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Nanofiller Modification and Incorporation into Fluoropolymer Nanocomposites and the Properties thereof

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Nanofiller Modification and Incorporation into Fluoropolymer Nanocomposites and the
Properties thereof

by

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A THESIS

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To:

My Beloved Parents

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Abstract

Polymer nanocomposites (PNC) are of great interest owing to the many potential property enhancements possible via introducing different types of nanofillers in polymer matrices. In recent decades, increasing attention has been paid to PNCs due to their light weight, low cost, and ease of processability compared to metal alternatives and due to their novel capability to tune properties. Depending on the end-use application, certain PNCs properties are targeted and the PNC formulation and processing can be manipulated to achieve the desired properties.

In this PhD thesis, different PNC properties have been improved by employing different strategies: (1) modification of nanofillers, (2) synthesis of novel nanofillers, (3) implementation of hybrid fillers, and (4) amendment of PNC production methods. For nanofiller modification, chemical treatment of nanoclay, multiwall carbon nanotube (MWCNT) and graphene nanoribbon (GNR) were performed. For the second strategy, GNR was synthesized from parent MWCNT to benefit from higher surface area and interaction of the novel nanofillers with the polymer chains. The main objective of these two strategies is to improve the affinity and dispersion of nanofillers in the host polymer to enhance PNC properties. Utilizing a secondary filler to further enhance the desired properties was the third strategy and was accomplished via a hybrid filler PNC consisting of MWCNT and nanoclay. Finally, the fourth strategy was to develop optimized PNC production methods. The aim of the last two strategies was to obtain an improved morphology for the nanocomposite and it is well known that nanocomposite structure can be used to control the final PNC properties.

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List of Symbols and Abbreviations

Symbols

A	Surface area
A_{α}	Infrared absorbance for α -phase
A_{β}	Infrared absorbance for β -phase
C	Electrical capacity
C_0	Capacitance of free space
C_p	Heat capacity at constant pressure
CR	Curing rate
d	Interlayer spacing
d_{001}	Interlayer (basal) spacing
E_c	Composite moduli
E_f	Filler young's modulus
E_m	Matrix young's modulus
G'	Elastic modulus
G''	Viscous modulus
G'_{∞}	Final elasticity
G'_0	Minimum elasticity
Hz	Hertz (frequency unit)
I	electrical current
I_C	Capacitive currents
I_R	Resistive currents
K_{α}	Infrared absorbance coefficients for α -phase

K_{β}	Infrared absorbance coefficients for β -phase
L	Length
M_H	Maximum torque
M_L	Minimum torque
N_2	Nitrogen
OH	Hydroxyl group
r	Radius
R	Electrical resistance
S	Scatter parameters
SE_A	Shielding by absorption
SE_R	Shielding by reflection
SE_{MR}	Shielding by multiple reflection
SE_{OA}	Overall shielding
t	Thickness
$\tan(\delta)$	Dissipation factor
t_{S2}	Induction (scorch) time
t_{C90}	Optimum cure time
T_c	Crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
T_{set}	Set point temperature
V	potential voltage
$vol.\%$	Volume fraction
$wt.\%$	Weight (mass) fraction

Z	Impedance
Z'	Real impedance
Z''	Imaginary impedance

Abbreviations

APAM	Alberta Polymer Asymmetric Minimixer
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
CB	Carbon Black
CCVD	Catalytic Carbon Vapor Deposition method
CNT	Carbon Nanotube
CNx-GNR	Nitrogen doped Graphene Nanoribbon
CNx-MWCNT	Nitrogen doped Multi-Walled Carbon Nanotube
COOH	Carboxyl group
CPC	Conductive filler/Polymer Composites
CPN	Clay Polymer Nanocomposites
CVD	Chemical Vapor Deposition method
D-TGA	differential Thermal Gravimetric Analysis
DSC	Differential Scanning Calorimetry
EMI	Electromagnetic Interference shielding
ESD	Electrostatic Discharge
FKM	Fluoroelastomer
FTIR	Fourier Transform Infrared

GNR	Graphene Nanoribbon
HFP	Hexafluoropropylene
HRTEM	High Resolution Transmission Electron Microscopy
IGC	Inverse Gas Chromatography
MAS	Magic-Angle Spinning
MDR	Moving Die Rheometer
MEK	Methyl Ethyl Ketone
Mnt	Montmorillonite
MWCNT	Multi-walled Carbon Nanotube
NMR	Nuclear Magnetic Resonance
O-CN _x -GNR	Oxidized Nitrogen doped Graphene Nanoribbon
PCP	Progressive Cavity Pump
PNC	Polymer Nanocomposites
PVDF	Poly Vinylidene Fluoride
rad	Radian
RPM	Revolutions Per Minute
SEM	Scanning Electron Microscopy
SWCNT	Single-Wall Carbon Nanotube
TAIC	Triallyl Isocyanurate
TEM	Transmission electron microscopy
TFA	TriFluoroacetic Acid
TFE	Tetrafluoroethylene
TGA	Thermal Gravimetric Analysis
TS	Tensile Strength

VDF	Vinylidene Fluoride
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
18CSI-Mnt	Octadecyltrimethoxysilane modified Montmorillonite
18CSI-SF-Mnt	Octadecyltrimethoxysilane-Fluorosurfactant modified Montmorillonite
2M2HT	Dimethyl-dihydrogenated Tallow

Greek letters

$\text{\AA}$	Angstrom
α	Phase constant
β	Phase constant
γ	Crystal type
γ_i	Surface tension of phase i
γ_i^d	Dispersion tension
γ_i^P	Polar tension,
δ	Crystal type
ε	Permittivity
ε'	Real permittivity
ε''	Imaginary permittivity
ε_0	Permittivity of free space
θ	diffraction angle
λ	Wavelength
μ	Chemical crosslink density

ρ_v	Volume resistivity
σ	Conductivity
ϕ^d	Interaction term for dispersion
ϕ^p	Interaction term for polar energies
ϕ_f	Volume fraction of filler
χ_1	Flory-Huggins interaction parameter
Ω	Electrical Resistivity unit
ω	Frequency

Chapter 1

Introduction

The main objective of this PhD thesis is to develop polymer nanocomposites (PNC), particularly fluoropolymer nanocomposites with enhanced physical properties, i.e. mechanical, thermal, and electrical properties. This has been accomplished through modifying the composite constituents and manipulating the fabrication methods. Different methods and modifications are used, depending on the end-use applications of the nanocomposites. Having a comprehensive understanding of the structure of PNC materials, different techniques have been examined to improve the morphology hence final properties such as swelling resistance, and mechanical and electrical performance. This chapter presents a general background, as well as the motivations in different parts of the current dissertation.

1.1. General back ground

According to IUPAC, a nanocomposite is a composite in which one of the phases has at least one dimension in the order of nanometers [1]. As usual, scientists are learning from Nature and developing nanocomposite materials by mixing two or more phases in nanoscale. A famous statement by Oriakhi, published in an article titled “Nano Sandwiches” in 1998, is that “Nature is a master chemist with incredible talent” [2, 3]. Many examples of nanocomposites can be found in natural surroundings, such as bone, shell, and wood [2]. In 1991, the first report of a commercial

PNC was by Toyota Motor Company in Japan for a nanoclay/Nylon-6 material used for a timing belt [2, 4].

Basically, the primary aspect of interest in nanocomposites is the reinforcement effect of nanofillers. However, there are many other potentials to improve properties of nanocomposites such as flammability resistance, polymer blend compatibilization, electrical properties, membrane, and barrier properties [5, 6]. In recent decades, the development of polymer based nanocomposites has attracted great interest due to their potential for a wide range of applications [2, 7-9]. Currently, PNCs are exciting and critical materials for major polymer compounds worldwide (Table 1.1) and are expected to comprise US\$ 9 billion market by 2025 [10].

Table 1.1. US Nanocomposites demand (million lbs) [11]

	2005	2010	2020	% Annual Growth (2005-2020)
Nanocomposites Demand	154	344	7030	29
Thermoplastic	152	329	5600	27
Thermoset	2	15	1430	55

PNCs will result only if the polymer macromolecules penetrate between the filler layers, or particles, resulting in a dispersion of separated layers at the nanometer level or the formation of individual particles, of nanosize dimensions, in the matrix [12-14]. The interest in PNC has been initiated by the incorporation of exfoliated nanoclay and, more recently, by other topics such as carbon nanotubes, graphene, carbon nanofibers, and nanocrystalline metals, etc. The modification of nanofillers are also under study [5]. For example, filler compatibilization (i.e. making the system chemically stable), filler's surface functionalization, substitution of some of the elements of the filler with atoms with different properties, etc. While incorporation of nanofillers, such as nanoclay, can improve the PNC's mechanical strength, a poor dispersion may cause the opposite effect [5].

Moreover, nanoparticle addition may lead to some drawbacks, such as brittleness [15]. The chemical compatibility of fillers and the matrix and final dispersion of nanofillers, therefore, should be considered carefully when making nanofiller-polymer composites.

1.1.1. Clay/Polymer Nanocomposites

Although the exploration of polymers with intercalated/exfoliated silicates appears to be very modern, clay/polymer composites have been known since the late 1950s [16, 17]. Initially, there were two major reasons for the interest in using clays in polymer industries: (1) to improve the polymer's physical properties; (2) to reduce the amount of polymer in the final part [2, 14]. The major advantage of nanoclay compared to other conventional micro-scale fillers, is their ability to yield outstanding properties at noticeably smaller loading amounts [18, 19]. Clay/polymer nanocomposites have received considerable interest in recent decades because of their extraordinary properties compared to pristine polymer or conventional (micro- or macro-) composites [14, 18, and 19]. These improvements include better mechanical properties (higher moduli or strength), higher heat resistance, better flame retardation, and lower permeability to liquids and gases [14, 19].

It is necessary for the nanoclay's silicate sheets to get separated and individually dispersed in polymer matrix at the nanometer scale to exploit the advantage of clay/polymer nanocomposite [20]. Nanocomposite properties depend on nanoclay dispersion, aspect ratio, and the interfacial interaction between the clay and polymer matrix [6, 21]. The presence of well-dispersed nanoclays in polymer matrices could result in extraordinary property enhancements for most applications [22-24]. In order to increase the strength of composites, two dominant factors should be considered: (1) the interfacial adhesion between nanoclay and polymer [12]; (2) the dispersion of nanoclay in polymer matrix, i.e. breaking up aggregates of clay layers [25].

Three main types of clay/polymer composites are illustrated in Figure 1.1: phase-separated, intercalated and exfoliated. In each case, the physical properties are different [4, 16, 21, 26, and 27]. Phase-separated refers to the state when polymer does not penetrate between the nanoclay silicate sheets; therefore, the properties are the same as conventional composites with micro-scale fillers [16]. In this case, the unseparated nanoclay silicate sheets are known as tactoid [2, 5, and 14]. The term intercalation is used when small amounts of polymer are introduced between clay sheets. In montmorillonite (Mnt), for example, the polymer causes layer separations of about 20-30 Å [14, 16]. When silicate sheets completely and uniformly delaminated and dispersed in the polymer matrix, this morphology is termed exfoliation, with galleries of 80-100 Å between layers [14, 16, and 20]. Studies show that several factors are contributing in degree of exfoliation of nanoclay-polymer nanocomposites, i.e. chemical compatibility, shearing forces, viscous forces and elastic forces of the polymer matrix, etc [2]. Exfoliation results if the shearing forces overcome the attractive forces, e.g. Van der Waals forces, between nanoclay layers in the clay galleries [2, 28].

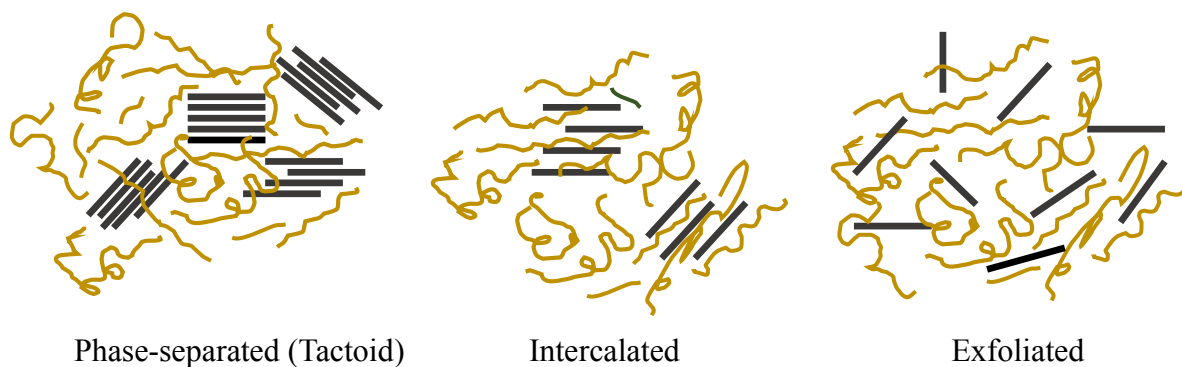


Figure 1.1. Morphologies of clay-polymer composite [adapted from 2, 16].

It is claimed that the exfoliated structure leads to noticeable improvements in the mechanical properties of polymeric systems [4, 29]. One of the most known amendment in properties of polymer/clay nanocomposites is solvent and gas resistance; the tortuous diffusion path created by the well-dispersed nanoclays reduces the permeation significantly [22, 30]. Incomplete exfoliation

has been shown to have adverse effects on reinforcement efficiency [29]. The nanocomposite structure depends on both processing conditions and the inherent nature of nanoclay and the polymer [31, 32]. Since clay intercalation and exfoliation play an important role in the final properties of nanocomposites, different methods of mixing and different mixing conditions should be investigated to obtain an optimum morphology for the PNC.

1.1.1.1. Nanoclay Modification

Depending on the compatibility of nanoclay and polymer, different mechanisms of dispersion are possible [16]. (1) By introducing chemically treated compatible clay, every processing condition should lead to a well-dispersed nanocomposite. (2) Marginally compatible clay and polymer requires the processing conditions to be optimized to achieve exfoliated nanocomposite. (3) For incompatible clay and polymer, the processing conditions should be optimized to at least gain the minimum tactoid or optimum intercalation, but it is unlikely to have even partial exfoliation [16].

Other than using optimized processing method and conditions, another factor which contributes in the degree of intercalation or exfoliation of nanoclays is the compatibility of clay sheets with the polymer [15]. The clay sheets are not compatible with most of organic polymers, due to their hydrophilic nature. It is important, therefore, to convert the hydrophilic surface of the clay to hydrophobic to obtain exfoliated polymer/clay nanocomposites [33]. The hydrophobic modification of nanoclay allows many hydrophobic guest molecules to be easily intercalated [8, 34]. To increase the compatibility of clays and polymer matrix, several modification approaches, using different modifiers have been reported in the literature such as using coupling agents or other appropriate functional groups [34].

1.1.1.2. Clay/Polymer Nanocomposites Production Methods

The major techniques used to produce clay/polymer nanocomposites production are: (1) in-situ polymerization, where nanoclays are dispersed in a monomer solution and then the polymerization is initiated; (2) solution mixing, where nanoclays are added to a dissolved polymer in its appropriate solvent and the solvent is extracted at the end; (3) melt-intercalation, which is preferred from an industrial perspective, using conventional polymer processing equipment [13]. This method has environmental and cost advantages [4, 12, 13, and 15].

Literature shows that different mixing parameters - including time, temperature, and shear rate - can affect the final nanocomposite morphology and properties [15-18, 35, 36]. Thus, the effect of mixing parameters on morphology and final properties of the clay/polymer nanocomposites, have been investigated as a part of this PhD dissertation.

1.1.2. Multi-walled Carbon Nanotube (MWCNT) and Graphene Nanoribbon (GNR)/Polymer Nanocomposites

One of the most interesting topics of nanotechnology is the design of advanced nanoscale devices for electronic applications. Within these areas, PNCs are of significant interest due to their extremely diverse applications, as well as their tunable properties, light weight, ease of processability, and low cost [5, 37]. In recent years, significant attention has been given to conductive filler/polymer composites (CPCs) for their application in electronics which arises from their unique combinations of properties, such as tunable electrical conductivity, charge storage, antistatic dissipation, ESD protection and EMI shielding [37]. CPCs are produced by incorporation

of different types of conductive fillers, such as carbon black, nanowire, carbon nanotube, or other graphene-based fillers, into a polymer matrix. Herein, MWCNT is selected as the ideal conductive filler because of high aspect ratio and remarkable electrical, thermal and mechanical properties for specific applications [38, 39].

Graphene nanoribbons (GNR) have been discovered as one of the most recent carbon-based nanofillers [40]. As will be discussed in Chapter 2, GNRs can be synthesized via different methods from graphene-based nanomaterials, such as carbon nanotube (CNT), graphite or graphene. They exhibit outstanding and unusual properties that can potentially lead to numerous applications, especially for electric devices [41, 42]. GNR is viewed as an attractive nanofiller for PNCs, due to its high electrical and mechanical properties similar to those found in CNTs. They also have the advantage of a higher interfacial area, which results in better adhesion with polymer matrices [43].

1.1.2.1. MWCNT and GNR modification

One of the most effective methods considered recently for tuning the MWCNTs properties is doping which means substitution of some of carbon atoms in MWCNT structure with elements such as nitrogen or boron [44-47]. Nitrogen-doped carbon nanostructures exhibit enhanced mechanical and electrical properties compared to un-doped original CNTs [47-50]. As this is a very recent development, there is limited research revealing fundamental understanding of this topic [44, 47].

1.2. State-of-the-Art

As discussed in previous sections, many diverse applications for PNC exist. Depending on certain applications of materials, different improvements in properties could be achieved through the incorporation of nanofillers, along with amendments in processing methods. In order to enhance the target properties, different types of strategies are investigated in this state-of-the-art as presented in the experimental strategy flowchart in Figure 1.2.

(I) Modification and synthesis of novel nanofillers

Chapter 4 explores nanoclay modification, with the goal of gaining improved dispersion in the elastomer matrix, resulting in better final PNC properties. Successful modification of nanoclay with different organic modifiers was carried in order for the montmorillonite (Mnt) clay to have better interaction with fluoroelastomer (FKM). An increase of $\sim 170\%$ in basal spacing of the clay was an indication of improved dispersion of the nanoclays in FKM which led to enhanced swelling resistance, and better thermal and mechanical performance of the nanocomposite. Moreover, excellent thermal stability of the modified clay could be achieved compared to the commercial available product.

Second strategy to synthesize a novel nanofiller, i.e. GNR, and also pursuing the first strategy for modification of MWCNT and GNRs was investigated in Chapter 5. A new class of GNR was synthesized from parent MWCNT. Moreover, different chemical treatments such as nitrogen doping and thermal reduction were tested to manipulate their application as nanofillers in FKM matrix. Based on literature, a significant issue that is important for crosslinked polymers - elastomers or rubbers - is the effect of nanofillers on the crosslinking density [5]. In this part of

dissertation, we discuss the role of MWCNT and GNR in their modified and non-modified state during the curing process of FKM. The aim of this investigation is to obtain improvements in the final electrical and mechanical performance of the PNCs. We were able to tune the crosslinking density by means of these novel synthesized nanofillers. In addition, adjusted surface properties of these nano materials will lead to superior performance as nanofillers for electrical and mechanical properties improvement.

(II) Implementation of hybrid fillers

One specific reason for the interest in CPCs for charge storage applications is having tunable dielectric properties [39]. In Chapter 6, electrical properties of a fluoropolymer, namely poly vinylidene fluoride (PVDF), were targeted for charge storage applications. The third strategy, i.e. using hybrid fillers, was proposed. We used nanoclay as a barrier layer to tune dielectric properties of MWCNT/PVDF. Hybrid composites of MWCNT/nanoclay/ PVDF could be successfully produced for the use of conductive polymer composite (CPC) as charge storage materials. For this specific application, the goal is high dielectric permittivity and low dielectric loss we accomplished this objective by incorporating an optimum level of nanoclay (1.0 wt. %) into MWCNT/PVDF nanocomposite. An interesting combination of ~670% increase in the dielectric permittivity combined with a considerable reduction in the relative dielectric loss (~ 68% less dissipation factor) was achieved. Also, the sharp insulator-conductor transition was muted as a consequence of using this third strategy.

(III) Amendment of PNC production methods

The last strategy was to optimize the fabrication methods. In Chapter 7, we investigate the effect of mixing parameters on morphology and final properties of nanoclay/FKM nanocomposite, prepared by the melt-intercalation method. By studying the effect of melt-mixing process conditions on curing behavior and mechanical performance of nanoclay/FKM nanocomposites, an optimum condition was obtained. This optimum process gave more effective crosslinking kinetics and better mechanical strength of PNC. Enhancements in tensile strength, elongation at break and modulus of 70%, 94%, and 405% respectively, were attained.

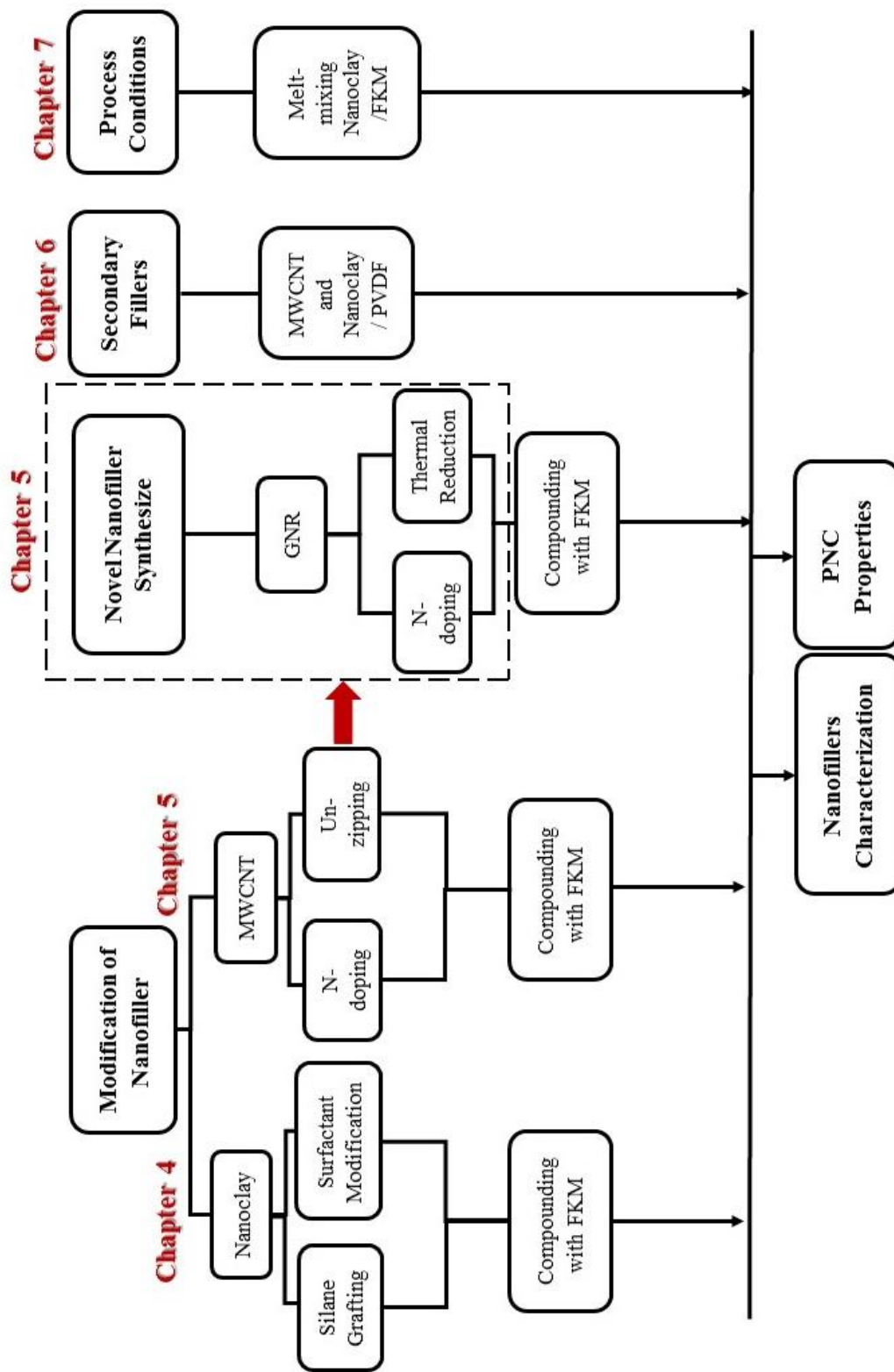


Figure 1.2. Experimental strategy flowchart

1.3. References

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Chapter 2

Literature Review: Materials

In order to investigate the effect of different strategies for polymer nanocomposite (PNC) properties improvement, several experiments have been done for nanofillers and PNCs production and characterization. In this thesis, we have focused on fluoropolymers, namely fluoroelastomer (FKM) and poly vinylidene Fluoride (PVDF) as the polymer matrices for PNC. Different types of nanofillers including nanoclay, multiwall carbon nanotube (MWCNT), and graphene nanoribbon (GNR) have been utilized based on the specific applications of PNCs. The significant properties and characteristics of the materials, and their desired behavior for specific applications are discussed in this chapter.

2.1. Fluoropolymers

The first fluoropolymer, polytetrafluoroethylene (PTFE), was discovered in 1938 by Dr. Roy Plunkett at Dupont Company [1, 2]. Generally, fluoropolymers are defined as polymers with a base of fluorocarbon. Fluoropolymers are particularly interesting and attractive compounds because of their versatility and their unique combination of relevant properties [3]. Table 2.1 summarizes the commercialization timeline of major fluoropolymers, as well as their processing and applications trade-offs.

Table 2.1. Commercialization timeline of major fluoropolymers [adopted from1]

Fluoropolymer	Monomer (s)/ Chemical Structure	Commercialization year	Trade-off	
			+	-
Polytetrafluoroethylene (PTFE)	$\left(\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{F} & \text{F} \end{array} \right)_n$	1947	Continuous use temperature 260°C	Non-melt processible
Poly(chlorotrifluoroethylene) (PCTFE)	$\left(\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{F} & \text{Cl} \end{array} \right)_n$	1953	Melt processible/ Non-melt processible	Maximum continuous use temperature 180°C
Fluorinated ethylene propylene (FEP)	$\left(\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{F} & \text{F} \end{array} \right)_n \left(\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{F} & \text{CF}_3 \end{array} \right)_m$	1960	Melt-processible	Maximum continuous use temperature 200°C
Polyvinyl fluoride (PVF)	$\left(\begin{array}{cc} \text{H} & \text{F} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right)_n$	1961	Thin film/ weatherable	Maximum continuous use temperature 107°C
Polyvinylidene fluoride (PVDF)	$\left(\begin{array}{cc} \text{H} & \text{F} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{F} \end{array} \right)_n$	1961	Melt processible	Maximum continuous use temperature 150°C
Ethylene ChloroTriFluoroEthylene (ECTFE)	$\left(\begin{array}{cccc} \text{H} & \text{H} & \text{Cl} & \text{F} \\ & & & \\ -\text{C} & - & \text{C} & - & \text{C} & - & \text{C}- \\ & & & \\ \text{H} & \text{H} & \text{F} & \text{F} \end{array} \right)_n$	1970	Hardness/ Toughness	Maximum continuous use temperature 150°C
Perfluoroalkoxy (PFA)	$\left(\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{F} & \text{F} \end{array} \right)_n \left(\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{F} & \text{O} \\ & \\ & \text{CF}_3 \end{array} \right)_m$	1972	Melt processible/ Continuous use temperature 260°C	Low molecular weight
Poly(ethene-co-tetrafluoroethene) (ETFE)	$\left(\begin{array}{cccc} \text{H} & \text{H} & \text{F} & \text{F} \\ & & & \\ -\text{C} & - & \text{C} & - & \text{C} & - & \text{C}- \\ & & & \\ \text{H} & \text{H} & \text{F} & \text{F} \end{array} \right)_n$	1973	Hardness/Toughness	Maximum continuous use temperature 150°C
Teflon® AF	Copolymer: Tetrafluoroethylene (TFE) and 2,2-Bistrifluoromethyl- 4,5difluoro-1,3-dioxole (PDD)	1985	Soluble in special halogenated solvents	High cost

Fluoropolymers can be thermoplastics, elastomers, plastomers, thermoplastic elastomers, Development of this class of polymers led to significant changes in the expected properties and fabrication process of polymers [1]. The notable properties of fluoropolymers originate from the replacement of hydrogen by fluorine in the polymer structure. Their basic properties arise from their low polarizability and strong electronegativity, small Van Der Waals radius (of the Fluorine atom), and strong C-F bond (552 kJ/mole) [3-5]. One fundamental property of fluoropolymers is their superior resistance to organic and inorganic chemicals [1]. In addition, these polymers exhibit some key beneficial mechanical, electrical, and thermal characteristics compared to other polymers [4]. Thermal stability of fluoropolymers is significant because of high processing temperatures required for these materials. Furthermore, fluoropolymers have a wide range of electrical applications, such as in wire coating and insulation for electrical components. Fluoropolymers have desired electrical properties, including dielectric constant, dissipation factor, and electrical resistivity [4].

2.1.1. Fluoroelastomer

Rubber materials, or elastomers, have been considered as critical components in many technical products, particularly when tougher, unforeseen environments demand special improved material performance such as high temperature stability and oil resistance for energy applications [6]. Normally, it is difficult to produce engineering polymers with both high strength and high toughness [7]. High strength is the ability of a material to sustain high loads, while toughness is the measure of the total energy that can be absorbed by a material before fracture. Lack of toughness shown by brittle polymers has been improved by the incorporation of rubbers through blending or

copolymerization [7]. Among fluoropolymers, fluoroelastomers have shown useful properties and have significant presence in modern industries [5, 8-10].

Fluoroelastomers (FKM) have been proposed for applications where rubberlike elasticity is needed in severe environments such as oil-well completion and oilfield services [6, 9]. The wide range of industrial applications of fluoroelastomers is due to their unique combinations of mechanical and compression properties, coupled with their excellent performance under conditions requiring resistance to high temperature and organic liquids such as fuels and oils [5, 8]. They also exhibit good resistance to flame propagation, oxidation, ozone and weathering [5]. Most companies involved in fluorine chemistry devote funds and research efforts to fluoroelastomers products, in spite of the high costs of these materials [5].

Applications of fluoroelastomers

FKM, and more specifically, the copolymers and terpolymers synthesized from vinylidene fluoride (VDF), hexafluoropropylene (HFP), and tetrafluoroethylene (TFE), are used widely in automotive, chemical, petrochemical, aerospace, and food processing industries, primarily as seals, gaskets, O-rings, and hoses [8-10]. These materials are fluoroelastomers, i.e. consisting of fluorine and carbon only. They are typically specified for sealing applications requiring high chemical and thermal resistance [8-12].

Three classes of fluoro-rubbers have been defined by ASTM: Tetrafluoroethylene/propylene dipolymers (FEPM), FKM, and perfluoro-elastomers (FFKM). Each has different types of molecular configurations and, hence, different final properties. An important issue is to determine up to what temperature and for how long the elastomer can be operated in severe environment and

maintain acceptable mechanical performance [12]. Generally, resistance properties such as high temperature and chemical resistances, increase with increasing fluorine content [5]. Most of the current research efforts are directed to improve the properties of fluoroelastomers and their processability. Different types of fluoroelastomers exhibit different performance.

One example is the specific application of an elastomer stator for Progressive Cavity Pump (PCP). The down-hole PCP pump is used for crude oil extraction [6]. It consists of two basic components: a single helical metal rotor and a double helical elastomer stator (Figure 2.1). The stator elastomer should be compatible with the reservoir fluid and down-hole conditions, as well as maintain good mechanical performance for the high shear applied during oil extraction at elevated temperatures. Among polymers, elastomers and, more specifically, fluoroelastomer (FKM), are recommended for this application due to their superior oil resistance. Having insufficient mechanical performance at high temperatures ($>150\text{ }^{\circ}\text{C}$), however, means its properties need to be improved.



Figure 2.1. Progressive Cavity Pump [13]

A main issue with nanocomposites is the level of the interfacial adhesion of filler to the matrix [14]. In addition to the nature and properties of nanofillers and the polymer matrix, the properties of nanocomposites depend on their morphology and the interfacial interaction between the filler and matrix [15]. Several studies show that different mixing parameters, including time, temperature, and shear rate, can affect the final nanocomposite morphology and properties [16-21]. One major part of this work corresponds to the improvement of FKM properties through nanoclay incorporation.

Properties of fluoroelastomers

I) Swelling Behavior

The stability of polymeric materials in aggressive liquid environments is of importance for their successful application [11]. It is well known that FKM is typically used in severe environments. For example, one of the most popular applications of FKM based seals is for use in submerged pumps [8]. Therefore, it is essential to investigate their swelling and solvent transport properties.

II) Thermal properties

As a class, fluoroelastomers are notably resistant to heat, as compared to other elastomers. Among them, VDF-based fluoroelastomers and fluorosilicones are capable of long-term service in dry heat at 200°C, while FKM elastomers are stable for many months at 260°C [5].

III) Mechanical properties

The tensile properties of the fluoroelastomers are generally satisfactory. In addition, the resistance to compression set is an important property of fluoroelastomers for their end-use as seals [5]. Other mechanical properties may be considered for various applications. The mechanical performance of some commercial fluoroelastomers is summarized in Table 2.2. It is worth noting that FKM compounds have limited low temperature flexibility and are not easy to process. These elastomers have moderate tensile strength at room temperature when compared with hydrocarbon rubbers and retain only a portion of it when used at high temperatures [10].

Table 2.2. Mechanical properties of different types of fluoroelastomers [5]

Property	Fluoroelastomers			
	FFKM	FKM	TFE/P	Fluorosilicone
100% Modulus (MPa)	6.2-13.1	2.1-15.2	2.5-3.5	1.0-6.1
Tensile strength (MPa)	14.5-16.8	9.0-18.6	18.0-20.0	6.2-8.6
Elongation (%)	120-240	100-500	250-350	100-500
Compression set (%) 70h, 200°C	35-50	≥10	45-50	60
Hardness (shore A)	70-95	90-95	65-75	50-75
Brittle temperature (°C)	-40 to -30	-59 to -18	-40	-66

Some of the commercial fluoroelastomer trademarks with different properties are listed in Table 2.3.

Table 2.3. Fluoroelastomers trademarks and properties [5]

Trademark	Co-monomers	%F	Advantage/drawbacks
Viton ®	VDF/HFP/TFE		Good chemical resistance at high temperature
Fluorel ®	VDF/HFP	64	Resistance to oxidation, solvents, flames
Tecnoflon ®	VDF/HFP/TFE	70	May swell
Dai-el ®	VDF/HFP/TFE		High thermostability, better resistance to swelling
FKM ®	VDF/HFP/TFE with CSM	67	Better mechanical properties
	VDF/HFP/TFE/E (5%)	variable	Protects from alkaly attack
	VDF/PAVE	variable	Resistance to oxidative attack
Tecnoflon ®	VDF/HCF=CFCF ₃	variable	Heat resistance, as above and to solvents
Kel F ®	VDF/TFE/ HCF=CFCF ₃	62-70	Vulcanization: better heat and chemical resistance
	VDF/CTFE	variable	
Atlas ®	TFE/P	54-57	Chemical, heat and pressure resistance

2.1.2. PVDF

Another class of fluorinated polymers are partially fluorinated. These polymers are distinguished from perfluoropolymers by some hydrogen atoms in the molecular structure in addition to fluorine and carbon [1]. One example is Poly(vinylidene Fluoride), PVDF, also called VF₂ and PVF₂. PVDF is a semi-crystalline thermoplastic with five distinct crystalline forms [22, 23]. The most common crystalline phase is α form with the trans-gauche conformation, in which hydrogen and fluorine atoms are located alternately on each side of the chain [24, 25]. The β crystalline form has an all-trans chain conformation, with fluorine atoms on one side of the chain

and hydrogen atoms on the other side of the chain [1]. The γ crystals, obtained from ultrahigh molecular weight PVDF, are less usual [26, 27] and δ crystals are generated as the result of distortion of the other crystalline forms [28].

PVDF is a type of electroactive polymer (EAP), which has drawn great attention due to its applications as a polar piezoelectric material [29-37]. Generally, electroactive polymers have special electromechanical and dielectric properties that make them ideal matrices for charge storage applications [23, 33]. EAPs are materials that exhibit deformation- such as change in size or shape- when an electric field is applied and exhibit an electrical response when subjected to deformation [33, 34]. Ferroelectric materials are substances with the ability to maintain electric permanent polarization that can be released or switched in an electrical field [35]. Piezoelectric materials are a class of ferroelectrics with the ability to generate voltage; hence, they exhibit electric current when a mechanical deformation, i.e. compression or expansion, is applied [33, 36]. Among different PDVF's polymorphs, the polar β -phase has gained the most interest because of its piezo-, pyro- and ferroelectric properties and subsequent better dielectric properties [37-40]. Besides having piezoelectric properties, PVDF is nonflammable and chemically resistant, and also has considerably high strength, wear and creep resistance [1, 3]. Its service temperature, however, is limited and its chemical resistance is lower than perfluoropolymers [1].

2.2. Nanofillers

Materials are considered to be in nanoscale when one of the dimensions of the materials (e.g. particle, platelet, fiber, nanowire, etc.) are in the range of 1–100 nm. Nanomaterials exhibit physical and chemical properties that are dramatically different from their micron scale counterparts, due to

their large surface area per volume [14, 15, 41, and 42]. These materials are typically classified by their geometry. The main three classes are particulate, fibrous, and layered [15, 41].

A fundamental morphological characteristic that is significant in relation to structure and properties of nanocomposites, is the surface area/volume, as illustrated in Figure 2.2 for different classes of nanofillers [41]. This ratio increases by three orders of magnitude as the scale changes from micrometer to nanometer [41].

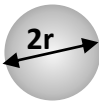
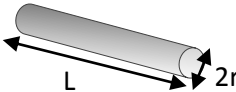
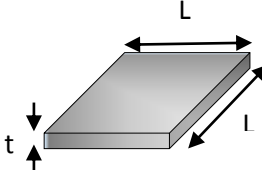
Geometry :	Particulate	Fibrous	Layered
			
Surface area/volume ratio:	$3/r$	$2/r + 2/L$	$2/t + 4/L$

Figure 2.2. Surface area/volume ratio for three different classes of nanomaterials [41]

The most commercially important and scientifically interesting aspect of the use of nanofillers is the very low amount of filler that has to be added to the polymer to yield improved properties [43]. The advantages of nanoscale particle incorporation can lead to a wide range of applications, including barrier properties, membrane separation, UV screens, flammability resistance, polymer blend compatibilization, biodegradable polymers, electrical conductivity, impact modification, and biomedical applications [14, 15]. Table 2.4 lists the most important nanofillers currently being used for the improvement of polymer material properties for different applications.

The first commercial example of polymeric nanocomposites, in automotive applications, was nanoclay/nylon-6 for making timing belt covers in Toyota Motor Company, 1991 [43].

Table 2.4. Examples of nanoscale filler incorporated in polymer composites [14]

Nanofiller	Property enhancement(s)	Application/utility
Exfoliated clay	Flame resistance, barrier, compatibilizer for polymer blends	Aerospace, automotive
SWCNT; MWCNT	Electrical conductivity, charge transport	Electrical/electronics/optoelectronics
Nanosilver	Antimicrobial	Wound dressings, biomedical
ZnO	UV adsorption	UV screens
Silica	Viscosity modification	Paint, adhesives
CdSe, CdTe	Charge transport	Photovoltaic cells
Graphene	Electrical conductivity, barrier, charge transport	Electrical/electronic
POSS	Improved stability, flammability resistance	Sensors, LEDs

2.2.1. Nanoclay

The term “clay” has been historically referred to as small parts of soil fractions (less than 2 μm) without any specific composition [15]. Every clay mineral is composed of layered silicates, containing two types of sheets: tetrahedral and octahedral [15, 44]. Each layer sheet’s thickness is about 1 nm and the lateral dimension varies from 30 nm to several microns. The aspect ratio is usually in the range of 10-1000 [15, 44]. Based on the structure of nanoclay silicate sheets, there are two main characteristics that are considered for nanocomposites: (1) ability to disperse individually and (2) ability to fine-tune their surface chemistry through ion exchange with organic/inorganic cations. It should be noted that polymer clay nanocomposites will result only if the layers are separated and dispersed in the polymer matrix at the nanometer level [42].

The most commonly used clays for nanocomposites are Hectorite, Saponite, and Montmorillonite (Mnt) [15, 44]. Among them, Mnt is the most frequently used clay for preparation of polymer clay nanocomposite (PCNs) [6, 15, and 42]. It consists of hundreds of silicate layers with cations in between the layers, as shown in Figure 2.3 [15, 42]. The plate-like nanolayers are held together by electrostatic forces.

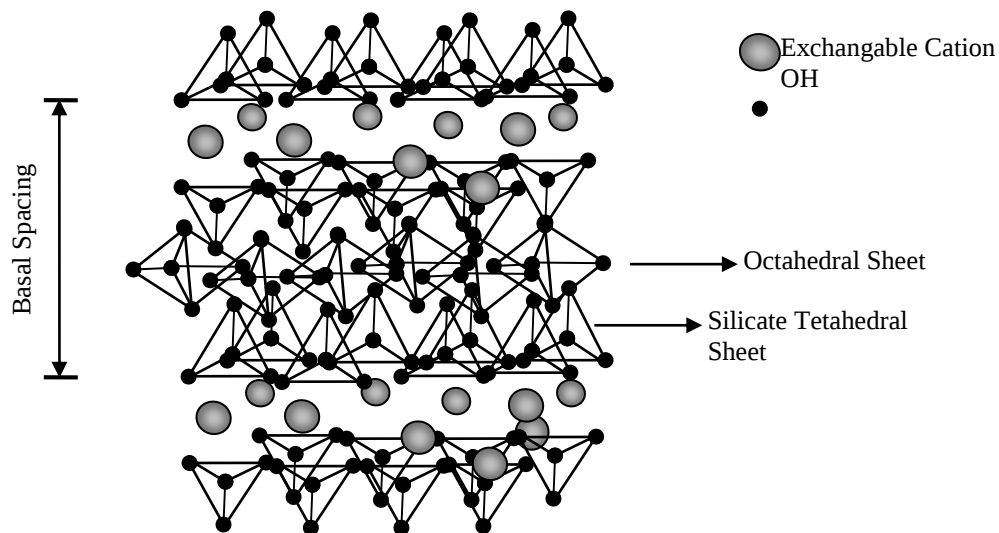


Figure 2.3. Montmorillonite structure [adopted from 15]

For the PCN parts of this thesis, we have synthesized several different modified Mnt. The modifications were done to make the filler chemically compatible with the polymer matrix. For example, we used alkyl silanes and a fluorosurfactant for compatibilizing Mnt with fluoroelastomer. Clay modifications are discussed in Chapter 4 entitled “*Modification of Montmorillonite with Alkyl Silanes and Fluorosurfactant for Clay/Fluoroelastomer (FKM) Nanocomposites*”.

2.2.2. Carbon nanotube

Carbon nanotube (CNT) was first synthesized by Iijima in 1991, a few years after the discovery of fullerenes [45-47]. Fullerene is a geometric cage-like structure of carbon atoms discovered in the 1980s by Smalley and co-workers at Rice University [47]. CNTs are a form of long, narrow fullerenes where the walls are graphite sheets (hexagonal carbon) that have been rolled to a tube [15, 41]. The diameter ranges from about a nanometer to tens of nanometers, with lengths up to centimeters [15]. Nanotubes exist in one of two structural forms: single-wall and multiwall [45, 41]. A single-wall nanotube (SWCNT) is a single graphitic sheet, rolled into a tube with a cap at either end, and with a diameter of approximately 1 nm [46]. Multi-walled carbon nanotubes (MWCNTs) consist of concentric single-walled carbon nanotubes (SWCNTs) held together with relatively weak van der Waals forces [41].

The morphology of a CNT is defined by the orientation and magnitude of the chiral vector in the original rolled graphite sheet [41]. There are two configurations for the atomic structure of CNTs, as illustrated in Figure 2.4: armchair and zigzag [41]. The chirality of the CNTs significantly affects their properties [41].

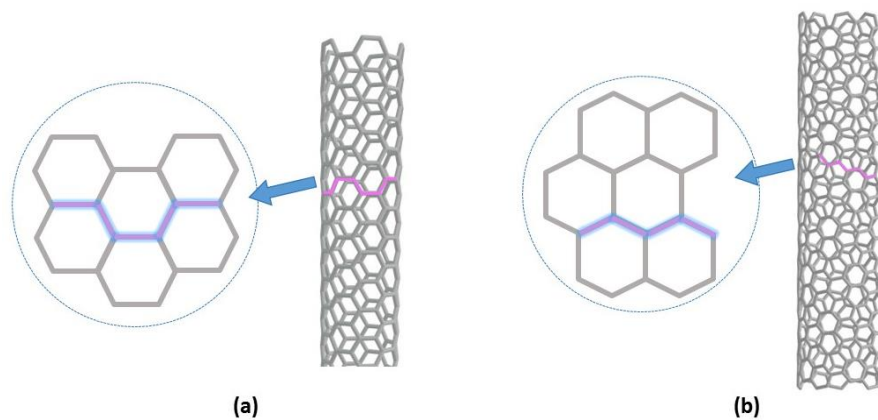


Figure 2.4. Atomic structures of (a) armchair and (b) zig-zag carbon nanotubes

Carbon nanotubes exhibit exceptional properties as a consequence of their symmetric structure [41, 48]. The very large aspect ratio of CNTs makes them an interesting nanofiller for reinforcement applications and for enhancement of the properties of nanocomposites [13, 15, 47-53]. CNTs are thermal stable up to 2800 °C (at vacuum), while the thermal conductivity is about twice that of diamond's [48]. In terms of electric properties, they are ideal conductive fillers for conductive polymer composites (CPCs), due to the high current-carrying capacity that is 1000 times higher than copper wires [13, 14, 31, 48, and 49]. The superior thermal and electrical properties are combined with outstanding mechanical performance, i.e. high specific stiffness and strength [16, 31, 47-50]. Many potential applications have been proposed for carbon nanotube composites, including conductive and high-strength composites, energy storage and energy conversion devices, hydrogen storage media, nanometer-sized semiconductor devices, electromagnetic interference shielding, probes and interconnects, sensors, electrostatic dissipation, charge storage and super capacitors, as well as various electrode applications [14, 15]. However, some challenges arise while using CNTs in polymer composites. The first is in the uniform dispersion of nanotubes. The existence of high Van der Waals attraction between CNTs causes aggregation and, consequently, an increase in the percolation threshold [13, 41, 49, and 51]. In addition, the efforts for improving the dispersion may affect other important properties, such as electrical, mechanical, and dielectric properties [13, 49, 52, and 53]. Some strategies for dealing with these types of problems are addressed in Chapters 5 and 6.

We used a commercial MWCNT (NanocylTM NC7000) for the MWCNT/clay/PVDF nanocomposites for charge storage application (Chapter 6). Homemade MWCNTs were used for GNR production and studying the curing behavior of MWCNT/FKM and GNR/FKM nanocomposites (Chapter 5). The synthesis method of MWCNTs and GNRs are explained in section 3.1.3.

2.2.3. Graphene nanoribbon

Graphene is the basic building block of all graphitic forms of carbon with a honeycomb structure, as illustrated in Figure 2.5a [54, 55]. Generally, the graphene-like structures are classified into three main types: (1) graphene, an infinite two-dimensional crystal (≤ 3 layers); (2) graphite, an infinite three-dimensional crystal made of more than three stacked layers (Figure 2.5b); and (3) graphene nanoribbons, finite one-dimensional graphene crystals (Figure 2.5c) [54].

Graphene nanoribbons (GNRs) can be synthesized through different methods, such as chemical vapor deposition, chemical treatment or mechanical exfoliation of graphite, epitaxial growth of graphene films on electrically insulating substrates, reduction of graphene oxide, chemical and electrochemical unzipping of CNTs [54, 56-75]. These one atom thick, sp^2 -hybridized carbon sheets have borders which can exhibit edge states and, consequently, result in different electronic, chemical and magnetic properties, depending on their size and type of the edges [54, 76, and 77]. For example, GNRs with a width of less than 10 nm behave as semiconductors, while for wider GNRs, the properties depend on the edge's chiral configurations, which could be either zigzag (30°) or armchair (0°) [54, 77-79].

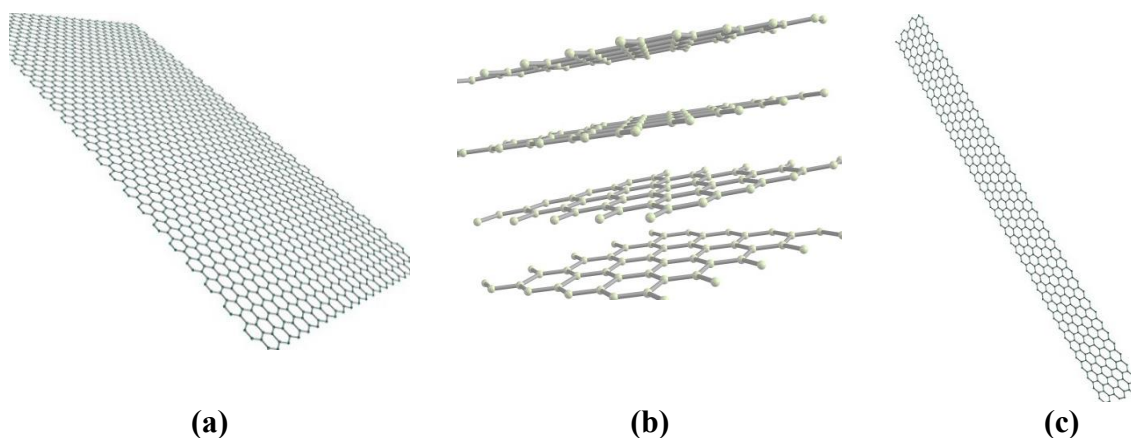


Figure 2.5. Structure of (a) graphene, (b) graphite, and (c) graphene nanoribbon

Typically, GNRs exhibit outstanding and unusual properties that can lead to numerous applications, especially for electrical devices [56, 80-82]. Having a higher interfacial area may cause better adhesion with polymer matrices, which is a significant hallmark for polymer nanocomposites [86]. Basically, graphene-based materials have superior electronic properties, having a very high intrinsic mobility of charge carriers and zero effective mass [84, 85]. On the other hand, in terms of mechanical properties, graphene is one of the strongest materials ever known [57] so they are attractive fillers for reinforcement applications. Also, graphene-based fillers are appealing because of their stiffness, strength, and thermal conductivity, combined with an impermeability to gases in nanocomposites [86-89].

In addition to the good electrical and mechanical performance of graphene, the shape of GNRs' makes them interesting materials for polymer nanocomposites. Particularly, the higher aspect ratio of GNRs and their shape facilitates their blending with polymers in the molten state and there is also the possibility to functionalize their edges [83]. As has been discussed previously, the GNRs' properties mainly depend on their shape, size and edges. Therefore, chemical or structural modification of GNRs is expected to modify their performance [57]. One of the recommended methods for modification of GNR properties is doping [69]. More specifically, Nitrogen-doping is considered for GNRs, as well as other graphene-like nanostructures [57]. It has been predicted in the literature that nitrogen doping of GNR could result in noticeable modifications in electronic and spin properties [56, 80]. In Chapter 5, titled "Tuning the curing behavior of Fluoroelastomer by incorporation of Nitrogen doped Multiwalled Carbon Nanotube and Graphene Nano Ribbon", we investigate chemical modification of GNRs and incorporation of GNR in fluoroelastomer nanocomposites. Nanocomposite properties and performance as a function of chemical

modification type and level is studied. GNRs for the study in Chapter 5, were produced from unzipping home-synthesized MWCNTs as described in section 3.1.3.

2.3. References

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Chapter 3

Processing and Characterization

The purpose of this Chapter is to provide introductory information about the laboratory equipment used in this work for fabrication and characterization processes of polymer nanocomposites (PNCs). A brief introduction to each of the processes presented here. This chapter is divided to two sections allocated to (1) PNC processing methods and (2) characterization tests conducted to evaluate the properties of PNCs.

3.1. Processing

3.1.1. Mixers

3.1.1.1. Melt mixing

Melt mixing is a well-known method for compounding polymer blends or composites. In this process, nanofillers are introduced into the polymer at a high temperature where the matrix is molten. Polymer macromolecules should move easily at high temperatures in their low viscosity state during the mixing process. Polymer chains are expected to penetrate between nanofillers, and intercalate the nanolayers or nanoparticles. The melt mixing process for the nanocomposites with different filler loadings was carried out using one of the following two mixers, Haake Batch Mixer

or Miniature Batch Mixer. The choice of mixer depended on the scale of the material, and included a defined and controlled temperature, time and rotor speed (shear).

Haake Batch mixer

Melt intercalation was performed in the Thermo-Fisher Haake Rheomix Series 600® internal batch mixer with twin Banbury blades (Figure 3.1a) to make polymer nanocomposites. The mixing volume is 70 cm³ and filling factor used is about 0.78 for most of the polymers.

Miniature batch mixer

Melt intercalation was performed in a smaller mixer custom developed in our laboratory. This batch mixer, as shown in Figure 3.1b, has exactly the same system and structure as the Haake Rheomix 600, but with a small chamber size of 2.4 cm³. This makes the mixer ideal for small scale experiments, with a limited material amount.

Alberta Polymer Asymmetric Minimixer (APAM)

Alberta Polymer Asymmetric Minimixer (APAM) is the name of another custom miniature mixer which was developed by our research group in 2004 (Figure 3.1c) [1]. This mixer was built to achieve flow regimes similar to industrial mixers and has temperature and rotation frequency (Revolutions per minute (RPM)) control in addition to torque and melt temperature measurement. Its complex flow pattern is the same as that observed in a standard, two-rotor laboratory internal batch mixer, such as the Haake Rheocord series 600, but in a simple, one-rotor configuration. The asymmetric design of the rotor exerts sufficiently high shear rates, elongational flow and reorientation to obtain both a well-dispersed and well-distributed material [1].

The small scale of the chamber's cavity volume of approximately 2 cm³ makes the mixer ideal for laboratory experimental purposes. The cup has an inner diameter of 13 mm and a height of 25

mm. The rotor, similar to a roller blade has a helical cut and a length of 25 mm, with an alternating diameter. The temperature of the chamber is measured and controlled to maintain a steady state via the heating band around the mixer and using temperature measured by the thermocouple in the outer cup.

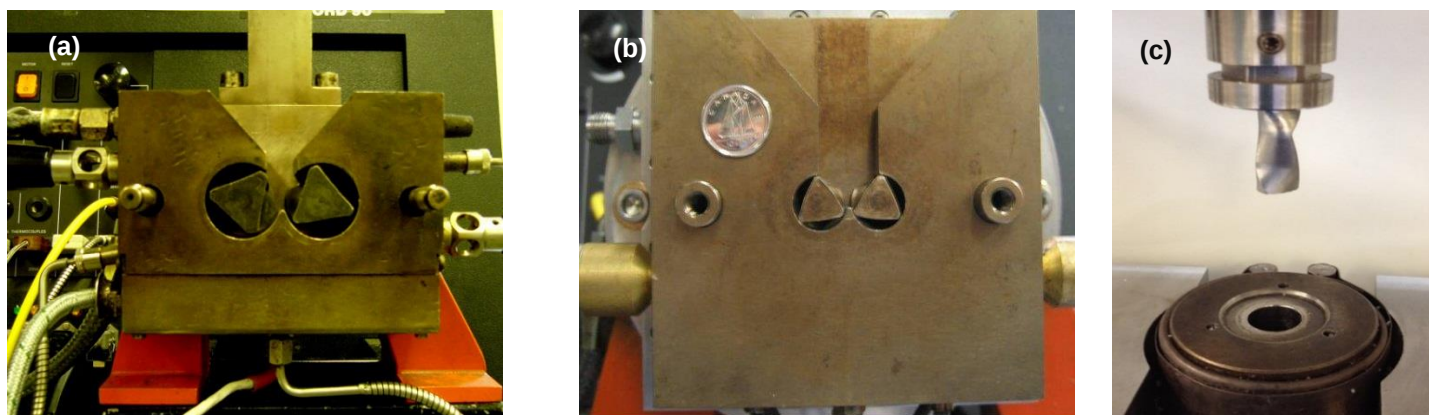


Figure 3.1. Melt-intercalation mixers; a) Haake internal, b) Miniature batch, and c) APAM

3.1.1.2. Solution mixing setup

Magnetic stirrers in beakers were used for dissolving the polymer in the appropriate solvent, for the dispersion of nanofillers in the solvents, and for solution mixing. Solution mixing temperature was controlled using a thermocouple immersed in the liquid. In addition, to have the best homogenous solutions for nanofillers, ultrasonication was also used. Figure 3.2 depicts the schematic of the solution mixing procedure used for making nanofiller/polymer nanocomposites.

3.1.2. Ultrasonication and Homogenizers

Generally, a very high van der Waals attraction exists between the nanofillers causing aggregations and, consequently, we cannot take advantage of their special properties with respect

to the high surface area. Among several physical and chemical strategies to overcome this problem, ultrasonication has been used in parts of our project to physically enhance the dispersion. Sonication is the method of applying sound energy to agitate, disperse, break up and sheer particles [2]. Sonication, with focused ultrasound frequencies (more than 20 kHz), are called ultrasonication. The ultrasonication may be applied for different purposes, such as homogenizing, disintegration, degassing or cleaning [3]. The following ultrasonic devices have been used for disaggregation and homogenizing the nanoparticles' dispersion prior to any modification reaction or compounding with polymers.

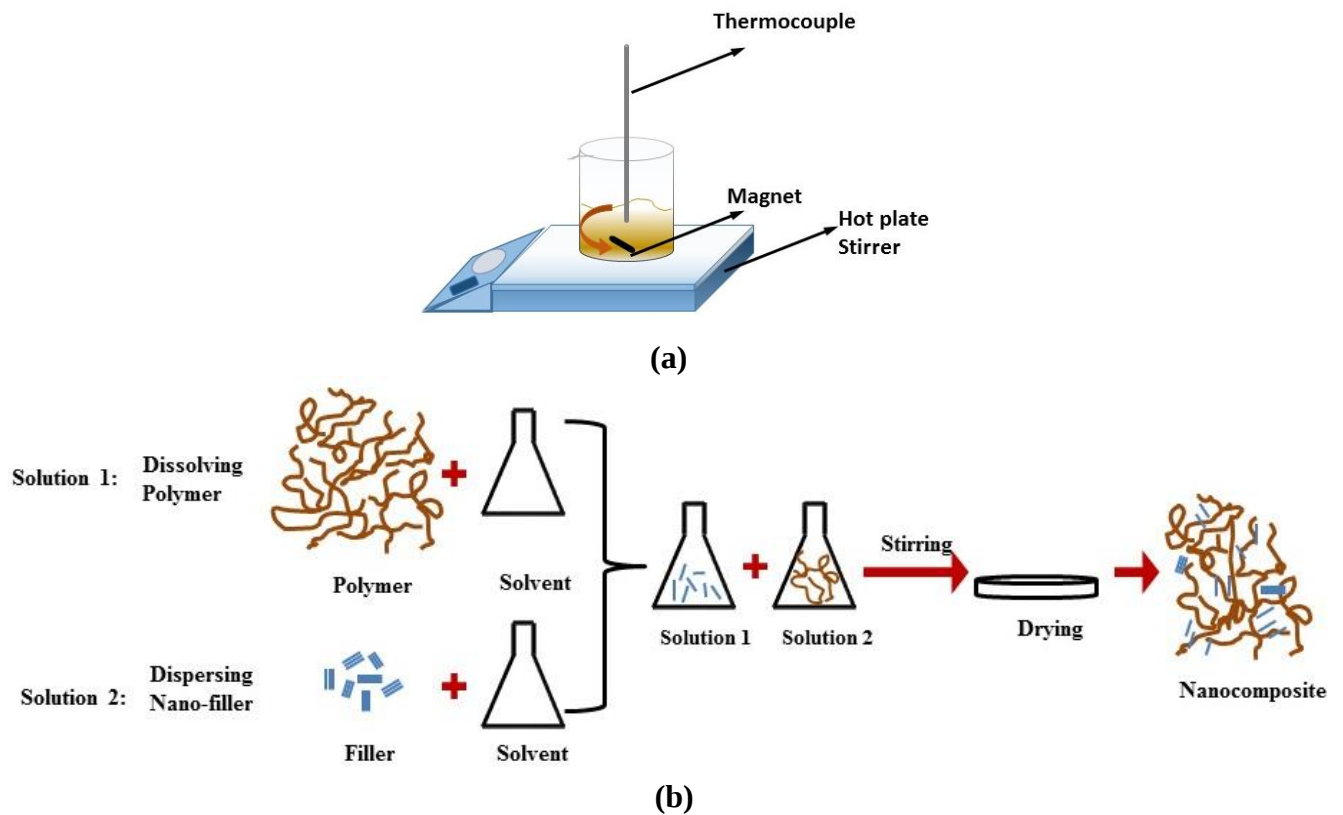


Figure 3.2. a) Stirrer, hot plate, and thermocouple, b) Schematic of solution mixing process

Bath sonicator

A VWR ultrasonic bath (Figure 3.3a), with temperature and time control, was used to disperse nanofillers well, particularly MWCNTs and GNRs, in the appropriate solvents to enhance the modification processes.

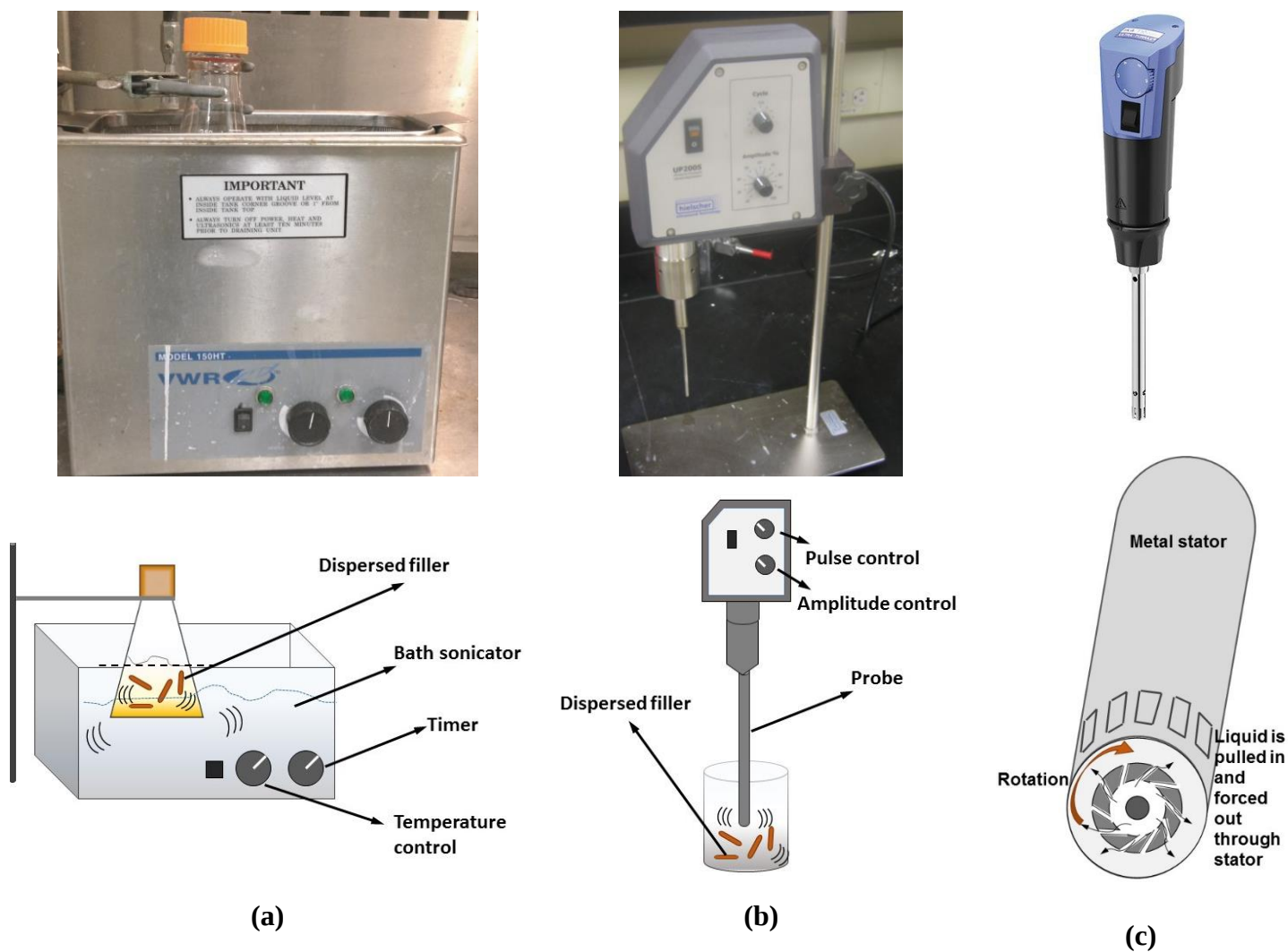


Figure 3.3. Photographs (top) and schematics (bottom) of; a) Bath sonicator, b) probe sonicator, and c) digital homogenizer [4]

Probe sonicator

The Hielscher ultrasonic processor UP200S (Figure 3.3b), with a power of 200 W and frequency of 24 kHz, was used as a homogenizer for the dispersion and de-agglomeration of particles in liquids, through ultrasonic power. Both the amplitude and pulse of the sonicator are adjustable from 20 to 100% and 0 to 100%, respectively. This device was used for the homogeneous dispersion of carbon nanotubes and graphene nanoribbons in the polymer solution while in the solution mixing process.

Digital Homogenizer

The IKA T-18 Ultra Turrax Digital Homogenizer (Figure 3.3c) was used for the homogenous solution mixing of the polymer and fillers. Its 500 W motor generates rotation rates of 500 to 25000 rpm, with stainless steel dispersion elements. This equipment was also used for homogenizing the product of the solution mixing process for carbon nanotubes and graphene nanoribbons with polymer dissolved in a suitable solvent.

3.1.3. Carbon Nanotube Synthesis Setup

We synthesized homemade multi wall carbon nanotubes (MWCNTs) and synthesized graphene nanoribbons (GNRs) from the parent MWCNTs with specific desired structures and properties [5-7], using the setup depicted in Figure 3.4. We used these custom MWCNTs in some part of this work.

Recently, one of the most effective methods considered for tuning the CNTs properties is doping with elements such as nitrogen or boron [5, 6, and 8]. Therefore, we used N-doping for our MWCNT and GNRs and incorporated them in the polymer nanocomposites. The method and setup

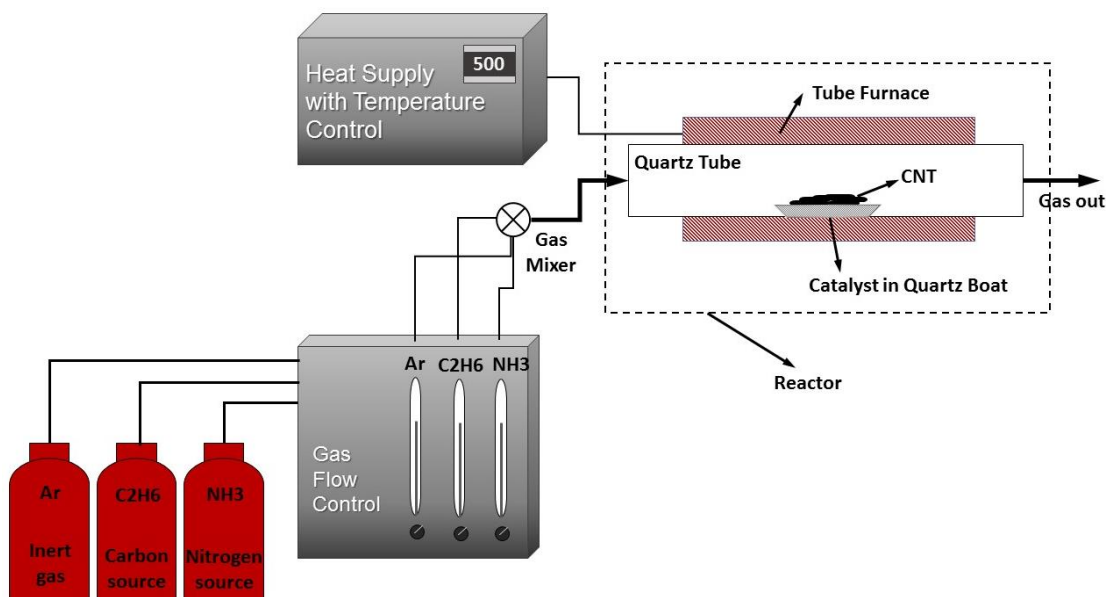
used for the synthesis of nitrogen doped CNTs and GNRs is described briefly in this section. More detailed information could be found in the literature [5-7].

Nitrogen doped Carbon Nanotube Synthesis setup

The N-CNTs were synthesized by a chemical vapor deposition (CVD) method using our carbon nanotube synthesis setup, as shown in Figure 3.4.



(a)



(b)

Figure 3.4. (a) Photograph and (b) schematic of CNT synthesis setup

A mixture of ethane (C_2H_6) as a source of carbon, ammonia (NH_3) as the source of nitrogen, and argon (Ar) as the inert environment, was used in the synthesis process. The flow rates of the gases were controlled by the gas flowmeters (Cole Parmer 150-mm 316 SS). A metallic catalyst, supported on alumina (M/Al_2O_3), was placed inside a quartz boat located inside a quartz tubular reactor with a diameter of 4.5cm. The reactor was placed inside a tube furnace (Thermo Scientific–Lindberg Blue M) set at a temperature in the range of 550 to 950 °C for 2 hours.

3.1.4. Graphene nanoribbon Synthesis Procedure

The longitudinal unzipping of MWCNTs (Figure 3.5), through chemical oxidation in a mixture of acids, has been proven to produce a high yield of low defect GNRs [7, 9]. In this PhD project, undoped and nitrogen doped GNRs were synthesized from the parent in-house synthesized undoped and nitrogen doped MWCNTs via chemical oxidation method [7] in our laboratory.

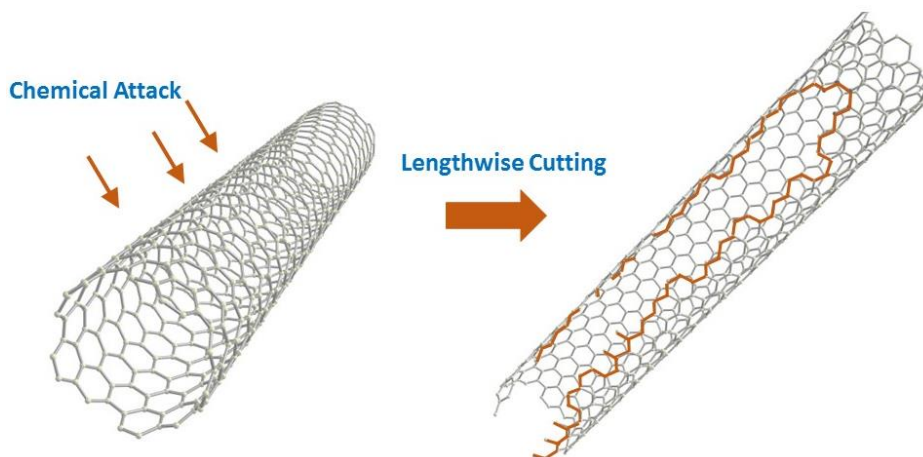


Figure 3.5. Schematic longitudinal unzipping of MWCNT

The oxidation procedure is illustrated in Figure 3.6; 150 mg of MWCNTs was stirred in 36 ml H_2SO_4 for 1 hour. Then, 4 ml of the second acid, H_3PO_4 or Trifluoroacetic acid (TFA), was added

to the mixture and stirred for 15 minutes. Next, 750 mg of KMnO_4 was slowly added to the mixture and stirred for 1 hour at room temperature, followed by another 2 hour stirring at 65 °C. Finally, the product was rinsed with 20% HCl and diethyl ether and vacuum filtered to obtain GNR flakes.

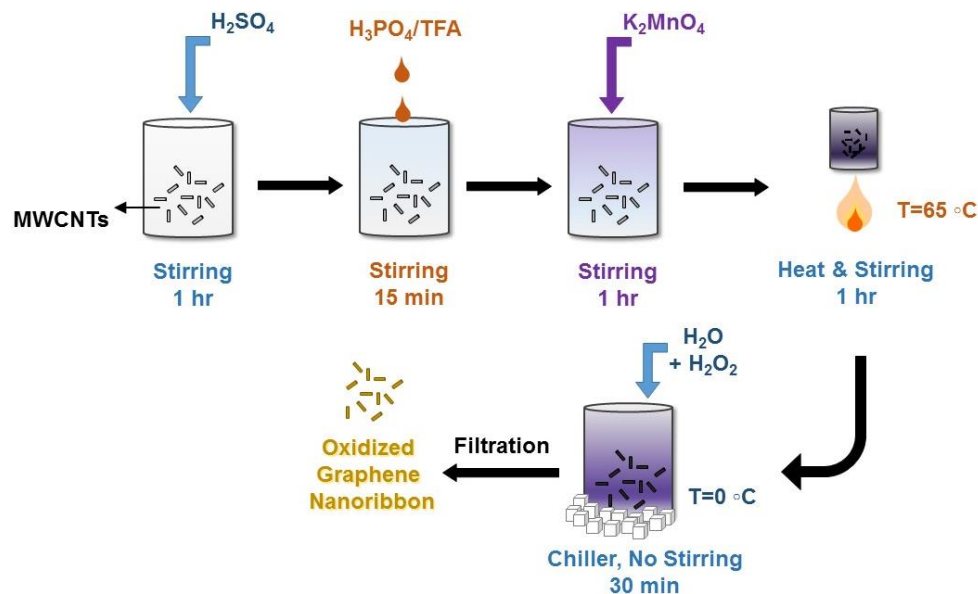


Figure 3.6. GNR synthesis process

3.2. Sample preparation techniques for characterization tests

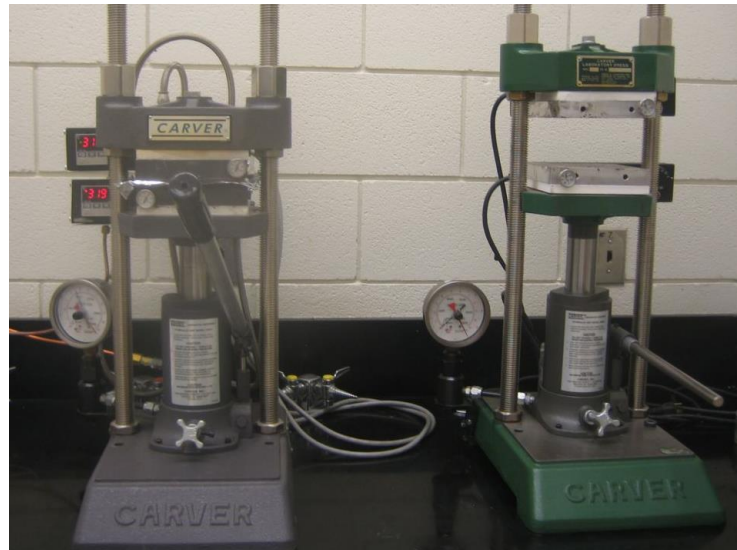
3.2.1. Molding

Different forming methods and equipment, such as injection molding or compression molding, were used to shape the polymer materials into samples for different tests and characterizations. In this thesis, all of molding was conducted using a hot compression press setup.

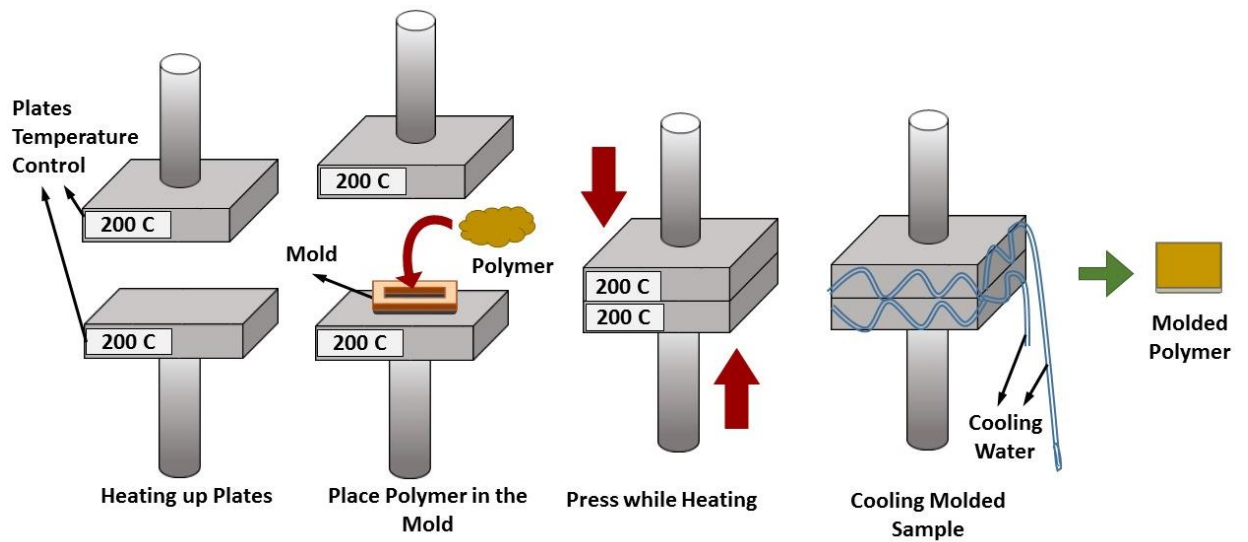
Compression molding

A Carver hot press with heating/cooling platens (Figure 3.7a) was used for both compression molding and curing of the polymer composites. The temperature and pressure of process were

controlled at the desired values according to the type and final purpose of the molded material. The heating system was a series of cartridges heaters. The cooling system of the press comprised of cold water flowing through tubes embedded in the mold. The compression molding steps are illustrated in Figure 3.7b.



(a)



(b)

Figure 3.7. (a) Hot press setup, and (b) Compression molding steps

One of the most important applications of this setup for this work is for the vulcanization process. Curing, or vulcanization, is a form of reaction used to crosslink elastomer. Crosslinks refer to the number of points that link each chain to other chains in the three dimensional network of rubbers [9]. The vulcanization process has been performed according to ASTM D5289.

3.2.2. Ultramicrotome

The filler/polymer composites should be cut to extremely thin sections, for microscopy visualization or imaging purposes. Sections should have thicknesses of about 70 nm for Transmission electron microscopy (TEM). Therefore, a Leica EM UC6 ultramicrotome (Figure 3.8) was used for ultrathin sectioning of the composites. This microtome may operate at either room temperature or at cryo-conditions, depending on the glass transition temperature (T_g) of the polymer. T_g is the temperature below which the polymer becomes hard and can be sectioned without deformation. Ultramicrotoming above T_g can lead to artifacts, thus sectioning is usually done at 50°C below T_g .

- **Room temperature** is used when the material is brittle enough to be easily cut as sections in room temperature.
- **Cryo-ultramicrotoming** is required for sectioning of the samples with a very low T_g , such as rubbers in our work. The temperature of the knife, cryo-chamber gas and the sample holder can be set and controlled at a range from -15 °C to -185 °C. The chamber is cooled through liquid nitrogen evaporation.



Figure 3.8. Ultramicrotome system for sectioning materials prior to microscopy

3.3. Characterization

3.3.1. Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was done using a TA instruments' Q-500 series was used to determine the thermal stability of nanocomposites. TGA tests can be performed under different atmospheres, such as air, H₂O or N₂, and also using different heating protocols, depending on the type of material and purpose of the test. For our composites, the tests were conducted under N₂ atmosphere. The important data obtained from the TGA are: (1) the thermal decomposition onset of the materials, which shows the thermal stability and (2) the amount of modifiers which are absorbed by the materials, which is particularly useful for the organo-modified clay in this work.

3.3.2. Differential Scanning Calorimetry

The crystallization behavior, detection of phase transition, and crosslinking procedure of materials are studied by differential scanning calorimetry (DSC) test. The test has been conducted

using a Q-500 TA Instruments DSC with different temperature rates and programs. Some of the most important results from DSC in our studies are: (1) melting temperature (T_m), (2) glass transition temperature (T_g) and (3) crystallization temperature (T_c). These data can be used to determine the amount and type of crystals and phase structure; gelation temperature, maximum curing temperature, changes in the heat capacity and enthalpy of reactions for curing behavior studies.

3.3.3. X-Ray Diffraction

Wide angle X-ray diffraction (XRD) was used to study the nanofillers' intercalation, composites morphology and crystalline structure of the polymer matrices. The tests were performed using a diffractometer with Co $K\alpha$ or Cu $K\alpha$ radiation, at wavelengths of 0.179 or 0.154 nm, respectively. The most important results obtained from XRD were the amount of intercalation and exfoliation of nanofillers, like nanoclay sheets, in the polymer matrix and the type and amount of crystalline structure. The interlayer space can be calculated from Bragg's law:

$$2d\sin\theta = n\lambda \quad \text{Eq. 3.1}$$

Where d is the interlayer spacing, in Angstroms, θ is the diffraction angle in degree and λ is wavelength in Angstroms.

3.3.4. Fourier transform infrared

Fourier transform infrared (FTIR) spectroscopy is a technique for performing qualitative and quantitative analysis of the molecular structure and chemical bonds of organic compounds, achieved by analyzing how the sample absorbs a light beam at each wavelength [2, 11]. The term

"infra-red" covers the range of the electromagnetic spectrum between 0.78 and 1000 μm . In the context of infra-red spectroscopy, wavelength is reported as "wavenumber" $\frac{2\pi}{\lambda}$, which has the unit cm^{-1} [11].

Attenuated total reflectance (ATR) is a sampling technique which is useful for liquid and solid materials without the need for further sample preparation. In this work, FTIR and FTIR-ATR spectroscopy were used to characterize the molecular structure of nanofillers, such as modified nanoclays, and the morphology of nanocomposites. The FTIR-ATR was recorded on an IL Nicolet NEXUS 470 FT-IR with Zn-Se detector.

3.3.5. Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) spectroscopy is a technique for the study of the molecular physics and crystals of materials, by analyzing the absorption and re-emission of electromagnetic radiations by the nuclei in a magnetic field [2]. Magic-angle spinning (MAS) is a technique often used to perform experiments in solid-state NMR spectroscopy [13]. The chemical shifts in NMR spectra, which are the resonant frequency of a nucleus relative to a standard, are diagnostic of the structure of a molecule [2]. Herein, the purpose of NMR is to identify the success of chemical modification and to confirm the grafting of the nanoparticles. Solid-state ^{29}Si MAS NMR was performed on a Bruker AMX spectrometer, operating at an applied magnetic field of 7.05 T, using a BL4 magic-angle spinning probe and 4 mm (o.d.) zirconia oxide rotors.

3.3.6. Microscopic Imaging

Electron microscopy imaging is a technique of imaging the ultrastructure of materials using electron beams. Two types of electron microscopy imaging were used in this work, transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

Transmission electron microscopy

Transmission electron microscopy (TEM) is based on the transmission of an electron beam through ultramicrotome-sectioned materials (i.e. 70 nm slices). The beam of electrons interacts with the specimen as it passes through and the image is formed from the interaction of the transmitted electrons with the electrons in the sample. TEM analysis was carried out on the ultramicrotomed sample sections with thickness of about 50-70 nm. There are two TEM facilities used for this work, depending on the desired resolution: the Hitachi H-7650, with 2 nm resolution and Tecnai TF20 G2 FEG-TEM, with higher resolution to 0.05 nm. The former works with 120 kV acceleration voltage, and the latter at a 200 kV. Tecnai TF20 has the standard single-tilt holder and its images were captured on a Gatan UltraScan 4000 CCD camera at 2048x2048 pixels [14].

Scanning electron microscopy

A scanning electron microscope (SEM) produces images by scanning a sample with a focused beam of electrons. The electrons interact with atoms in the sample and produce detectable signals which contain information about the sample's surface topography and composition [96]. This method of imaging provides information about external morphology, chemical composition, crystalline structure, and orientation of materials. The SEM analysis for this thesis was done by the FEI XL30 at an accelerating voltage adjustable between 0.5 kV and 30 kV [13].

3.3.7. Electrical properties

Composites made by incorporating conductive nanofillers in polymer matrices are known as conductive polymer composites (CPC). The major applications of CPCs are charge storage, electromagnetic interference (EMI) shielding and electrostatic discharge (ESD) dissipation [2, 15]. A range of electrical conductivity is required for each of the applications [16]. We have, therefore, measured these properties for our conductive fillers (namely MWCNT and GNR) polymer composites, using the following equipment and methods.

Electrical conductivity

Electrical conductivity is defined as the ordered movement of charges (electric current) when an electric field is applied. In other words, it is the ability of a material to conduct an electric current. An alternative for measuring this material property is electrical resistivity. Electrical resistivity is how strongly a material opposes the electrical current [17]. With respect to conductivity, materials are categorized into three main groups: conductive, semi-conductive and insulative. Materials with a conductivity of less than $10^{-12} \text{ S.m}^{-1}$ are known as insulators, while the conductivity range of 10^{-12} to around 10^{+2} S.m^{-1} corresponds to semi-conductors. Conductive material (semi-metals and metals) have conductivity of more than 10^{+2} S.m^{-1} [5]. Figure 3.9 shows the conductivity range for typical polymer composites.

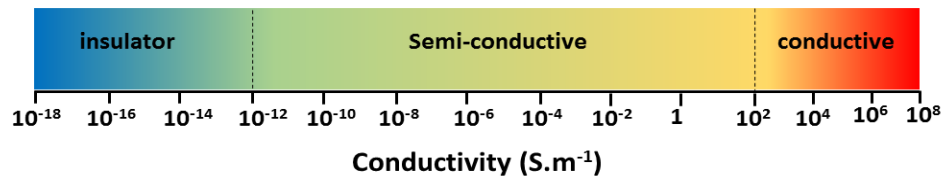


Figure 3.9. Electrical conductivity range for polymer composites [18]

Conductivity (σ) is inversely related to volume resistivity(ρ_v).

$$\sigma = \frac{1}{\rho_v} \quad \text{Eq. 3.2}$$

The volume resistivity can be calculated as follow:

$$\rho_v = \frac{RA}{t} \quad \text{Eq. 3.3}$$

$$R = \frac{V}{I} \quad \text{Eq. 3.4}$$

Where R is the measured resistance, A and t are the surface area and average thickness of the sample, V and I are potential voltage and electrical current, respectively.

Different systems were used to measure the volume resistivity of our polymer composites. Measurements were performed for rectangular molded samples (42x25x1 mm³) with the applied voltage of 10V. A Loresta GP resistivity meter (MCP-T610 model, Mitsubishi Chemical Co., Japan), connected with a four-pin probe (Figure 3.10a), was used for in-flow volume resistivity of less than 10⁴ Ω·cm, according to ASTM 257-75. For in-flow volume resistivity of more than 10⁴ Ω·cm, the measurements were carried out using a Hiresta-UP resistivity meter (MCP-HT450 model, Mitsubishi Chemical Co., Japan) connected with a piece of URS probe (Figure 3.10b).

For the 4-pin probe method, as shown in the schematic in Figure 3.11a, 4 needle-type electrodes are placed linearly on a sample. A voltage potential will be formed between 2 inner pin probes (2 and 3) is measured. Having the electrical current flow between the 2 external pin probes (1 and 4), the resistance can be estimated [19]. For the ring electrode probe, as illustrated in Figure 3.11b, the current flows across the sample and a potential voltage would be between probes. Again, the volume resistivity can be calculated using Equation 3.4.



(a)

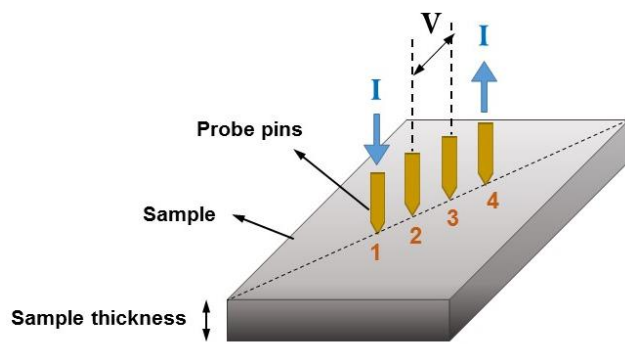


(b)

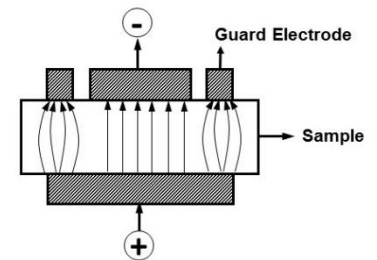
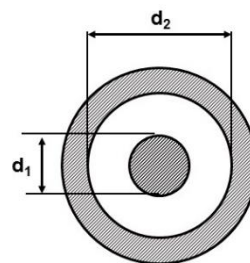


(c)

Figure 3.10. Resistivity measurement setup; a) Loresta (4 point probe in inset), b) Hiresta (ring electrode probe in inset), and c) Keithley



(a)



(b)

Figure 3.11. (a) 4-Pin probe for and (b) Ring electrode probe resistivity measurement [19]

Through thickness volume resistivity measurements were performed using a Keithley 2400 source meter for less than $10^4 \Omega \cdot \text{cm}$ and a Keithley 6517A electrometer for more than $10^4 \Omega \cdot \text{cm}$. Both types of Keithley were connected to a Keithley 8009 test fixture (Figure 3.10c). The sample is placed as insulator between two electrodes as shown in an equivalent circuit in Figure 3.12. Applying a voltage potential across opposite side of the insulator and measuring electric current through the sample, the volume resistivity can be calculated (Equation 3.4).

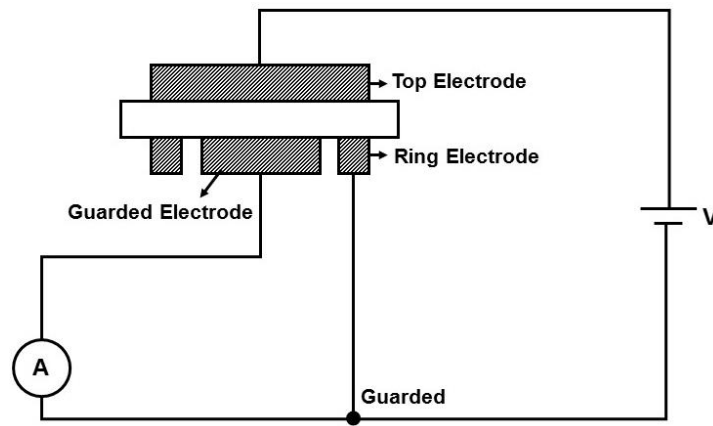


Figure 3.12. The equivalent circuit for Keithley 8009 Test Fixture [20]

Electromagnetic interference (EMI) shielding

Electromagnetic signals are induced by many electronic devices. The electromagnetic interference (EMI) shielding refers to the reflection and/or adsorption of electromagnetic radiation by a material that acts as a shield against those signals [19]. EMI shielding properties of the conductive filler/polymer composites in this work were measured by a WR-90 rectangular waveguide, using an Agilent programmable network analyzer, PNA Model E8364B (Figure 3.13), in the X-band (8.2 – 12.4 GHz) frequency range. Scatter parameters, also called S-parameters, were used to calculate shielding parameters in the EMI shielding setup [21].

The EMI shielding mechanism consists of three main mechanisms: reflection, absorption and multiple-reflection [21-23]. Therefore, the overall EMI shielding, SE_{OA} , is defined as the sum of shieldings by reflection, absorption and multiple-reflection:

$$SE_{OA} = SE_R + SE_A + SE_{MR} \quad Eq. 3.5$$

Where SE_R is shielding by reflection, SE_A is shielding by absorption, and SE_{MR} is shielding by multiple reflection. The network analyzer used to measure the EMI shielding properties consists of a signal source, a receiver and a display. The source dispatches a signal at a single frequency to the material under test. The receiver is adjusted to that frequency to detect the reflected and transmitted waves from the material. The magnitude and phase data will be measured for each signal. The source then switches to the next frequency and the measurement is repeated. Finally, the reflection and transmission measurement responses as a function of frequency will be displayed.

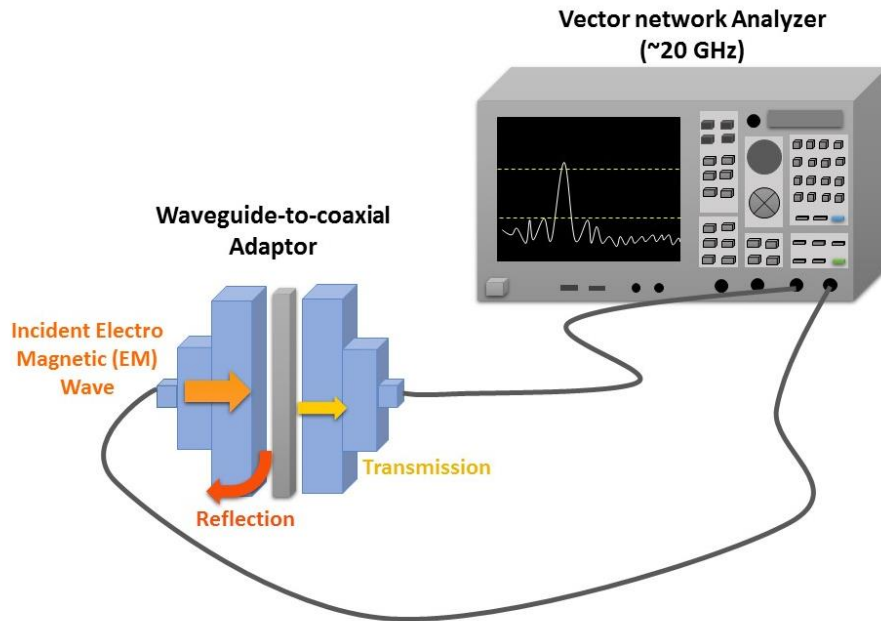


Figure 3.13. EMI shielding and dielectric permittivity measurement setup

The Scatter parameters (S-parameters) describe the performance of a two-port EMI shielding setup completely [15, 24]. S-parameters are defined as:

$|S_{11}|$: Reflected voltage magnitude divided by the incident voltage magnitude in port 1

$|S_{12}|$: Transmitted voltage magnitude from port 2 to port 1 divided by incident voltage magnitude in port 2

$|S_{21}|$: Transmitted voltage magnitude from port 1 to port 2 divided by incident voltage magnitude in port 1

$|S_{22}|$: Reflected voltage magnitude divided by the incident voltage magnitude in port 2

If the material is homogeneous, S_{11} should be equal to S_{22} , and S_{21} also should be equivalent to S_{12} . Since power of each signal is proportional to square of field strength, $|S_{11}|^2$ is equivalent to reflected power divided by incident power in port 1 and $|S_{12}|^2$ is equivalent to transmitted power from port 1 to port 2 divided by incident power in port 1.

Having S-parameters from the analyzer, the reflectance (R) and transmittance (T) are calculated as follow:

$$R = |S_{11}|^2 = |S_{22}|^2 \quad \text{Eq. 3.6}$$

$$T = |S_{12}|^2 = |S_{21}|^2 \quad \text{Eq. 3.7}$$

Then, shieldings by reflection and absorption and the overall shielding can be calculated as follow;

$$SE_R = 10 \times \log_{10} \left(\frac{1}{1-R} \right) = 10 \times \log_{10} \left(\frac{1}{1-|S_{11}|^2} \right) \quad \text{Eq. 3.8}$$

$$SE_A = 10 \times \log_{10} \left(\frac{1-R}{T} \right) = 10 \times \log_{10} \left(\frac{1-|S_{11}|^2}{|S_{12}|^2} \right) \quad \text{Eq. 3.9}$$

It is worth mentioning that no device has been developed to measure shielding by multiple-reflection separately; therefore, SE_{MR} is inherent in SE_R and SE_A . The overall shielding can be calculated as

$$SE_{OA} = SE_R + SE_A \quad Eq. 3.10$$

Dielectric Permittivity

Dielectric permittivity is material's ability to transmit (permit) the electric field and a measure of how easily a dielectric polarizes in response to an electric field. This property is important for charge storage applications of CPCs.

Permittivity has two components; real permittivity (ϵ') and imaginary permittivity (ϵ''). Real permittivity shows the amount of energy which has been stored in a material from an external field. Imaginary permittivity is the measure of dissipation of the external electric field's energy by the material. Therefore, permittivity is defined as a complex quantity as given below;

$$\epsilon = \epsilon' - i\epsilon'' \quad Eq. 3.11$$

Dissipation factor ($\tan(\delta)$) is the ratio of the dissipated energy to the stored energy and has great importance in industry as it links the capacitive and resistive currents in a material. High dissipation factor ($\tan(\delta) \gg 1$) shows a good conductor material while very low dissipation factor ($\tan(\delta) \ll 1$) indicates a good insulator. This factor is defined as below:

$$\tan(\delta) = \frac{\epsilon''}{\epsilon'} = \frac{\text{Energy dissipated/cycle}}{\text{Energy stored/cycle}} \quad Eq. 3.12$$

The S-parameters of each sample were recorded one at a time and used to calculate the complex permittivity with the Nicolson-Ross-Weir method [25]. Dielectric permittivity measurements were also done by using the Agilent programmable network analyzer, PNA Model E8364B.

The impedance of nanocomposites was calculated using the following equations:

$$Z = \frac{V}{I} \quad \text{Eq. 3.13}$$

$$I = I_R + I_C \quad \text{Eq. 3.14}$$

$$Z = Z' + iZ'' \quad \text{Eq. 3.15}$$

Where Z is impedance, V is AC voltage, I is total current, Z' , Z'' . I_R and I_C are real impedance, imaginary impedance, resistive and capacitive currents, respectively. Substituting I_R and I_C the final equations will be:

$$\varepsilon' = \frac{1}{\omega C_0} \left[\frac{-Z''}{(Z'^2 + Z''^2)} \right] \quad \text{Eq. 3.16}$$

$$\varepsilon'' = \frac{1}{\omega C_0} \left[\frac{-Z'}{(Z'^2 + Z''^2)} \right] \quad \text{Eq. 3.17}$$

$$C_0 = \varepsilon_0 \frac{S}{d} \quad \text{Eq. 3.18}$$

Where, ω is angular frequency, C_0 is the capacitance of free space, ε_0 is permittivity of free space, S and d are area and thickness of the sample, respectively.

3.3.8. Tensile test

Mechanical behavior and properties of the composites were examined by tensile tests. The schematic of the tensile test is shown in Figure 3.14a. The tensile strength tests were carried out using a TensiTech machine (Figure 3.14b) and followed the ASTM D412 standard for dumbbell specimens with the dimensions according to the standard and thickness of 2 mm [26]. Average values of the tensile strength (TS), elongation at break, and modulus of the composites were investigated in this study to explore the mechanical performance of materials.

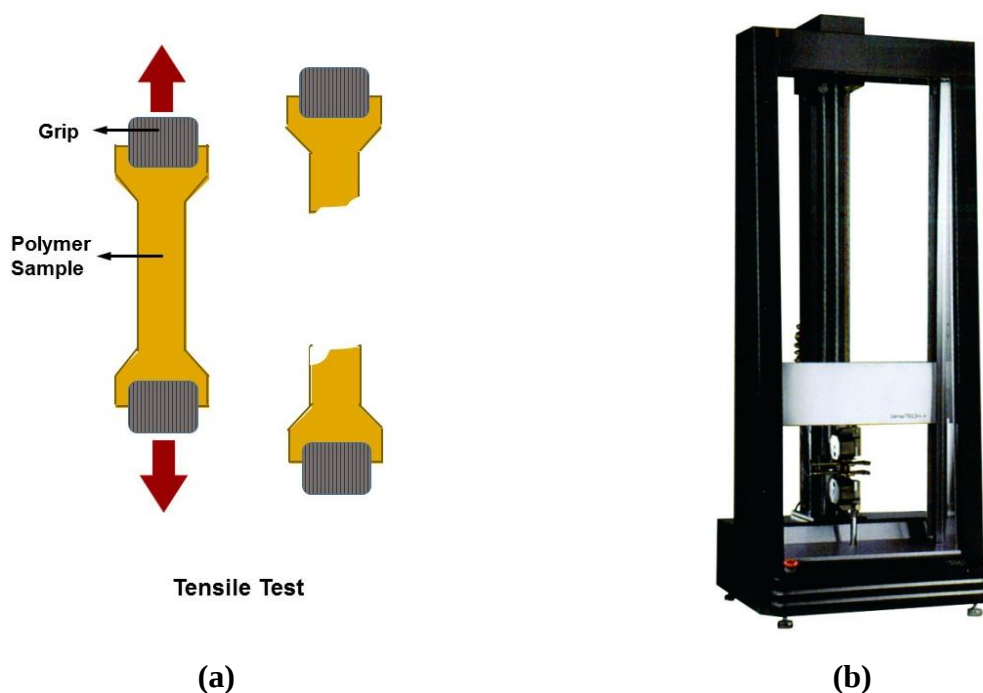


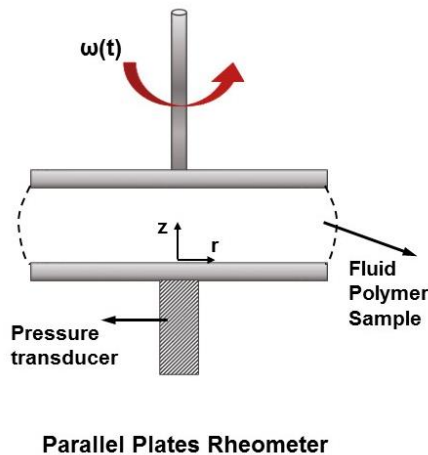
Figure 3.14. (a) Schematic of tensile test, and (b) TensiTech machine [27]

3.3.9. Rheometry

The elasticity and crosslinking processes were studied through rheometry. Two different rheometers were utilized for the investigation of rheological and vulcanization behavior of our nanocomposites.

- Non-isothermal curing behavior of MWCNT/FKM and GNR/FKM was studied using MCR 302 Anton Paar rheometer (Figure 3.15b). The viscoelastic characterization of elastomer composite materials, as a function of frequency, was determined using this equipment according to ASTM 4440. All measurements were performed utilizing parallel plate geometry (Figure 3.15a), with a diameter equal to 25mm. Samples for rheometry were pre-molded at 100 °C and 5000 psia for 10 minutes; they had a thickness of 0.9 ± 0.05 mm after removing from the mold and being cooled to room temperature. The non-isothermal curing behavior of composites was monitored by temperature sweeps from 90 °C to 250 °C in linear viscoelastic regime.

- For clay-polymer nanocomposite samples, the vulcanization and rheological behavior were studied using TechPro Moving Die Rheometer (MDR+), which was performed at 160 °C and with an oscillating frequency of 1.66 Hz, with 0.5 deg arc (ASTM D5289), for 20 minutes. The rheological characterization samples were disks, with 25 mm diameter and 2 mm thickness, prepared by compression molding at 90 °C and 10 MPa for 2 minutes.



(a)



(b)

Figure 3.15. (a) Parallel plate rheometry schematic, and (b) MCR 302 Anton Paar Rheometer [28]

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Chapter 4

Modification of Montmorillonite with Alkyl Silanes and Fluorosurfactant for Clay/Fluoroelastomer (FKM) Nanocomposites*

4.1. Presentation of the Article

The focus of this article is chemical treatment of a nanoclay, namely montmorillonite (Mnt), and effect of the modifications on the morphology and properties of Mnt/fluoroelastomer (FKM) nanocomposite. In the first section of this project, different types of modifiers including saturated and non-saturated organosilanes, and an ammonium quaternary surfactants were tested through different modification procedures. In addition to higher clay basal spacing for the modified clays, another interesting result was better thermal resistance of the modified Mnt versus the commercial available product. In the second section of this work, nanoclay/FKM nanocomposites were produced via melt-mixing process. Improved interaction of the modified Mnt with FKM led to noticeably enhanced dispersion of clay in polymer matrix and ameliorated properties such as swelling resistance, and mechanical and thermal performance of the nanocomposite. The main part of this work has been done by Maryam Khajehpour, Dr. U. Sundararaj has supervised the work, and Dr. Genaro Gelves (now with 3M, Canada) helped with interpretation of the results.

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Modification of Montmorillonite with Alkyl Silanes and Fluorosurfactant for Clay/Fluoroelastomer (FKM) Nanocomposites

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4.2. Abstract

The main objective of this work was to functionalize nanoclays with organosilanes and surfactant in order to facilitate the dispersion of the nanofillers in the host fluoroelastomer (FKM) polymer matrix. The better dispersion was achieved by improving interaction between the clay polymer nanocomposite (CPN) constituents. In the first part of this work, modification of montmorillonite (Mnt), using different saturated and unsaturated alkyl silanes and an alkyl hydrocarbon ammonium quaternary surfactant was investigated. Silicon magic angle spinning nuclear magnetic resonance (²⁹Si MAS NMR) spectroscopy, thermal gravimetric analysis (TGA), elemental analysis, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the silane-grafted clays. Results indicated that the amount of silane grafting was dependent on the specific structure of the silane. Silane-grafted Mnt was also modified with ionic surfactants intercalated between the clay sheets. A 169% increase in the clay basal spacing (from initial spacing of 1.00 nm up to 2.69 nm) could be achieved. In the second part of this work, fluoroelastomer (FKM) nanocomposites, containing custom-functionalized Mnt were

successfully synthesized, with the aim of producing reinforced high-performance materials. The effect of clay modification on the morphology and thermal properties of the CPN were studied using XRD, TGA, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The CPN made with the modified clay exhibited higher thermal stability relative to the CPN of the commercially available modified Mnt (an onset degradation point of about 40°C higher was obtained).

4.3. Introduction

In recent decades, interest in inorganic nanofiller polymer nanocomposites [1, 2] has increased. The most important advantage of nanofillers over conventional micro-particles is the remarkable improvement in the final clay polymer nanocomposites' (CPN) properties, with very low filler content, due to the interaction between polymer and filler on the nano scale [3-5]. Among nanofillers, silicate layers have gained specific attention since the 1950s, stemming from nanoclays' interesting structural features and their high aspect ratios [1, 6-9].

Nanoclay incorporation can enhance mechanical, thermal and barrier properties of polymers [7, 10, and 11]. The key factor for this improvement is the clay sheets' chemical compatibility and uniform dispersion in the host polymer [6, 12-15]. A complete delamination of the layered clays increases the interfacial interaction between the polymer chains and the nanoclays, leading to exfoliated clay/polymer nanocomposites [15, 16]. Although the hydrophilic nature of silicate layers is generally incompatible with organic polymers [2, 7, 8, 11, 16, 17-20], with active sites, such as hydroxyl groups and exchangeable interlayer cations, clay can be modified to be compatible with an organic polymer matrix [7].

Previous studies have explained that the superior properties of CPN are dependent on the clay's dispersion, the aspect ratio, and the interfacial interaction between the clay and polymer matrix [11,

14, and 20]. Large clay particles and low affinity of natural clays to most organic polymers diminish their reinforcing ability in CPN [9]. Therefore, it is important to make them compatible via organophilization of clays to facilitate their intercalation with the hydrophobic polymer macromolecules [2], so as to improve the clay sheet dispersion in the matrix and enhance efficiency in modifying the final properties [2, 14, 17-19, and 21-24] . While both the basal spacing and chemical affinity of silicate layers are important for their dispersion, two approaches are used for clay modification: interlayer ion exchange with surfactant and, treatment of functional groups on the clay surface and edges by organic compounds, such as silane [8, 9, 14, 18, and 22-25].

Montmorillonite (Mnt) is one of the most commonly studied clay minerals for polymer nanocomposites and is also the most used in different applications of CPN [9, 26]. One of the most successful ways for organophilizing clay is silane grafting, which is possible through the reaction between the alkoxy groups of silane and the hydroxyl groups of Mnt [9]. Grafting of clays with bifunctional silanes not only improves interfacial interaction, but also enables chemical reactions between clays and functional groups in the macromolecules [12, 16]. The end groups of the grafted silanes can react with monomers before polymerization and/or with polymer chains during melt mixing or vulcanization [14].

The thermal stability of Mnt/polymer nanocomposites can be improved by replacing ion exchanged ammonium intercalants with covalently bonded silane [14, 16]. Enhanced mechanical properties and an increased crystallization temperature are expected as a result of edge grafting of clay with silane [16]. While the size of the surfactant molecules is much larger than the cations that are normally placed between the silicate layers in pristine clay, the replacement of cations with surfactant should help to open up the interlayer spaces.

The reinforcement of elastomers by clay incorporation has a wide range of applications, due to their light weight, higher processability relative to metals [27], and enhanced mechanical properties

compared to traditional elastomers [27 ,28]. Although many studies have been done on CPN with thermoplastics and thermosets, much less attention has been paid to elastomers [29]. Most applications of elastomers, however, are impossible without reinforcement [10]. Fluoroelastomer (FKM) is a type of elastomer that exhibits excellent performance when high temperatures and chemical resistance are required [30]. These materials are proposed for applications where elastic behavior is needed for severe environments demanding special improved material performance such as high temperature stability and oil resistance [31].

In this work, modification of Mnt with the purpose to be more compatible with, and well dispersed in FKM was investigated using both organosilane as chemical compatibilizer and surfactant as dispersion-aid. Herein, the effectiveness of silane grafting and the use of surfactant for increasing intercalation in the clay is investigated and reported. The modification was carried out using saturated and unsaturated alkyl silanes, namely, vinyltrimethoxysilane, octadecyltrimethoxysilane, 7-octenyltrimethoxysilane, and 10-undecenyltrimethoxysilane; and a quaternary ammonium surfactant was used as cation exchanger. Incorporating the modified nanoclay in FKM, the nanocomposite was produced, and its properties were studied. The unsaturated functionalities in the silane-modified clays provide for better interaction between clays and polymers, and make it easier to fabricate reinforced elastomer nanocomposites that are vulcanized through free radical mechanisms.

4.4. Experimental

4.4.1. Materials

Montmorillonite clay, Nanofil 116 (pure unmodified Mnt), and Cloisite 20A (organo-modified Mnt with dimethyl dihydrogenated tallow quaternary ammonium surfactant) were obtained from Southern Clay Products Inc, TX, United States. The structure of unmodified Mnt is available in

literature (He et al, 2005; Herrera et al, 2004; Hussain et al, 2006). Octadecyltrimethoxysilane (90%) was purchased from Sigma-Aldrich Chemistry Company Inc., ON, Canada, and 7-octenyltrimethoxysilane (95%) and 10-undecenyltrimethoxysilane from Gelest, Inc., PA, USA, Vinyltrimethoxysilane (SCA972 silane coupling agent) was kindly provided by Struktol, ON, Canada. Masurf® FS-1620 fluoroaliphatic quaternary fluorosurfactant and Viton® fluoroelastomer (grade GF-200S) were supplied by Mason Chemical Company, OH, USA and DuPont, ON, Canada, respectively.

4.4.2. Clay modification

The two main methods of Mnt modification examined in this study as illustrated in Figure 4.1: (1) silane grafting, and (2) ion exchange with surfactant. Silane grafting is the reaction of alkoxysilane Si-O-R functionalities with hydroxyl groups on the edges of the clay forming Si-O-Si bridges with elimination of alcohols (R-OH) [9]. Typically, adding surfactant reduces the surface and interfacial tension. In this work, four different silanes were used for silylation: octadecyltrimethoxysilane, 7-octenyltrimethoxysilane, 10-undecenyltrimethoxysilane and vinyltrimethoxysilane. The exchangeable cations between the clay layers were replaced by a cationic surfactant (trimethyloctadecyl ammonium chloride) to increase the basal spacing between layers.

With both silane and surfactant used in Mnt modification, two different procedures were tested. In method 1, the surfactant was added first, followed by the silane. In method 2, silane was added to the clay prior to the surfactant. Modification procedures, using 100 mL of a mixture of methanol (90 vol. %) and water (10 vol.%) as the dispersing medium for 1 g of clay, were carried out at 70°C. 1 mL of the organosilane and/or surfactant was used per 1 g of clay and the time for the silane reaction and cation exchange with the surfactant was 4 h and 1 h, respectively. Above a certain

concentration of surfactant, there is no effect of concentration on the layer spacing, and 1mL of surfactant was above the critical amount required for this system. The modified clay was dried in a vacuum oven at 60°C for 24 h, milled in a mortar and sieved through a mesh to less than 63.5 micrometers with a USA standard test sieve.

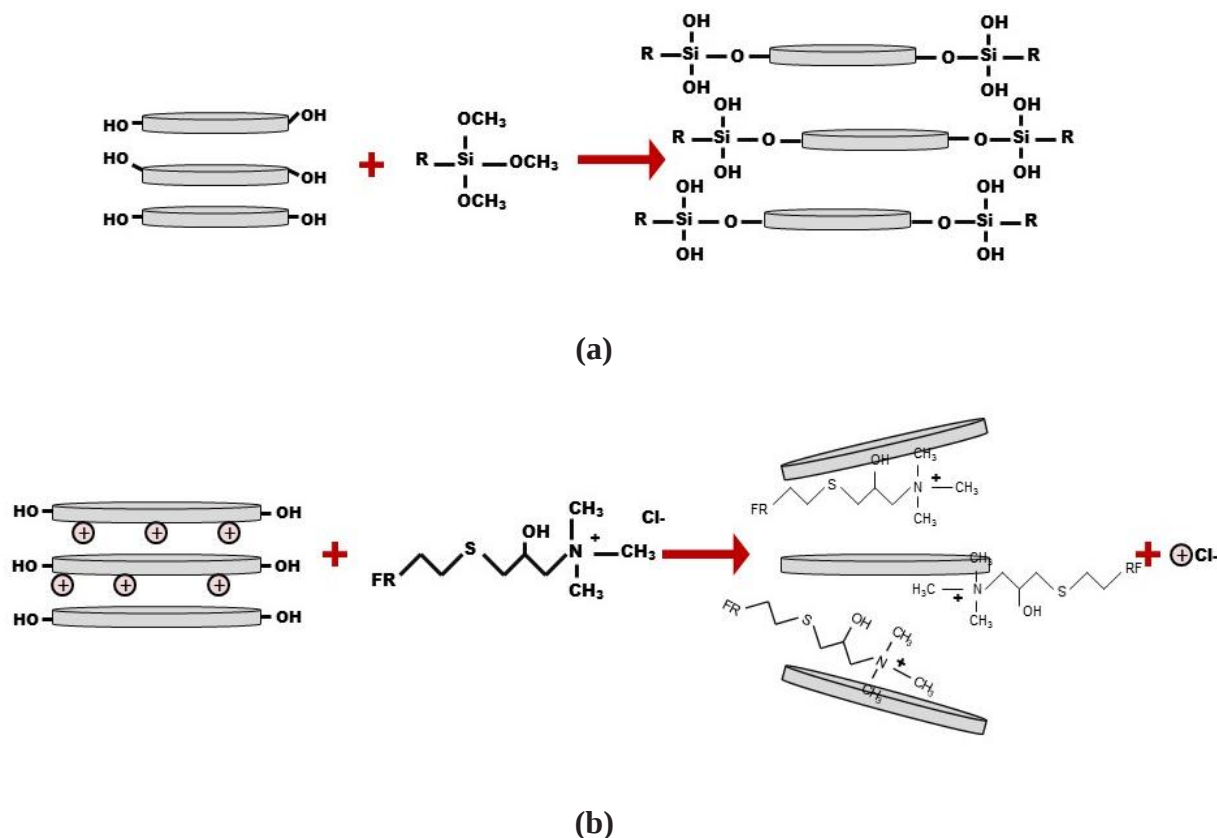


Figure 4.1. Schematics for (a) Mnt modification with alkylsilanes and (b) Mnt modification with surfactant.

4.4.3. Clay polymer nanocomposite preparation

Organically treated Mnt from the previous phase was used for FKM nanocomposite preparation. Melt intercalation is the most favored method in industry [5, 6, and 29] and, as such, was chosen for the production of CPN in this work. Two common, commercially available fillers used for making elastomeric nanocomposites are carbon black and Cloisite 20A [15, 28]. Some comparisons

were made between the results using these fillers and those of the synthesized clays using the same mixing conditions.

Melt compounding was done with a Haake internal mixer. The elastomer was first masticated for 3 min, and the clay (at a concentration of 10 phr) was added to the polymer and melt mixed for about 17 min. The mixer temperature was set at 50°C; however, elastomer mastication caused the melt temperature to rise to 80°C. The modified clay dispersion in the polymer matrix is illustrated schematically in Figure 4.2.

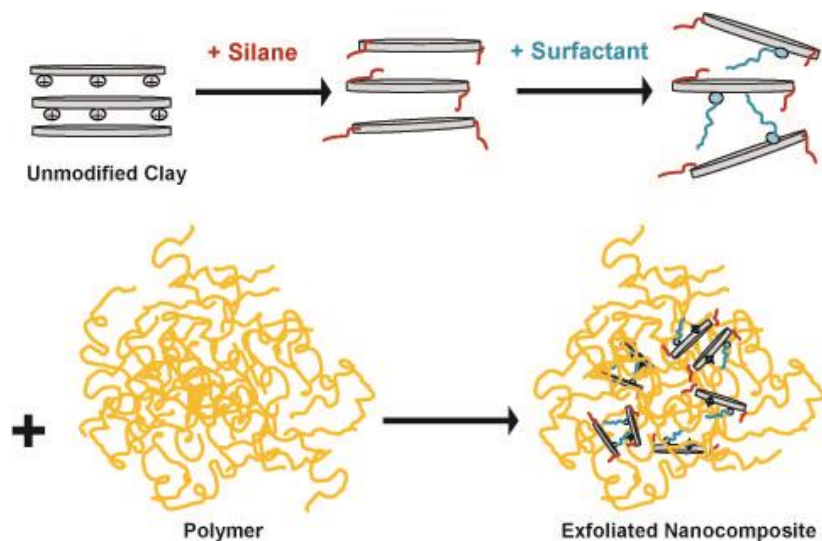


Figure 4.2. Modified clay/FKM nanocomposite preparation

4.4.4. Characterization

A TA Instruments' Q500 series (New castle, DE, USA) thermogravimetric analyzer was used to determine the thermal stability of the modified clay and CPN. The TGA testing was done on a 10-mg sample under a nitrogen (N₂) atmosphere at a heating rate of 20°C/min from 30°C to 850°C. The FTIR technique was used to characterize the modified clay. Clay samples were prepared as potassium bromide (KBr) discs (~20mm diameter) using compression molding about 2 mg of the

clay mixed with KBr. FTIR spectroscopy was run on a Nicolet Nexus 470 FT-IR ESP (Thermo Fisher Scientific Inc., MA, USA) with a cesium iodide (CsI) detector. Solid-state ^{29}Si MAS NMR spectroscopy was performed with a Bruker AMX spectrometer, operating at an applied magnetic field of 7.05 T, using a BL4 magic-angle spinning probe and 4 mm (OD) zirconia oxide rotors. ^{29}Si MAS NMR spectra were referenced to an external sample of DSS at 8.8 ppm. Clay samples were packed and spun at the magic angle at a frequency of 4.0 kHz. Elemental analysis was done using a Perkin Elmer Model 2400 series II instrument to analyze the CHN (carbon, hydrogen, nitrogen) content.

The basal spacing of clay layers and the intercalation level of clay/FKM nanocomposites were estimated from the XRD test (Rigaku Ultima III, Scottsdale, AZ, USA) with Cu K α radiation and $\lambda = 0.154$ nm. For XRD characterization, CPN samples, with a diameter of 25 mm and thickness of 2 mm, were compression molded at 90°C and 6 MPa for 2 min. The generator operated at 40 kV and 44 mA. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to examine the morphology of the CPN. TEM was carried out using a Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, OR, USA), at 200 kV acceleration voltage with the standard single-tilt holder. Cryo ultra-microtome sectioning of the samples for TEM was done with a Leica EM FC6 at -160°C using liquid nitrogen. TEM images were captured on a Gatan UltraScan 4000 CCD (Gatan, Pleasanton, California, USA) camera at 2048x2048 pixels from samples with the thickness of 50-70 nm. SEM was carried out using a SEM, FEI XL30 (FEI, Hillsboro, OR, USA) with adjustable voltage between 0.5-30 kV. The surface of the samples for SEM image was trimmed with the microtome and were coated with gold before imaging.

4.5. Results and discussion

4.5.1. Clay modification

4.5.1.1. Silane grafting

The three methoxy groups in the silane structure can be hydrolyzed in the presence of methanol/water mixtures, and the resulting hydroxyl (OH) groups enable grafting reactions with the OH groups on the clay. In this work, silane compounds, containing saturated (octadecyltrimethoxysilane) and unsaturated (10-undecenyltrimethoxysilane, 7-octenyltrimethoxysilane) alkyl chains, were successfully grafted to Mnt and their effects were compared.

From the TGA results (Figure 4.3) for unmodified and silane-modified Mnt, and the commercially available alkyl-ammonium modified clay (Cloistie 20A) a loss of mass below 200°C was observed, which corresponds to the residual solvents, organics and gases absorbed onto the clay. In the range of 100°C to 400°C, pristine Mnt typically showed decomposition of water absorbed inside the platelets (interlayer) and of water hydrating the cations that were intercalated in the interlayer. The dehydroxylation of the aluminosilicate typically occurred between 500°C and 700°C [32].

The onset temperature of degradation (Table 4.1) is defined here as the temperature at which the modified clays lost 5 mass%. Moreover, the specific molar amount of silane grafted on the functionalized clays can be calculated from the mass loss percentage using this formula (Table 4.1);

$$X = \frac{(\text{mass\% loss of modified clay}) - (\text{mass\% loss of pure Mnt})}{100 - \text{dividend}} \times \frac{1}{MW}$$

Where X is the molar amount of grafted silane per gram of Mnt, and MW is the molecular weight of the organosilane used as modifier. The unmodified Mnt used in this study exhibited a mass loss

of 1.8 % up to 200°C and a loss of 8.2% between 200°C and 700°C. The TGA of silylated clays showed that the most significant mass loss took place at 460°C for 7-octenyltrimethoxysilane-modified Mnt (Figure 4.3b), 505°C for octadecyltrimethoxysilane-modified Mnt (Figure 4.3c), and 510°C for 10-undecenyltrimethoxysilane-modified Mnt (Figure 4.3d).

The onset temperature of degradation is defined here as the temperature at which the modified clays lost 5 mass%. Moreover, the specific molar amount of silane reacted with the clay can be calculated from the mass loss percentage. These parameters for the functionalized Mnt are summarized in Table 4.1. The unmodified Mnt used in this study exhibited a mass loss of 1.8 % up to 200°C and a loss of 8.2% between 200°C and 700°C. The TGA of silylated clays showed that the most significant mass loss took place at 460°C for 7-octenyltrimethoxysilane-modified Mnt (Figure 4.3c), 505°C for octadecyltrimethoxysilane-modified Mnt (Figure 4.3a), and 510°C for 10-undecenyltrimethoxysilane-modified Mnt (Figure 4.3b).

According to the mass loss results (Table 4.1), vinyltrimethoxysilane/Mnt only had a 6.3% of mass loss, indicating that the reaction used in this study did not lead to any strong evidence of Mnt grafting with this silane. The mass loss of the unmodified Mnt in the range of 200°C to 700°C was about 8.2%. Silane-grafted Mnt, in the same temperature range showed mass losses of 13.1% for 7-octenyltrimethoxysilane- Mnt 18.9% for 10-undecenyltrimethoxysilane- Mnt and 39.8% for octadecyltrimethoxysilane- Mnt. Assuming that the same amount of dehydroxylation occurred for silane-grafted Mnt, the difference between the mass losses from 200°C to 700°C would correspond to the amount of silane grafted on Mnt for each compound.

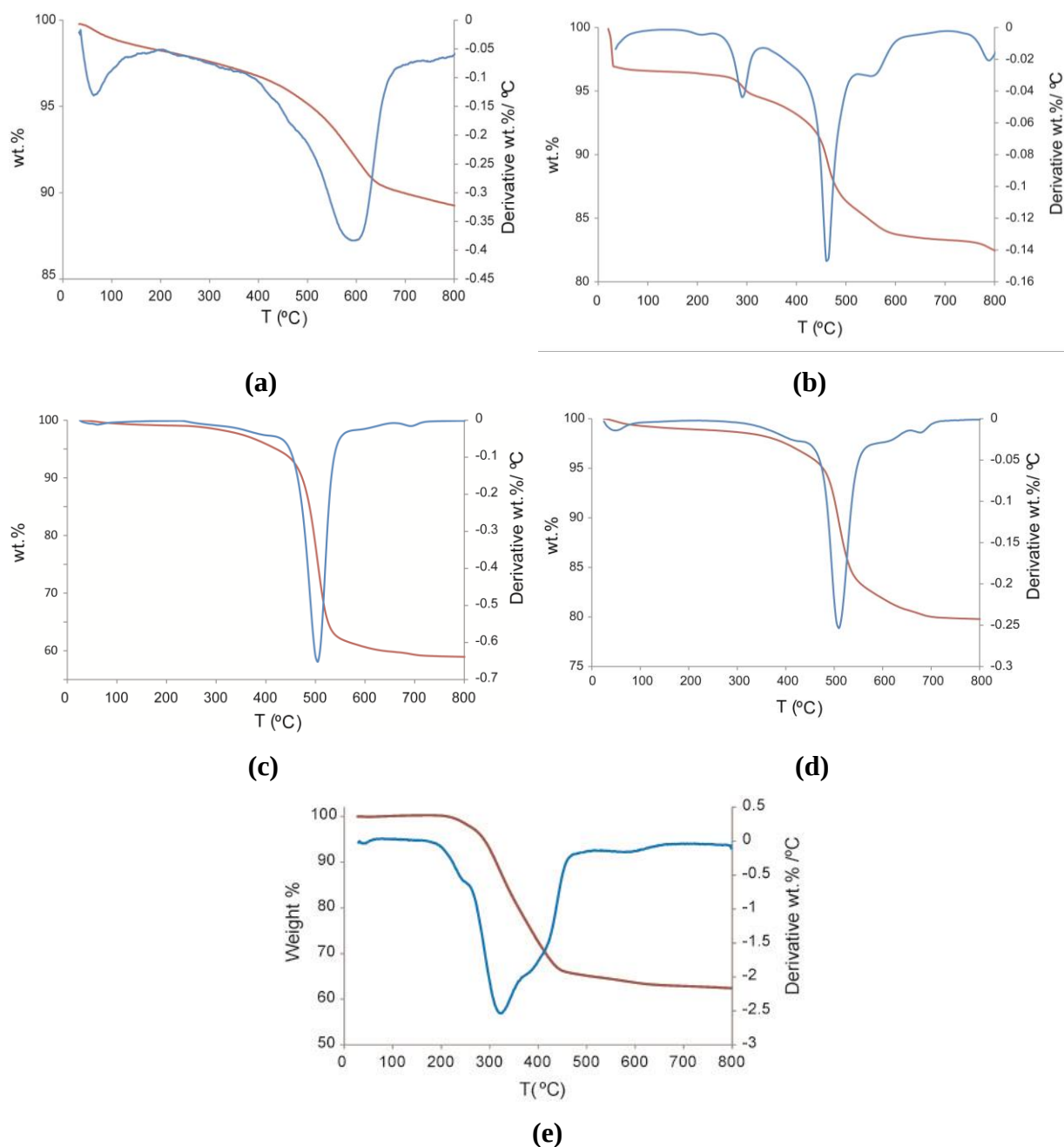


Figure 4.3. TGA (red lines) and differential TGA (blue lines) results for (a) unmodified Mnt, (b) Mnt modified with 7-octenyltrimethoxysilane, (c) Mnt modified with octadecyltrimethoxysilane, (d) Mnt modified with 10-undecenyltrimethoxysilane, and (e) Cloisite 20A.

The differential TGA (D-TGA) results show that the thermal degradation for unmodified Mnt occurred in the range of 400°C to 700°C, due to the dehydroxylation of the structural OH units of Mnt. Silane-modified Mnt exhibited decomposition in the range between 400°C and 600°C. The thermal dehydroxylation of the aluminosilicate, therefore, should overlap with the decomposition

of the silane from the clay surface. For comparison purposes, the onset temperature, based on the same criteria for a commercial Mnt modified with dimethyl dihydrogenated tallow quaternary ammonium surfactant (i.e. Cloisite 20A), is 287°C. As can be observed in the results, strong evidence exists of better thermal modification for the clay by the silanes, relative to the commercially available alkyl-ammonium modified clay (Cloisite 20A). The TGA and D-TGA results indicate that the order of thermal stability for the silane modified clays was 10-undecenyltrimethoxy > octadecyltrimethoxy >> 7-octenyltrimethoxy > Cloisite 20A.

Table 4.1. Degradation onset points for modified Mnt and the amount of silane reacted with the clay surface for different organosilane modifiers

Clay	Temperature at 5% mass loss (°C)	mass loss % (200-700°C)	mmoles of silane/ grams of Mnt
10-undecenyltrimethoxysilane- Mnt	475	18.9	0.849
octadecyltrimethoxysilane- Mnt	420	39.8	1.233
7-octenyltrimethoxysilane- Mnt	300	13.1	0.64
Cloisite 20A	287	38	-

The onset temperatures for silane-grafted Mnt demonstrated the higher thermal stability of these clays versus those modified with quaternary ammonium surfactants. The silicon-oxygen-silicon (Si-O-Si) bonds formed between the clay surface and the silane were more thermally stable than the ionic bonds formed between ammonium- or phosphonium-based surfactants typically used for modification of clays for polymer nanocomposites. Thus, grafting of Mnt with silane led to modified clays with increased thermal stability and, consequently, greater thermal stability of the polymer nanocomposite materials.

The elemental analyses (Table 4.2) confirm the silane grafting on clay's surface, and indicate that the amount of modifier grafted on the clays. One conclusion can be that the amount of silane grafting was higher for silanes with longer chains.

Table 4.2. Elemental analysis of unmodified and silane-modified Mnt

Clay	Actual element (%)	
	Carbon	Hydrogen
Mnt	0.96	1.50
Octadecyltrimethoxysilane- Mnt	31.86	5.78
10-undecenyltrimethoxysilane- Mnt	13.08	2.57
7-octenyltrimethoxysilane- Mnt	9.62	2.09

FTIR spectra of pure Mnt and silylated clays (Figure 4.4) show evidence of the organosilane grafting for the modified Mnts. The peaks in the range of 1000 cm^{-1} to 1130 cm^{-1} and the signal at about 1430 cm^{-1} were attributed to Si-O-Si bonds [33, 34] that existed for both the unmodified and modified clays. More specifically, the peak around 1040 cm^{-1} corresponded to Si-O-Si stretching [28]. The absorption at around 900 cm^{-1} was related to OH deformation, which is linked to cations; and, the peak at 1635 cm^{-1} corresponded to hydrogen-oxygen-hydrogen (H-O-H) deformation [35].

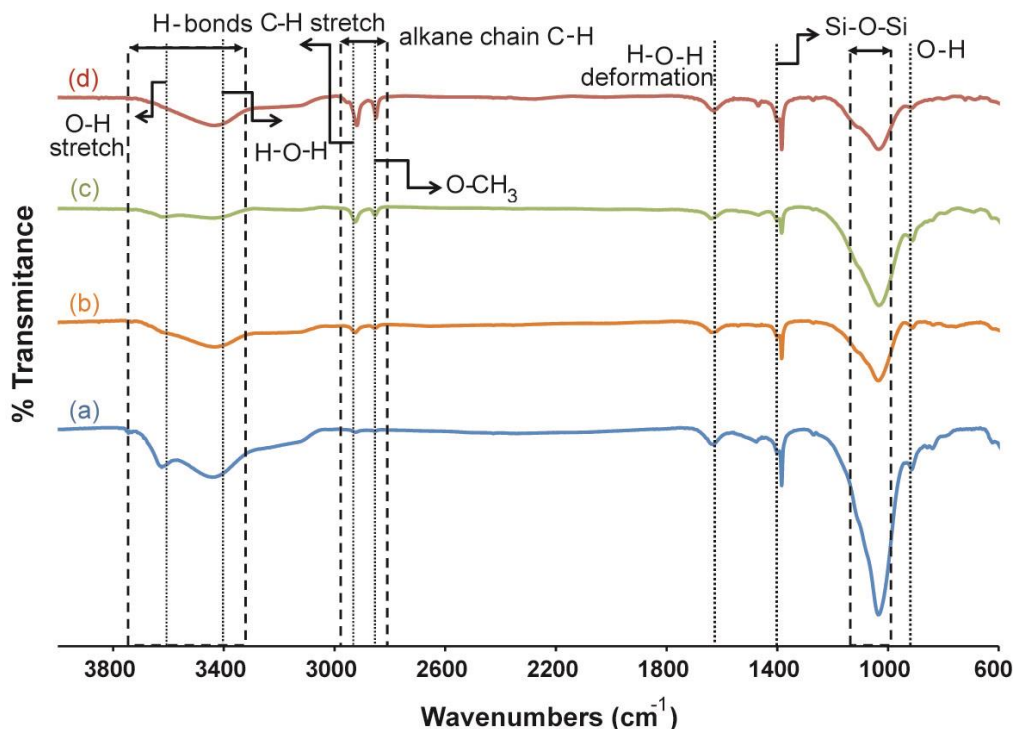


Figure 4.4. FTIR results for (a) unmodified Mnt (blue line), Mnt modified with (b) 7-octenyltrimethoxysilane (orange line), (c) 10-undecenyltrimethoxysilane (green line), and (d) octadecyltrimethoxysilane (red line)

Generally, the absorption peaks in the range of 2850 cm^{-1} to 2960 cm^{-1} can be attributed to C-H (carbon-hydrogen) from alkyl chains [36]. The peak at 2940 cm^{-1} showed the C-H stretch [37] for C atoms that are bound to OH groups. The peak at 2830 cm^{-1} confirmed the oxygen-methyl (O-CH₃) bond [38], but this may also indicate unreacted methoxy groups of the silane. Also the peak at 2850 cm^{-1} can be related to CH₂ stretching modes [39], which is again an indication of alkyl chains of the grafted organosilanes. The broad peak in the range of 3200 cm^{-1} to 3500 cm^{-1} can be assigned to intermolecular H bonds, which could be seen for unmodified clay [40], whereas the peak at 3400 cm^{-1} corresponded to H-O-H hydrogen-bonded water [35], which existed in both the octadecyltrimethoxy and vinyltrimethoxy silane-modified clays. This may be due to the O-H bonds on the platelet surface and substitution of methoxy groups of the silane after synthesis. The same is true for the peak at 3634 cm^{-1} , which can be attributed to O-H stretching vibration [35].

²⁹Si MAS NMR spectroscopy (Figure 4.5) was used to confirm the grafting of Mnt with different silanes. The chemical shifts are summarized for both the unmodified and silane modified clays (Table 4.3). The spectrum for unmodified Mnt displayed only one peak at -86.8 ppm; whereas silane-grafted Mnt exhibited additional peaks at -68.2 ppm and -61.1 ppm for octadecyltrimethoxy silane, -55.11 ppm and -44 ppm for undecenyltrimethoxy silane and -53.4 ppm and -51.2 ppm for octenyltrimethoxy. The resonance signal at -86.8 ppm corresponded to Q³ [Si(OSi)₃O(Al, Mg)], which is characteristic of the silicon atom forming the layered silicate. No signal was detected for Q⁴ [Si(OSi)₄], indicating that silica was not present in the clay while also demonstrating the purity of the Mnt [41]. Generally, signals in the range -80 to -120 ppm show Q¹, Q², Q³ or Q⁴ silicon types with 4 attached Oxygens which by substitution of any methyl group would be shifted to T types in the range of -70 to +10 ppm (Process NMR Associates webpage, 2012). The resonance signals that appeared at about -60 to -70 ppm for octadecyltrimethoxysilane- Mnt correspond to T³

[Si(OSi)₃R] [42], where R corresponds to the alkyl chain of the silane used for grafting. The signals at -55 ppm and -44 ppm for undecenyltrimethoxysilane- Mnt are due to T² [Si(OSi)₂(OH')R] and T⁰, respectively. T⁰ is an indication of hydrolyzed intermediate with no condensed Si-OH groups [42]. Also, the signals between -50 and -55 for the octenyltrimethoxysilane- Mnt should be related to T² and T³ [Si(OSi)₃R]. Taking the NMR spectra results into account, the appearance of new signals and decrease in the intensity of Q³ signals confirms the condensation reaction of the clays 'surface silanol groups [41] and grafting of different organosilanes on Mnt.

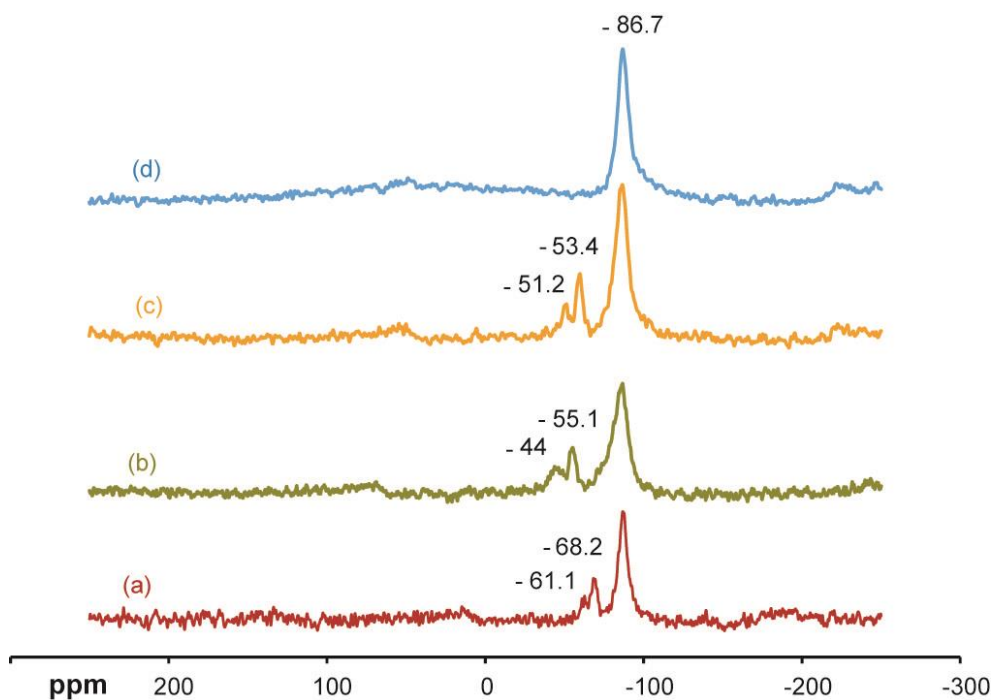


Figure 4.5. NMR results for (a) Mnt modified with octadecyltrimethoxysilane (red line), (b) Mnt modified with 10-undecenyltrimethoxysilane (green line), (c) Mnt modified with 7-octenyltrimethoxysilane (orange line), and (d) unmodified Mnt (blue line).

Table 4.3. NMR chemical shifts for silane-modified and unmodified Mnt

Sample	Chemical Shifts (ppm)
Mnt	-86.708
octadecyltrimethoxysilane- Mnt	-86.76, -68.2, - 61.1
10-undecenyltrimethoxysilane- Mnt	-86.70, -44, - 55.11
7-octenyltrimethoxysilane- Mnt	-86.52, -53.4, - 51.18

Basal spacing for different silane grafted Mnt and the pristine unmodified Mnt (Table 4.4) can be calculated from wide angle XRD results using Bragg's law, $2d \cdot (\sin\theta) = n\lambda$, where d is the basal spacing in angstroms, θ is the diffraction angle in degrees, and λ is the wavelength in angstroms and is equal to 1.54 Å for Cu K α radiation. The d for Mnt has been reported in the literature as 0.95 nm to 1.17 nm [43, 28]. The results of this work indicate that the initial interlayer space (i.e. 1.00 nm) was slightly increased after silane grafting. Some amount of silanes, therefore, had been intercalated between clay sheets while the rest of silane were grafted at the edges via a condensation reaction with hydroxyl groups at the clay edges [7].

Table 4.4. Basal spacing for modified and unmodified Mnt

Sample	d_{001} (nm)
Mnt [28, 43]	0.95-1.17
Mnt (experimental result)	1.00
Octadecyltrimethoxysilane/ Mnt	1.22

4.5.2. Effect of surfactant modification

Previous studies on the silane modification of clay reported the possibility of a blockage of the interlayer spaces between the clay platelets by silane molecules grafted on the clay edges [7]. Experiments with a quaternary ammonium surfactant were carried out in this study to determine if the silanes at the clay edges prevent intercalation. The outcomes of different clay treatment

procedures were different, depending on the order of the two steps of modification (i.e. the order of adding the silane and the surfactant). In Method 1, surfactant was added first and in Method 2, silane was added first.

The XRD results (Figure 4.6) show a significant increase in the basal spacing for the Mnt that was modified with both silane and surfactant than that of unmodified clay. The basal spacing (d_{001}) was observed that has been considerably increased in both orders of modification, indicating that the surfactant was successfully intercalated in the clay. While the modification of the clay with both species can be carried out in either order to result in intercalated/silinated clay, a larger interlayer space was achieved with Method 2. Method 2 showed an additional expansion of 0.3 nm over Method 1, which was an increase of about 30% based on initial basal spacing. The reason for the difference may be that the surfactant increased the interlayer space initially in the first method; however, with the addition of silane, some surfactant was flushed out from the interlayer spaces.

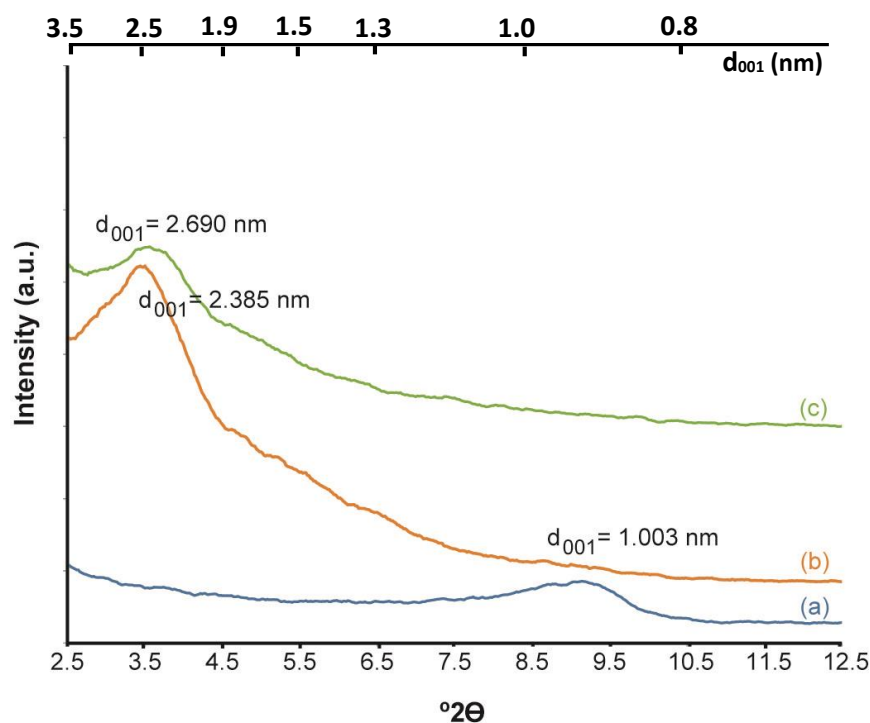


Figure 4.6. XRD results for (a) unmodified Mnt (blue line) and (b) modified Mnt using method 1-surfactant addition prior to that of silane-(orange line), and (c) modified Mnt using method 2 - silane addition prior to that of surfactant-(green line).

FTIR results for both the modified and unmodified Mnt (Figure 4.7) show the effect the two methods of modification on chemical bonds of the clays. The peaks in the range of 2800 cm^{-1} to 3000 cm^{-1} show the alkyl chain of both the surfactant and silane, indicating their attachment to the clay surface. The decrease in the intensity of peaks at $3200\text{--}3600\text{ cm}^{-1}$ region, which is correspond to stretching vibration H-bonded Si-OH groups, comparing to unmodified Mnt is due to organic surfactant intercalated into the Mnt interlayers. The decrease of peaks at 3450 and $3600\text{--}3730\text{ cm}^{-1}$, which correspond to the stretching vibration of surface Si-OH groups confirms the reaction of modifiers with the surface of clay [44, 45].

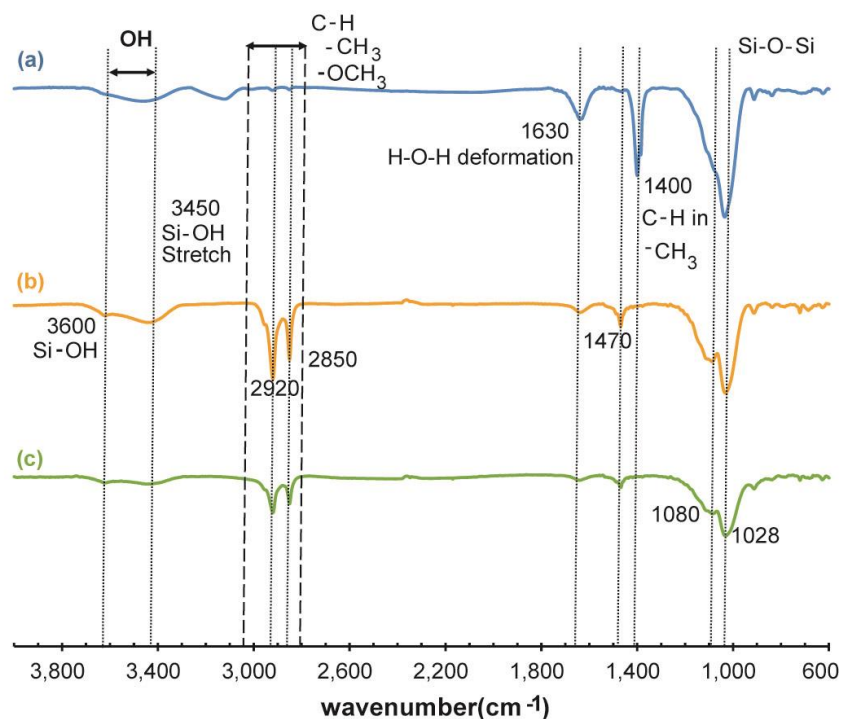


Figure 4.7. FTIR results for (a) unmodified Mnt (blue line) and modified Mnt using silane and surfactant with (b) method 1-surfactant addition prior to that of silane-(orange line), and (c) method 2-silane addition prior to that of surfactant-(green line).

The development and increase in the intensity of the peaks at 2850 and 2930 cm^{-1} are an indication of O-CH_3 and -CH_2 groups giving evidence of the attachment of the alkyl chain of the organic modifiers on the clay surface [45]. The development and increase in the intensity of the

peaks at 2850 and 2930 cm^{-1} are the indication of O-CH_3 and $-\text{CH}_2$ groups [45] or can be corresponded to symmetric and antisymmetric CH_2 stretching modes [39]. With either ways of interpretation, these peaks are evidence of attachment of the alkyl chain of the organic modifiers on the clay surface.

Generally the peaks between 1000 and 1260 cm^{-1} correspond to Si-O bonds that can be from silica, silane-silica or silane-silane sources [46]. However, the appearance of the new shoulder at 1080 cm^{-1} in modified Mnt is a proof of existence of Si-O-Si and is another indication of grafting of organosilanes on Mnt surface [42]. It is a possibility that the surfactant has been a factor in creating these Si-O-Si bonds since the shoulder at 1080 cm^{-1} is not visible in Figure 4.4. Up to this point, the characterization results have strongly indicated that Mnt was both modified at the clay edges by alkylsilanes and at the interlayer space by ionic surfactants.

4.6. Modified clay/FKM nanocomposites

4.6.1. Dispersion and morphology

The intercalation of FKM in CPN is reported as the interlayer space (d_{001}) of clay layers in the FKM matrix (Table 4.5) demonstrate that larger basal d-spacing can be obtained for modified clays than for unmodified clay. The treatment of the clay by surfactant, in addition to silane modification, caused slightly higher intercalation of clay. However, when introduced in the polymer matrix, the final basal spacing for the nanocomposites was similar for all the clays. This may be a consequence of interaction of clay and polymer during CPN production. The decrease in basal spacing for the 18CSI-SF-Mnt/FKM may have been due to unbound surfactant that was in the clay galleries that were pushed out by the polymer chains during intercalation.

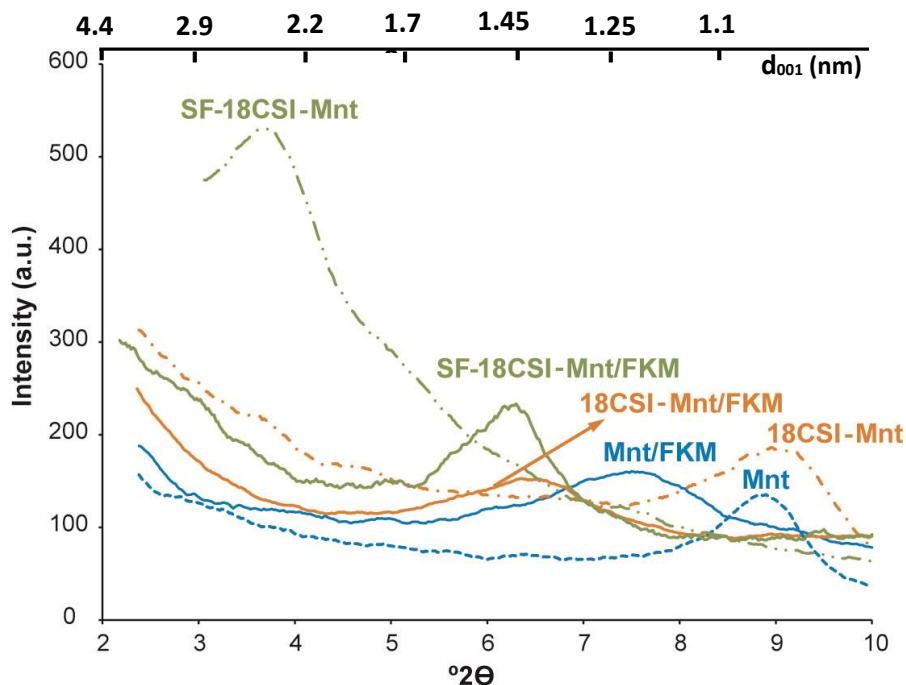


Figure 4.8. XRD results for unmodified Mnt (blue dashed line), octadecyltrimethoxysilane-Mnt clay; 18CSI-Mnt (orange dashed line), clay modified with silane and surfactant; 18CSI-SF-Mnt (green dashed line), and the respective nanocomposites with FKM (continues lines with same color as for the clays).

Table 4.5. Intercalation of modified and unmodified Mnt/FKM nanocomposites

Sample	Filler	d_{001} (nm)
18CSI-SF-Mnt/FKM	octadecyltrimethoxysilane-fluorosurfactant-Mnt	1.447
18CSI- Mnt /FKM	octadecyltrimethoxysilane-Mnt	1.417
Mnt/FKM	Mnt	1.168

The effect of these modifications in d_{001} is observed to be more significant for pristine clay, which was not introduced into the polymer matrix. This may be a consequence of interaction of clay and polymer during CPN production. One possible mechanism for this phenomena is the excess unbounded fluorosurfactant intercalated in the gallery between clay sheets. These unbounded excess molecules cause an increase in the interlayer space of the clay sheets while they will be flushed out by polymer molecules during melt-mixing process.

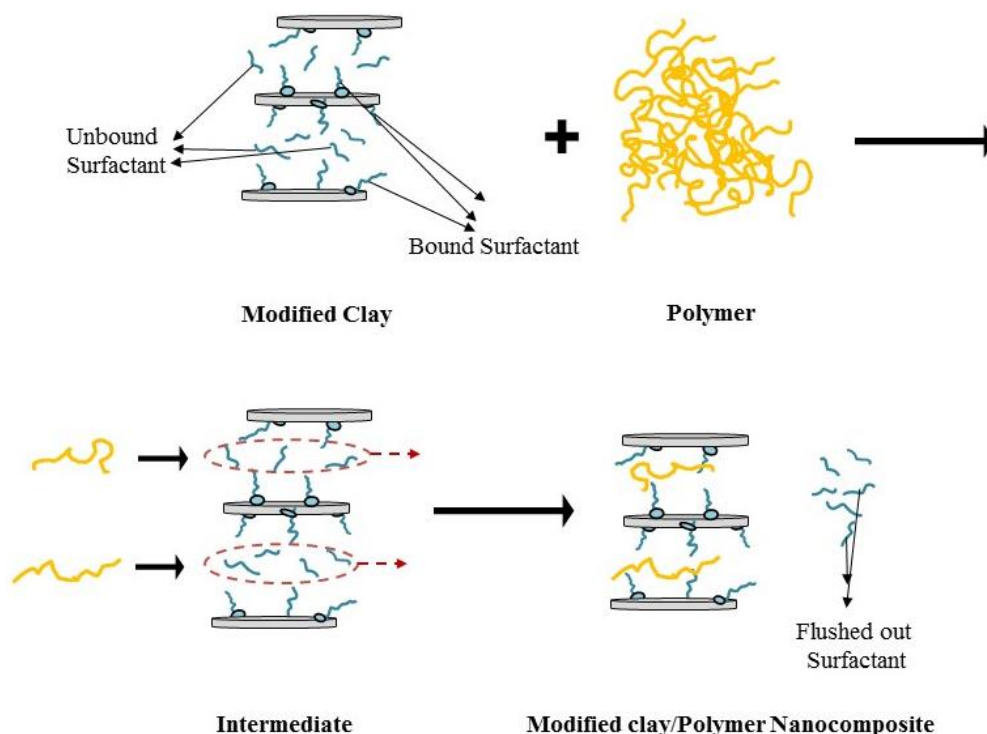


Figure 4.9. d-spacing decrease during nanocomposite production

As has been illustrated in the schematic of Figure 4.9, some of the surfactant molecules are bounded with the clay and some other excess amount are not. Having high affinity with the fluoroelastomer polymer matrix, these unbounded amount may be flushed out of the gallery to the polymer matrix hence, the basal spacing between clay sheets will be reduced.

Through the investigation of the morphology of different fillers and FKM nanocomposites, significant improvement in the dispersion of nanoclays into the FKM matrix was obtained by combined silane grafting and surfactant treatment. From TEM images (Figure 4.10) less agglomeration was observed for the silylated Mnt than the unmodified one. Consequently, improved distribution and higher intercalation can be achieved by silane modification of nanoclays.

The effects of surfactant on the dispersion of modified clay were also investigated by TEM and SEM imaging. The effect of surfactant modification of nanoclays, as can be observed from TEM images (Figure 4.11), confirms that the ion exchange in clays by surfactant resulted in an enhanced

intercalation of clay particles into the CPN. Also, noticeably better dispersion for the surfactant-silane-modified clays than the silane-modified clays in the FKM matrix was observed in SEM images (Figure 4.12). This is due to higher intercalation between the clay layers because of the existence of surfactant molecules in the interlayer space. As a result of enhanced dispersion of fillers improved mechanical properties [20] and oil or chemical resistance are expected.

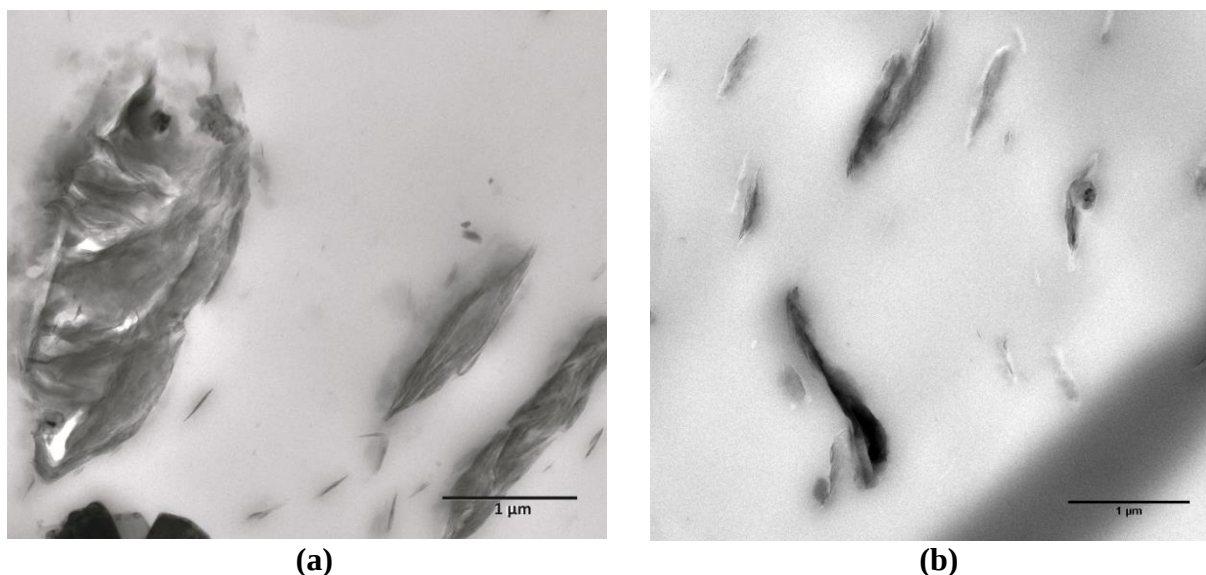


Figure 4.10. TEM image of (a) unmodified Mnt /FKM, (b) organosilane-modified Mnt /FKM

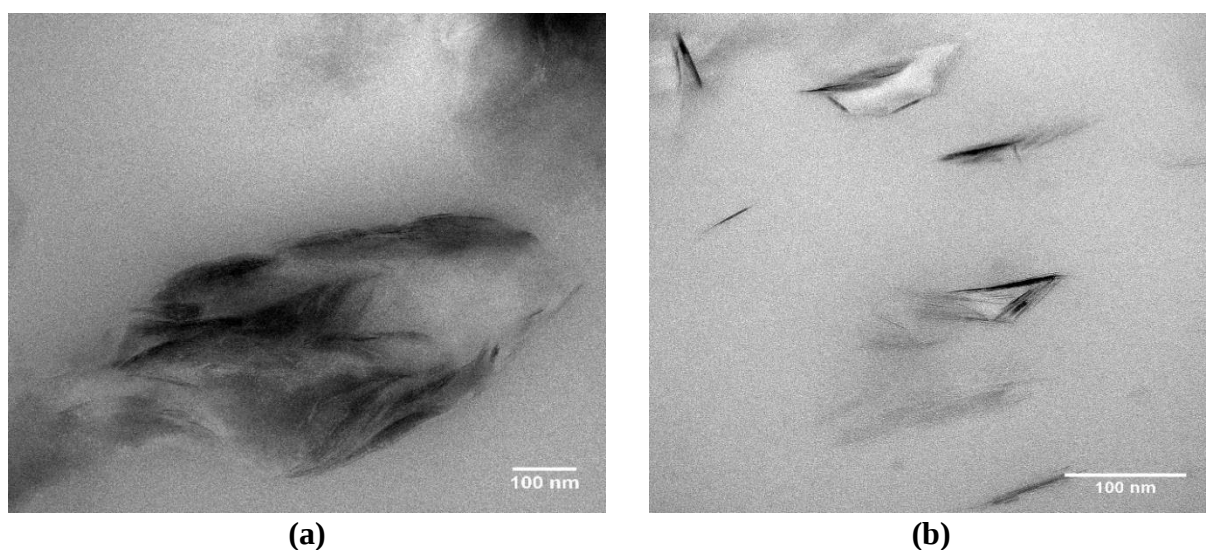


Figure 4.11. TEM images of (a) silane-modified Mnt /FKM and (b) surfactant and silane modified Mnt /FKM

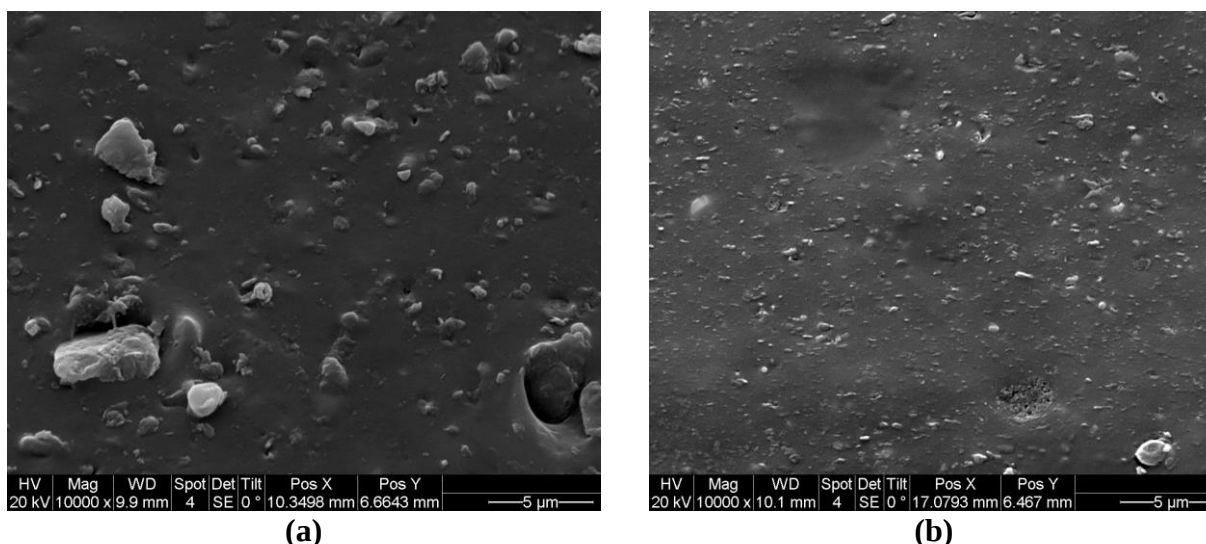


Figure 4.12. SEM images of (a) silane-modified Mnt /FKM and (b) silane and surfactant modified Mnt /FKM

4.6.2. Thermal stability

Another important property of CPN is its thermal resistance for high-temperature applications. The effect of the applied modifications on the thermal stability of the resultant CPN, therefore, was also studied. In this regard, TGA testing for the different clay/FKM nanocomposites was conducted (Table 4.6). The filler concentration for all the CPN was 10 phr, and the method of compounding was melt intercalation in a ThermoFischer Haake internal batch mixer.

Considering a mass loss of 5% as the onset degradation point, one may conclude that silane modification brought about an increase in the thermal stability of the CPN, relative to commercially modified clays (Cloisite 20A). The use of ammonium ions as surfactant for clay treatment, however, has a negative effect on the thermal stability of the CPN [47]. Moreover, the use of carbon black as the second filler caused a decrease in the temperature where degradation started. The optimum treatment of the clay, therefore, depends on the final application and the favored properties of the elastomer nanocomposite to which the clay is incorporated.

Table 4.6. 5% mass degradation start point for modified and unmodified Mnt /FKM nanocomposites

Clay Polymer nanocomposite	Filler	T (°C)
18CSI-Mnt/FKM	octadecyltrimethoxysilane- Mnt	425
CB-18CSI-Mnt/FKM	Carbon black /octadecyltrimethoxysilane - Mnt	415
18CSI-SF-Mnt/FKM	octadecyltrimethoxysilane-fluorosurfactant- Mnt	390
Cloisite 20A / FKM	Cloisite 20A	386
FKM	N/A	416

4.7. Conclusion

Considering the fact that both chemical compatibility and dispersion of nanoclays in polymer affect the final properties of CPNs, simultaneous modification using organosilane and surfactant have been successfully performed in this work via two different methods. Mnt with both intercalated fluorosurfactant and silane modification on the edges were produced. This is the first report of using both fluorosurfactant and silane for clay functionalization. By using different saturated and unsaturated silanes on Mnt, it was found that the amount of silane grafting and the thermal stability of the clay both vary depending on the silane chemical structure. Results demonstrated that surfactant and silane addition could noticeably increase the basal spacing for montmorillonite (Mnt) from an initial spacing of 1.00 nm up to 2.69 nm; essentially, a 169% increase. This is one of the few studies that investigated different length silanes for modification of clay surfaces. Silanes with longer alkyl chains were more readily grafted on the clay edges relative to those with shorter alkyl chains. The thermal stability of silane-modified Mnt was much higher than the commercially available modified Mnt, which was modified by a tallow surfactant. Further modification of clay, with a fluorosurfactant to increase the spacing between the clay layers, was successfully performed. These materials were also more thermally stable than the commercially available Mnt. A significant increase in clay interlayer spaces was achieved with the ion-exchange reaction as the result of surfactant modification of Mnt; this increase in basal d-spacing has been

shown to lead to a better dispersion of clays in the nanocomposites (Bukka and Miller, 1992). Enhanced interaction between the modified clay and the FKM, and hence, improved dispersion of the nanoclay in polymer matrix was achieved. The best intercalation and exfoliation of the clays was obtained by clay modification with surfactant prior to silane grafting.

4.8. References

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Chapter 5

Tuning the curing behavior of fluoroelastomer by incorporation of nitrogen doped graphene nanoribbons*

5.1. Presentation of the Article

In this chapter, we report synthesis of a novel nanofiller, namely graphene nanoribbon (GNR), from parent multiwalled carbon nanotubes (MWCNT). In addition, nitrogen doping and thermal reduction of the GNRs and MWCNTs were performed via chemical and thermal treatments. In the next step, the customized nanofillers, i.e. GNRs and MWCNTs, have been incorporated in fluoroelastomer (FKM) matrix through a solution mixing/melt mixing protocol. The surface chemistry of both nanofillers and nanocomposites are investigated through X-Ray Photoelectron Spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). The effect of both modified and non-modified GNR and MWCNT on the final properties and curing behavior of GNR/FKM and MWCNT/FKM nanocomposites are discussed. The main target was to tune the crosslinking density of GNR/FKM nanocomposites via surface modification of the nanofillers. Curing process, rheological and elastic behavior of the samples studied using differential scanning calorimetry (DSC) and rheometry. The main part of experiments in this work for production and characterization of the samples has been done by Maryam Khajepour, Mr. S. Sadeghi helped with the rheology and results interpretation, Mr. A. Zehtab Yazdi helped with nanofiller synthesis and results interpretation, and Dr. U. Sundararaj has supervised the project.

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Tuning the curing behavior of fluoroelastomer (FKM) by incorporation of nitrogen doped graphene nanoribbons (CNx-GNRs)

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5.2. Abstract

Graphene nanoribbons (GNRs), obtained by different methods from carbon nanotubes (CNTs) or graphene, are attractive materials for polymer nanocomposites due to their considerably high interfacial area, as compared to CNTs. Consequently, a better adhesion with a polymer matrix is anticipated for GNRs. Also, surface modification of these nanofillers, such as nitrogen doping, is known to be an efficient method to improve their properties. In this work, fluoroelastomers (FKM) were used as the polymer matrix to host GNRs. Undoped and nitrogen doped GNRs (CNx-GNR) were synthesized from the parent multiwall carbon nanotubes (MWCNTs). MWCNT/FKM and GNR/FKM nanocomposites were prepared via a solution mixing/melt mixing protocol.

Adding nanofillers can affect the crosslinking density of crosslinked polymers, such as elastomers and rubbers. The effect of interfacial interaction between the functional groups on the surface of the GNR and FKM matrix have been studied in this project. Our results showed that the concentration and type of the surface functional groups were the main contributors in determining

the cure behavior of the nanocomposites. While reduced CN_x-GNR had a similar cure behavior as neat FKM, oxidized GNRs had relatively slower cure kinetics. These observations were found to be correlated with the presence of a hydroxyl functional group on the surface of oxidized GNRs (O-CN_x-GNR).

5.3. Introduction

Fluoroelastomer (FKM) has been used in many industrial applications, such as gaskets, seals and O-rings, due to its unique combination of mechanical properties and excellent resistance to chemicals and heat [1-3]. End-use requirements usually dictate the type of fluoroelastomers, vulcanization system and the fillers to be used [4]. Vulcanization is the process through which individual linear polymer chains convert to a three dimensional cross-linked network [5]. The network structure significantly affects the elasticity and properties of rubbers; a homogenous three dimensional network leads to considerably higher ultimate properties [6]. Likewise, filler incorporation in the elastomeric compound can affect the vulcanization process, as well as the final properties [7].

For decades, silicas and carbon blacks have proven their capabilities in meeting a wide range of requirements in the rubber industry. Functional groups, introduced on the surface of fillers, are believed to induce differences in the cure behavior by changing both the cure reaction mechanism [8] and the cure reaction kinetics [9]. There is long-standing literature on cure enhancement by incorporation of carbon blacks in rubber compounds. The presence of functional groups, such as carboxyl, quinone, phenol and lactone groups, alongside other surface properties, was considered as the main reason behind improved effects. Filler surface properties, including total surface area,

porosity, surface roughness and surface activity, play major roles in determining final physical and mechanical properties of elastomeric compounds. Although filler surface activity is poorly defined, this term has been widely used in the filled polymer research area. Highly structured carbon blacks, with high surface activity, are known to have a significant effect on cure behavior and crosslink density. Adding silica-containing binding systems [10], graphitization and polymer grafting [11, 12] are some of the frequently used methods to alter the surface activity of carbon blacks. Carbon black halogenation has also been reported to have an appreciable effect on cure efficiency and final crosslink density [13]. Using inverse gas chromatography (IGC) measurements, it was demonstrated that the main contribution to the surface energy for studied commercial carbon black grades comes from a dispersive component [14-16]. The reinforcing effects, therefore, induced by the carbon black presence, is controlled by filler-rubber interactions, while the weak filler network has a minor effect.

To date, several attempts have been made to develop CNT reinforced-rubber nanocomposites [17] with enhanced properties for different applications. Although there has been considerable interest in carbon nanotubes (CNTs) as ideal fillers for the property enhancement of polymer nanocomposites [18-21], CNT dispersion state and interfacial adhesion between elastomeric composite components has remained problematic. For instance, poorly dispersed nanofillers hinders the reactive species mobility, resulting in a heterogeneous crosslink topology [22].

Recently, graphene nanoribbons (GNRs), one dimensional graphene based nanomaterials, were obtained from synthesis methods such as chemical vapor deposition (CVD) [23], lithographic patterning, plasma etching, oxidation of graphite, and unzipping CNTs [24-29]. Unzipping CNTs can be performed via different methods, including catalytic nanoparticles, electron beam, potassium vapor, and sodium/potassium intercalation [19, 22-24]. The longitudinal unzipping of MWCNTs,

through chemical oxidation in a mixture of acids, has been proven to produce a high yield of low defect GNRs [23, 30, and 31]. Generally, GNRs are attractive materials for polymer nanocomposites due to their higher interfacial area and, hence, their better adhesion with the polymer matrix and enhanced properties, as compared to CNTs [32].

Altering the carbon-based nanofillers' surface chemistry would be beneficial to enhance interfacial adhesion, by providing a strong interaction between the filler and the polymer matrix. For example, substituting carbon atoms with other atoms, as dopants, is known as an efficient method to improve the properties of CNT [24, 25, and 33]. Despite the importance of the subject, literature is scarce in reporting the effect of surface chemistry of the carbon-based nanofillers on the cure behavior of elastomeric nanocomposites. Few research works have reported the effect of CNT pre-treatment on physico-mechanical properties of the final nanocomposite for other reactive systems, such as thermosetting resins, which can only be usable for comparative purposes. In an attempt to elucidate the cure behavior of chemically reduced graphene/natural rubber nanocomposite with a sulfur cure system [34], authors reported a pronounced acceleration effect at low loading of the nanofiller. Such an effect was completely suppressed at higher concentrations, which was interpreted to be a result of the hindered mobility of reactive species. In this work, undoped and CN_x-GNR, synthesized from the parent multiwall carbon nanotubes (MWCNTs) via a chemical route, were used as nanofillers. FKM, a copolymer of vinylidene fluoride (VDF), hexafluoropropylene (HFP), and tetrafluoroethylene (TFE), was used as the polymer host. MWCNTs and GNRs, with and without nitrogen doping, were incorporated as fillers in the FKM matrix and the curing behavior of the nanocomposites was investigated. To the best of our knowledge, this is the first report on GNR/FKM nanocomposites.

5.4. Experimental

5.4.1. Materials

In-house synthesized undoped and nitrogen doped MWCNTs (CNx-MWCNT) were produced in our laboratory through catalytic carbon vapor deposition (CCVD) process [18]. The undoped MWCNTs have an average diameter of 25 nm and a length of 3.7 μm . The CNx-MWCNTs have a bamboo structure with an average diameter of 45 nm, a length of 2.5 μm and nitrogen doping of 2.31%. Undoped and CNx-GNR were synthesized from the parent multiwall carbon nanotubes (MWCNTs) via a chemical route [31], based on the developed protocol proposed by Tour's group [30]. In this method [31], 150 mg of MWCNTs was stirred in 36 ml H_2SO_4 for 1 h. Then 4 ml of the second acid, H_3PO_4 or Trifluoroacetic acid (TFA), was added to the mixture and stirred for 15 min; 750 mg KMnO_4 was slowly added to the mixture and stirred for 1 h at room temperature, followed by another 2 h stirring at 65 $^\circ\text{C}$. Finally, the product was rinsed with 20% HCl and diethyl ether, then vacuum filtered to obtain GNR flakes. The undoped GNR and CNx-GNR, with about 1.75 wt% of nitrogen, were produced from the original undoped and CNx-MWCNT, respectively. The reduced GNR, with a high 8.45 wt% of nitrogen, was synthesized from the CNx-GNR through a thermal reduction of CNx-GNR. The thermal reduction process was performed at 500 $^\circ\text{C}$, using NH_3 gas. Viton[®] fluoroelastomer, grade GF-200S, was supplied by Dupont. Triallyl Isocyanurate (TAIC), ZnO, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane were obtained from Cray valley, U.S.ZINC, and VAROX[®] respectively, for the curing process. Methyl Ethyl Ketone (MEK) was purchased from VWR.

5.4.2. Method

5.4.2.1. Nanocomposites preparation

GNR/FKM and MWCNT/FKM nanocomposites were produced using a solution mixing/melt mixing protocol. First, FKM was dissolved in MEK; the MWCNTs and GNRs were separately dispersed in MEK via ultrasonication in a bath sonicator for 30 min. The filler solution, either MWCNT or GNR, was added to the FKM solution, drop wise, while using probe sonication (Hielscher UP200S ultrasonic processor) with 50% amplitude and 50 pulse cycles for 15 minutes. The curing agents, TAIC (2 phr), ZnO (3 phr), and 2,5-dimethyl-2.5-di(t-butylperoxy) hexane (2 phr), were added to the composite solution and the mixture was homogenized by using an IKA T10 homogenizer, at 10,000 rpm, for 10 minutes. The solution was dried for 24 hours, under the fume hood, at room temperature and annealed in the vacuum oven at 60 °C for 6 hours. The last step was melt-mixing using an Alberta Polymer Asymmetric Minimixer (APAM), a specialized 2 mL miniature mixer developed in our research group in 2004 [29]. Melt compounding was performed at 120 °C, with the rotor speed of 50 rpm for 5 minutes.

5.4.2.2. Characterization

The vulcanization and rheological behavior of MWCNT/FKM and GNR/FKM was studied using a MCR 302 Anton Paar rheometer. All measurements were performed using parallel plate geometry, with a diameter equal to 25 mm. Samples for rheometry were pre-molded at 100 °C and 5000 psia for 10 minutes; they had a thickness of 0.9 ± 0.05 mm after unmolding and being cooled to room temperature. The non-isothermal curing behavior of composites was monitored by temperature

sweeps from 90 °C to 250 °C, in a linear viscoelastic regime with a heating rate of 0.5 K/min. High resolution transmission electron microscopy (HRTEM) analysis was carried out on the ultramicrotomed sample sections using a Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, Oregon, USA), at a 200 kV acceleration voltage with the standard single-tilt holder. The images were captured on a Gatan UltraScan 4000 CCD camera (Gatan, Pleasanton, California, USA) at 2048x2048 pixels. Differential scanning calorimetry (DSC) was conducted via a Q-500 TA instrument, with a heating rate of 10 K/min from -50 to 250 °C. Glass transition temperature measurements were also performed upon heating, before and after the cure process. X-Ray Photoelectron Spectroscopy (XPS) were conducted via a Physical Electronics PHI VersaProbe 5000-XPS to determine the elemental composition of the nanofillers. A 200.0 µm diameter beam from a monochromatic aluminum source, at 1486.6 eV and 49.3W, was used for spectra. The double neutralization beam consisted of a low energy electron beam and a low energy Ar⁺; the chamber analysis pressure was 2.0×10^{-7} Pa during spectra acquisition. Samples were pressed on indium foil and, for each of the samples, a high sensitivity mode spectrum was taken with a wide binding energy range of 0–1350 eV. Then, a narrower binding energy window, with a pass energy of 23.50 eV, was used to gather high energy resolution spectra to determine the chemical environment of the elements. The binding energies were reported relative to C1s at 284.8 eV.

5.5. Results and discussion

5.5.1. TEM images

HRTEM images in Figure 5.1 depict the successful unzipping process that occurred through the chemical treatment of MWCNTs to produce GNRs. Images 5.1(a) and 5.1(b) show undoped

MWCNT before and after oxidation, respectively. Here, a longitudinal unzipping mechanism can be easily realized. CNx-MWCNTs with bamboo structures (Figure 5.1(c)), however, are observed to be unzipped via a helical mechanism, as shown in Figure 5.1(d).

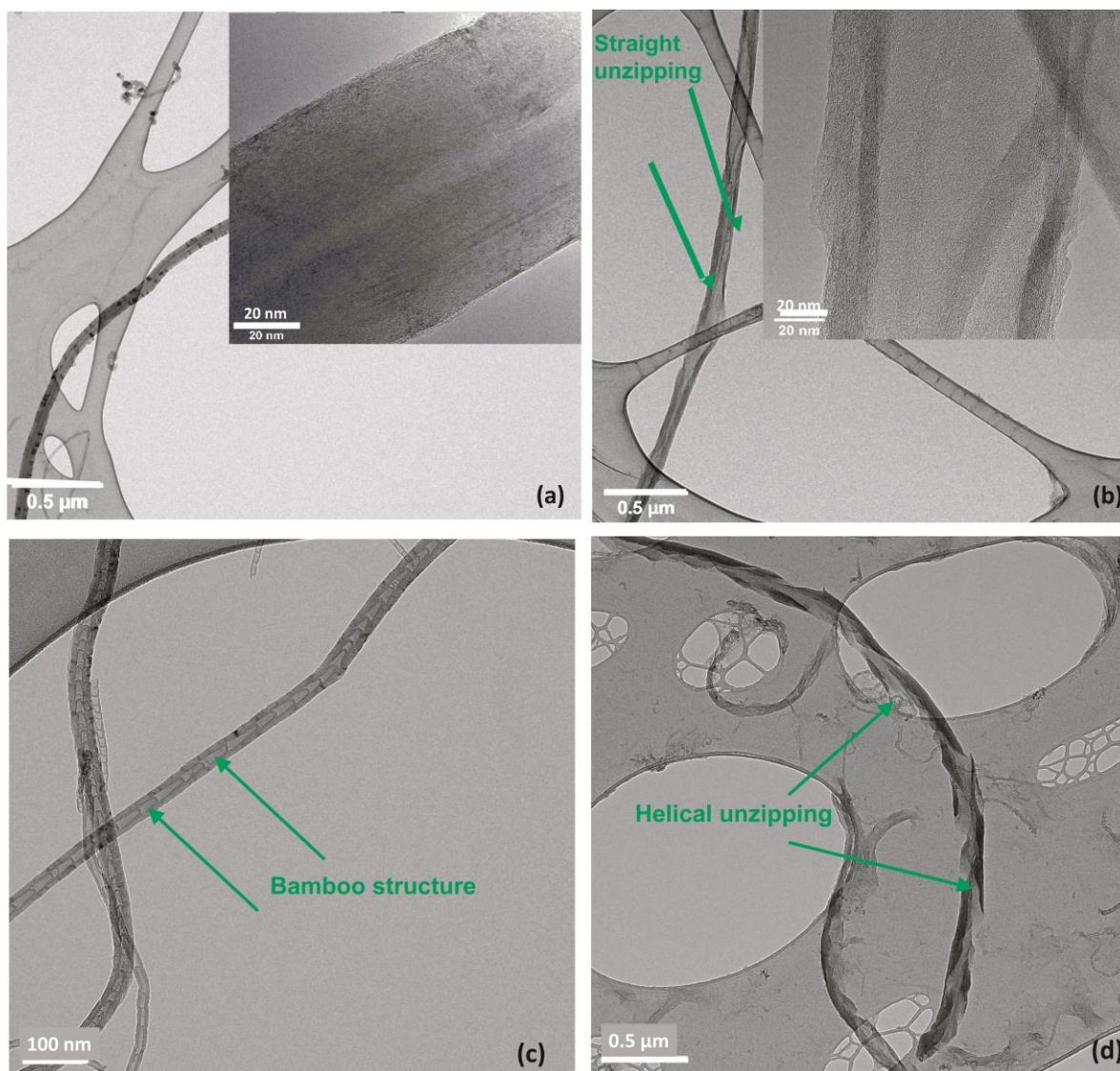


Figure 5.1. TEM images of (a) undoped MWCNT before unzipping, (b) undoped MWCNT after unzipping, (c) N-doped bamboo structure MWCNT before unzipping and (d) after unzipping [31].

Both the geometrical complexities of bamboo compartments and chemical doping of nitrogen species within the sp^2 graphitic network may be responsible for these substantially different mechanisms. MWCNTs and GNRs were then compounded with FKM. According to TEM images for the GNR/FKM and MWCNT/FKM nanocomposites (Figure 5.2), well-dispersed GNRs were observed in the FKM matrix and a considerably less aggregated structure was obtained for GNR particles relative to MWCNTs.

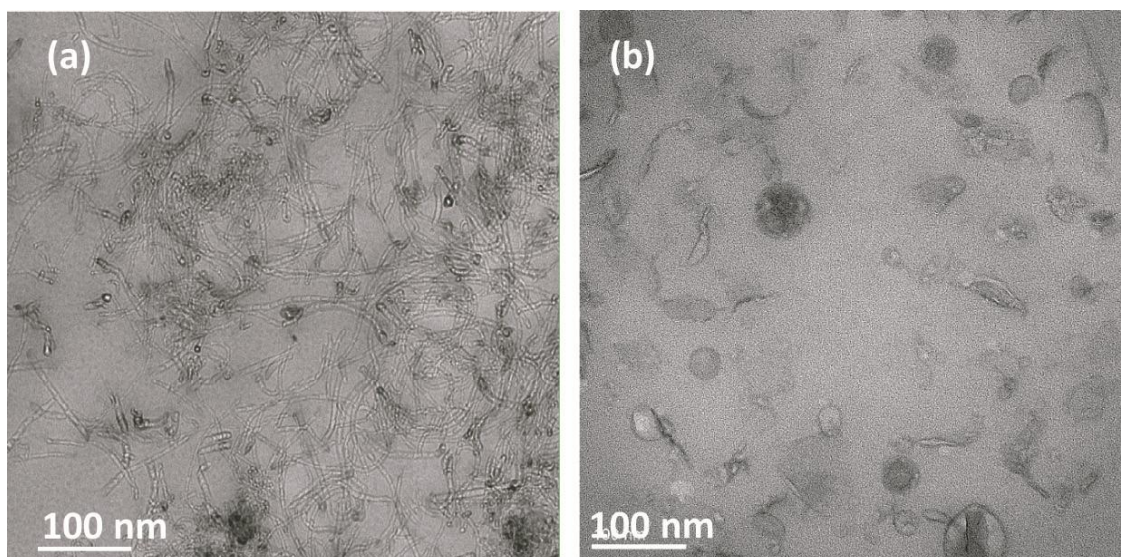
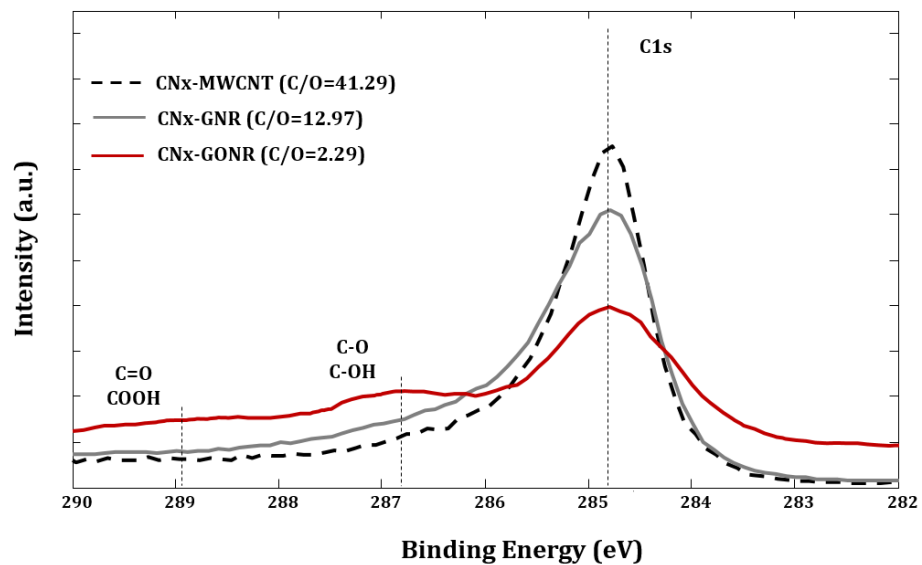


Figure 5.2. TEM images of (a) CN_x-MWCNT /FKM and (b) O-CN_x-GNR/FKM nanocomposites after curing.

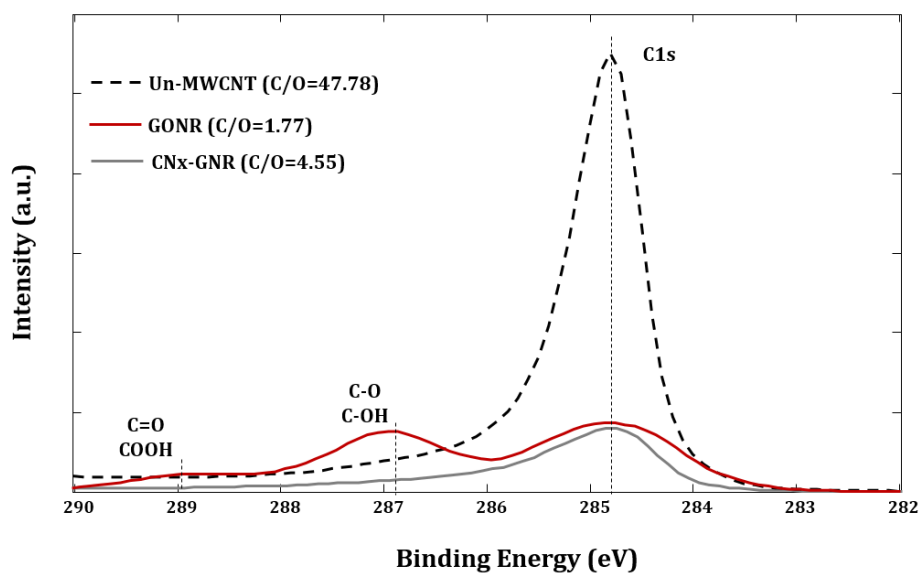
5.5.2. Surface Chemistry of Nanoparticles

To study the oxygen and nitrogen surface functionalities, all samples were analyzed by XPS. The high resolution C1s spectra of original CN_x-MWCNTs, CN_x-GONRs and CN_x-GNRs are given in Figure 5.3(a). The deconvolution of C1s peaks, based on a Lorentz-Gauss algorithm, indicates that the oxygen functional species exists predominantly in the form of hydroxyl (C—OH, 286.2-286.5 eV) and/or epoxy (C—O, 286.7-287.0 eV) groups. A few of them are carbonyl (C=O, 287.6-

287.8 eV) and carboxyl ($\text{O}=\text{C}-\text{OH}$, 288.8-289.1 eV) groups. Note that all spectra is calibrated with a binding energy of 284.8 eV for $\text{C}-\text{C}$ bond.



(a)

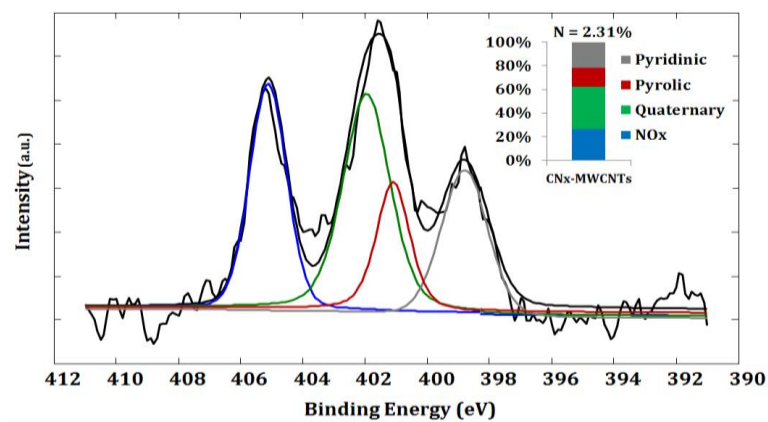


(b)

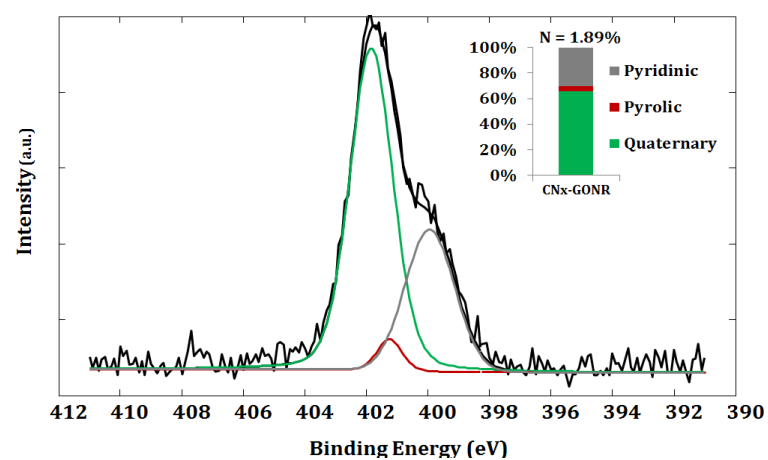
Figure 5.3. $\text{C}1\text{s}$ XPS spectra for (a) CNx-MWCNTs, oxidized, reduced, and (b) Un-MWCNTs, oxidized, reduced

According to the generally accepted Lerf-Klinowski model for graphene oxides, hydroxyl and epoxy groups predominately attached to the graphene basal plane, while carbonyl and carboxyl groups located presumably at the edges [35]. Figure 5.3(b) also displays the C1s XPS spectra of Un-MWCNTs after oxidation with a second acid. This figure clearly demonstrates the formation of larger amounts of epoxy and hydroxyl groups inside the graphene basal plane, rather than carbonyl and carboxyl groups on the edges of OGNRs. After reduction in ammonia, the peaks associated with the oxygen functional groups almost disappeared.

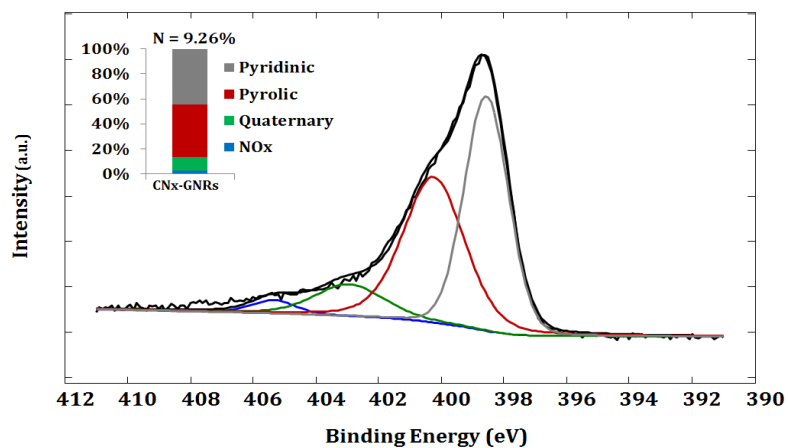
Figure 5.4 also shows the high resolution N1s spectra of CNx-MWCNTs samples after oxidation and reduction. Based on the deconvoluted peaks of CNx-MWCNTs (Figure 5.4(a)), nitrogen may incorporate into the hexagonal carbon structure in four main configurations: pyridinic (398.3–399.8 eV), pyrrolic (400.1–400.5 eV), quaternary (401.0–401.4 eV) and intercalated nitrogen molecules (404.0–405.6 eV) [18]. The removal of nitrogen molecules trapped inside the nanotube structure after oxidation could be an indication of successful unzipping, thus creating more edges in the structure (Figure 5.4(b)). Reduction of the same sample in ammonia not only removed most of the oxygen functional groups, but also simultaneously, nitrogen doped the sp^2 carbon structure (Figure 5.4(c)). In this case, most of the nitrogen species are characterized as pyridinic groups. The presence of more edges in the faceted structure of unzipped samples may increase the overall nitrogen content, peak intensity and, thus, the amount of pyridinic groups. The ratios and percentages of the functional groups of GNRs, obtained from XPS spectra analysis, are summarized in Table 5.1.



(a)



(b)



(c)

Figure 5.4. N1s XPS spectra for (a) N-MWCNT, (b) after oxidation, and (c) after reduction

Table 5.1. Functional groups for the nanofillers (XPS results)

Filler	C/O ratio	N%	N functional groups	O functional groups	%
Undoped oxidized GNR	1.35	0	-	COOH, Carboxyl	5
				C=O, Carbonyl	12
				C-O, Epoxy	20
				C-OH, Hydroxyl	15
				C-C, C=C	49
N-doped oxidized GNR (CN _x -GNR)	1.93	1.75	Quaternary (70%) Pyrrolic (10%) Pyridinic (20%)	COOH, Carboxyl	4
				C=O, Carbonyl	7
				C-O, Epoxy	12
				C-OH, Hydroxyl	6
				C-C, C=C	72
N-doped reduced GNR (R-CN _x -GNR)	7.5	8.45	NO _x (10%) Quaternary (20%) Pyrrolic (30%) Pyridinic (40%)	COOH, Carboxyl	0
				C=O, Carbonyl	0
				C-O, Epoxy	5
				C-OH, Hydroxyl	0
				C-C, C=C	95

5.5.3. DSC

Numerous research works [30] reported deviation in the glass transition temperature (T_g) of polymer nanocomposites from that of the pure polymer matrix. In a simplified overview, this behavior is thought to be associated with interfacial surface energy which controls the polymer chain mobility in the interphase region. In other words, at the same dispersion state, the polymer chain dynamic, in the interfacial region, is determined by the interaction between the matrix and the nanoparticle surface. It was observed that the nanocomposite T_g shifted to either higher or lower temperatures due to attractive/ non-attractive interactions in the interfacial region [36].

Table 5.2 summarizes the T_g for different uncured nanocomposite samples, with different fillers and filler loadings. All samples exhibited an increase in T_g , with respect to the FKM matrix. This

implies the existence of hindered dynamics in the interfacial region. The C_p step at T_g remained almost unchanged among all samples.

Table 5.2. ΔC_p and T_g for uncured compounds measured upon heating with the rate of 10 K/min

Filler wt. %	ΔC_p (J/g.°C) ^a				T_g (°C)			
	Undoped MWCNT	CNx- MWCNT	Undoped GNR	CNx- GNR	Undoped MWCNT	CNx- MWCNT	Undoped GNR	CNx- GNR
0	0.1882	0.1882	0.1882	0.1882	-22.46	-22.46	-22.46	-22.46
0.1	0.1864	0.141	0.1259	0.1677	-11.94	-14.63	-11.12	-9.72
0.2	0.164	0.1796	0.1477	0.1696	-13.57	-14.25	-10.28	-11.24
0.5	0.0977	0.2741	0.1845	0.1313	-9.9	-14.3	-11.45	-10.5
0.7	0.1097	0.1522	0.1174	0.1375	-10.2	-13.46	-11.2	-12.28
1	0.1277	0.1758	0.267	0.1461	-11.5	-12.18	-12.7	-11.34

a: ΔC_p values are normalized with respect to the polymer content.

The T_g always shifted to higher temperatures upon the cure reaction [37]. This well-known trend can possibly be explained in terms of additional stiffness arising from the crosslinks. The increase in T_g upon cure reaction, ΔT_g , is plotted as a function of filler loading in Figure 5.5. Different values for ΔT_g for different nanocomposite samples may be a consequence of differences in segmental dynamics caused by topological differences in the cured rubber network. The highest ΔT_g was observed for N-doped CNT samples. This can be considered as an indication for relatively higher crosslink density achieved in these samples. GNR and undoped CNT samples had apparently smaller ΔT_g , probably as a result of lower crosslink density. These observations can be attributed to the dominance of side reactions of the cure process in GNR samples. The dominance of side reactions could lead to networks with a lower density of crosslinks and higher content of non-elastic defects [38, 39]. Under such circumstances, the spatial distribution of crosslink density should be highly inhomogeneous down to very local scales.

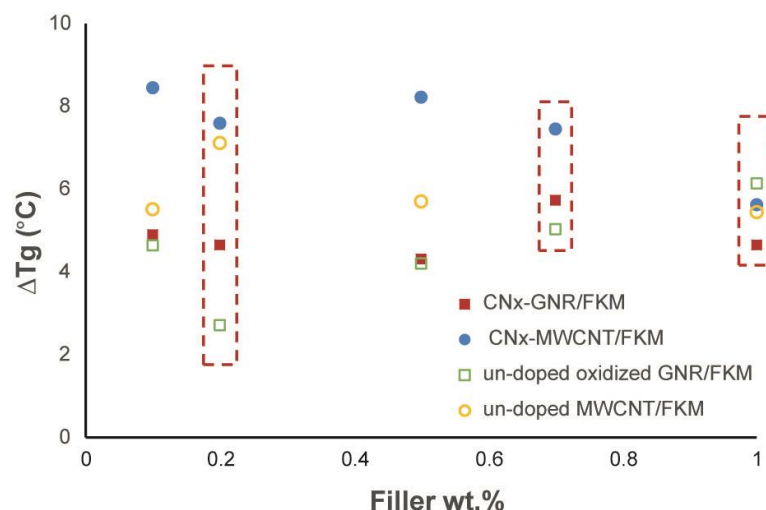
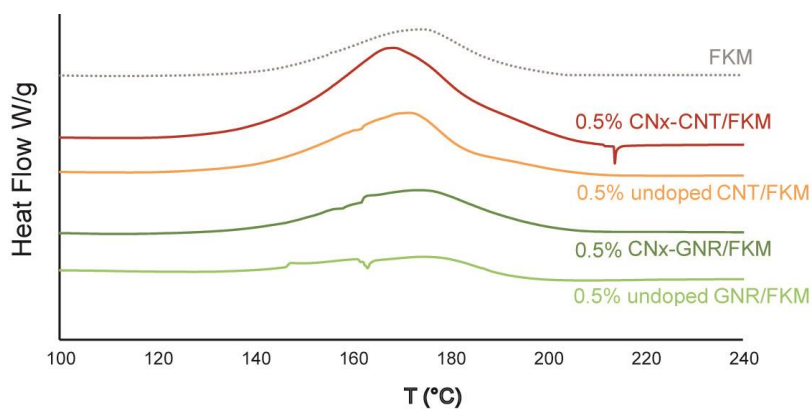
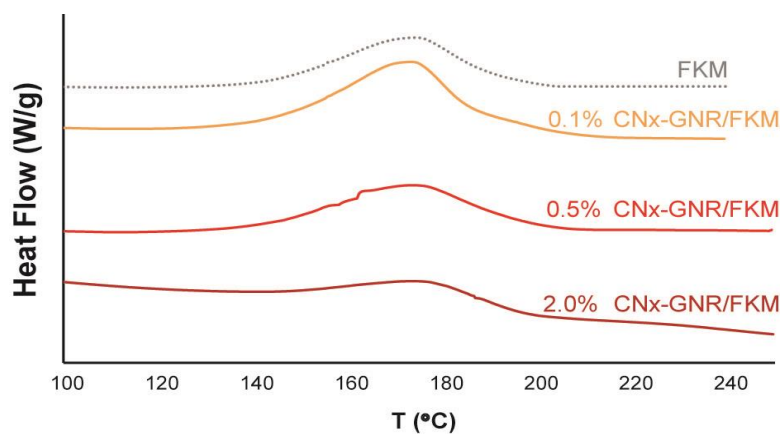


Figure 5.5. ΔT_g over curing reaction as a function of filler loading for N-doped MWCNT/FKM, undoped MWCNT/FKM, CNx-GNR/FKM, and undoped GNR/FKM nanocomposites

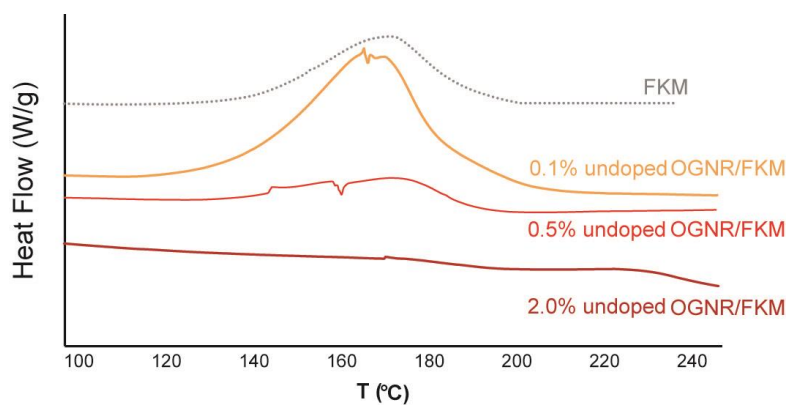
To provide further evidence of the crosslinking process, non-isothermal DSC experiments were performed. Figure 5.6 depicts non-isothermal DSC thermograms of FKM gum and nanocomposite samples. The observed exothermic peak broadened as the filler concentration was increased for both un-doped and CNx-GNR/ FKM samples. This exothermic peak corresponds to crosslink formation and cure process side reactions [40]. The heat produced by the cure reaction also had a descending trend as a function of filler concentration. It is also noticeable that un-doped oxidized GNR had a relatively more deleterious effect. This is mostly the effect of GNRs; such behavior was not observed for CNT nanocomposite samples (Figure 5.6(a)). This can be a result of higher crosslinking efficiency achieved in CNT nanocomposite samples.



(a)



(b)



(c)

Figure 5.6. DCS results for curing process heat flow for; (a) 0.5 wt% filler/FKM nanocomposites (fillers: CNx-doped MWCNT, undoped MWCNT, CNx-doped GNR, and undoped GNR/FKM) (b) different loadings of CNx-GNR/FKM nanocomposites, and (c) different loadings of undoped GNR/FKM nanocomposites

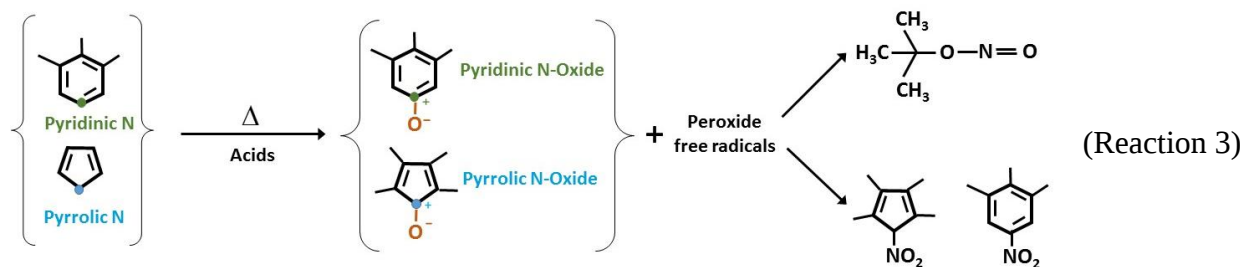
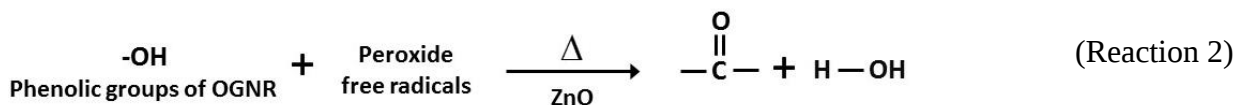
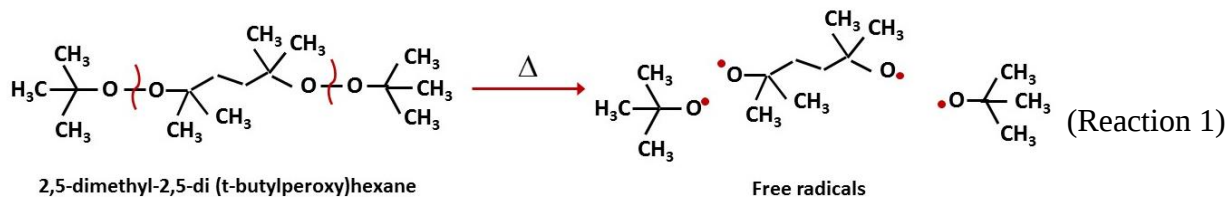
For highly complex reactions of curing, it is well-known that side reactions may interfere with the crosslinking process by either peroxide consumption in a non-productive manner or chain scission. Considering the surface chemistry of GNRs, one possible side reaction - consuming peroxide in a non-productive way - would be between the hydroxyl group on the surface of GNRs and the organic peroxide (see Table 5.1).

According to XPS data, more hydroxyl groups exist on the surface of un-doped OGNR as compared to the nitrogen-doped O-CN_x-GNR. This would explain the less harmful effect observed for O-CN_x-GNR. It is also previously reported that acidic fillers may adversely affect the peroxide efficiency in the crosslinking process due to acid-catalyzed decomposition of the peroxide [8, 9]. In the next section, our observation of side reactions, found through spectroscopic techniques, will be discussed extensively. To summarize the hypothesis: we may conclude that by having more hydroxyl groups, we anticipate more harmful effects for curing reactions induced by the presence of oxidized GNRs.

5.5.4. Fourier transform infrared spectroscopy (FTIR) and reactions

Several cure process side-reactions can be assumed for different GNRs with different functionalities. First, peroxide is decomposed to primary alkoxy radicals (Reaction 1), which are necessary to initiate further reactions, including curing or other side reactions. The next step for oxidized un-doped GNRs, might be a reaction between the free radicals and oxygen functional groups on the GNR surface (Reaction 2). The hydroxyl and carboxyl groups, especially the phenolic hydroxyl groups, in the presence of a high temperature and using ZnO as a catalyst, will react and

produce Ketone groups and H₂O. The possible reactions for the CN_x-GNR occurred between Pyridinic or Pyrrolic nitrogen atoms, substituted for carbon atoms, in the graphene structure. In the presence of heat and residual acids from the unzipping process, some nitrogen-oxygen bonds will be created, resulting in different N-O or N=O bondings with different energies.



Based on the FTIR results for the different GNRs/FKM nanocomposites (Figure 5.7(a) and 5.7(b)), we analyzed the chemical bonds before and after the curing reaction for different fillers/FKM nanocomposites. The association/dissociation of chemical bonds validates the reactions between GNRs' surface functional groups and the peroxide. The peaks at 1130 and 1190 cm⁻¹ correspond to C-F bonds. No noticeable change is seen in the intensity of these peaks, before and after the curing reaction for neat FKM and R-CN_x-GNR/FKM composites, appears.

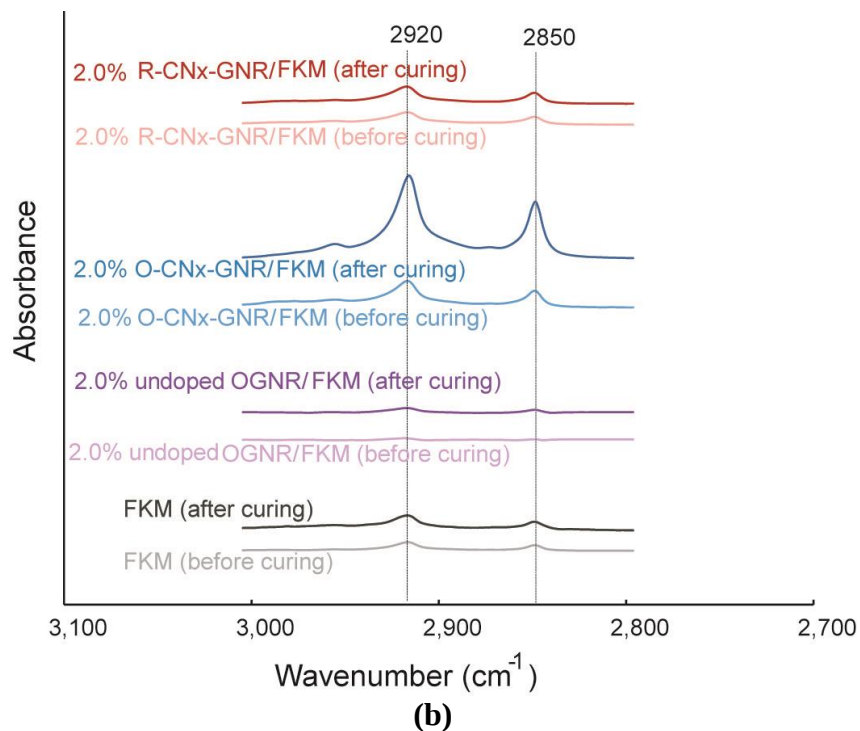
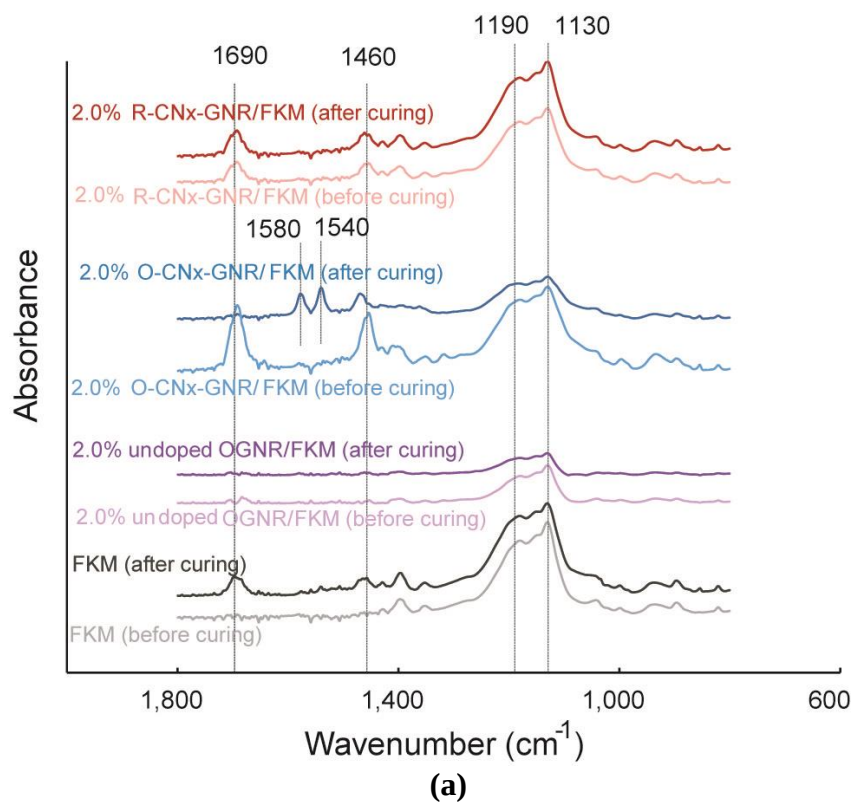


Figure 5.7. FTIR results for FKM and GNR/FKM nanocomposites (a) 800 to 1800 cm^{-1} , and (b) 2800 to 3000 cm^{-1}

We did observe a decrease in the intensity of peaks at 1190 cm^{-1} for undoped OGNR/FKM and O-CN_x-GNR/FKM, which can be a consequence of side reactions rather than crosslinking, resulting in a decrease of the relative amount of C-F. Moreover, two peaks, at 1540 and 1580 cm^{-1} for N-GNR/FK, are attributed to the N-O and C=C bonds, respectively. The association of the N-O bond may be due to the reaction of nitrogen on the GNR surface during the curing process. The peak at 1580 may be the consequence of the dissociation of C=N (peak at 1690 cm^{-1}) and the production of some C=C bonds. Peaks at 2850 cm^{-1} and 2920 cm^{-1} (Figure 5.7(b)), correspond to C-H and O-H groups, which were unchanged for neat FKM and R-GNR/FKM. For undoped GNR/FKM, a small increase in the intensity of these peaks can be observed; for N-GNR/FKM, a big increase is apparent. Having more hydroxyl groups on the surface of the un-doped oxidized GNRs, compared to CN_x-GNRs, the difference in the intensity of peaks related to O-H groups, before and after curing, is less visible for the former samples. This is due to the overlap of broad peaks which correspond to different O-H groups. Generally, peaks in the range of $2500\text{--}3500\text{ cm}^{-1}$ can be related to different types of O-H.

5.5.5. Rheology

Rheological measurements can provide valuable information about the cured rubber network structure and kinetics of crosslink formation [41]. Small amplitude oscillatory time/ temperature sweep can be performed to monitor the cure process [42]. The increase in sample elasticity, as a result of the curing process, can be used as a quantitative assessment of the crosslink density and organic peroxide efficiency [43]. Contrary to DSC, rheology is only affected by the formation of crosslinks contributing elastically to the cured rubber network and not by non-elastic defects (loops, isolated chains and dangling chains) [40]. Consequently, compared to other techniques like DSC

and solvent extraction, rheology is minimally impacted by cure process side reactions [43]. Figure 5.8 shows the frequency dependence of elastic modulus for uncured rubber compounds. It is observed that the CNx-doped MWCNT sample exhibited higher elasticity in the terminal region as compared to other nanocomposite samples. This can be attributed to the relatively stronger filler network formed in this sample, resulting in a higher terminal elasticity compared to OGNR/ FKM nanocomposites.

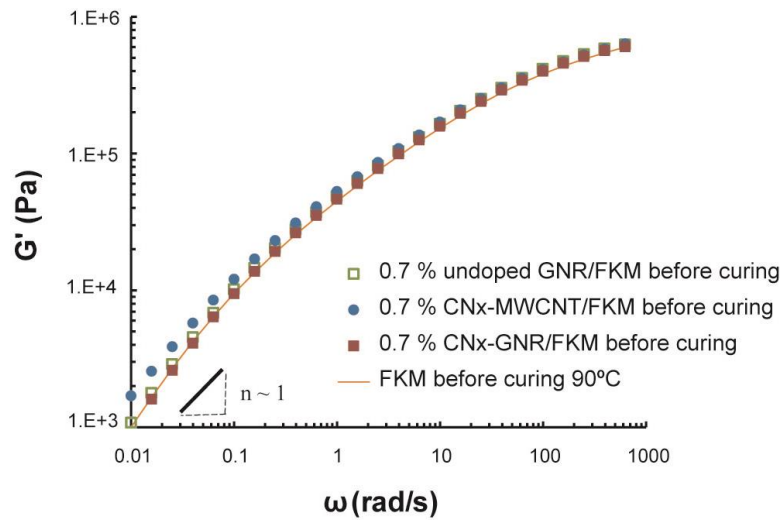


Figure 5.8. Frequency dependence of elastic modulus for uncured MWCNT/FKM and GNR/FKM compounds before curing at 90 °C

Figure 5.9 shows the elastic modulus of FKM gum and nanocomposite samples as a function of temperature. Different features are distinguishable on the curing curve. Based on these results, it is possible to determine the gel point temperature (G' - G'' cross over which is not shown here): the point at which a percolating three-dimensional gelled network structure is forming. Based on the definition, the gel point of a crosslinking polymer coincides with a G' - G'' crossover only if the loss and storage modulus are equal over the whole spectrum of frequencies and follow the power law correlation defined by $G' \sim G'' \sim \omega^{1/2}$.

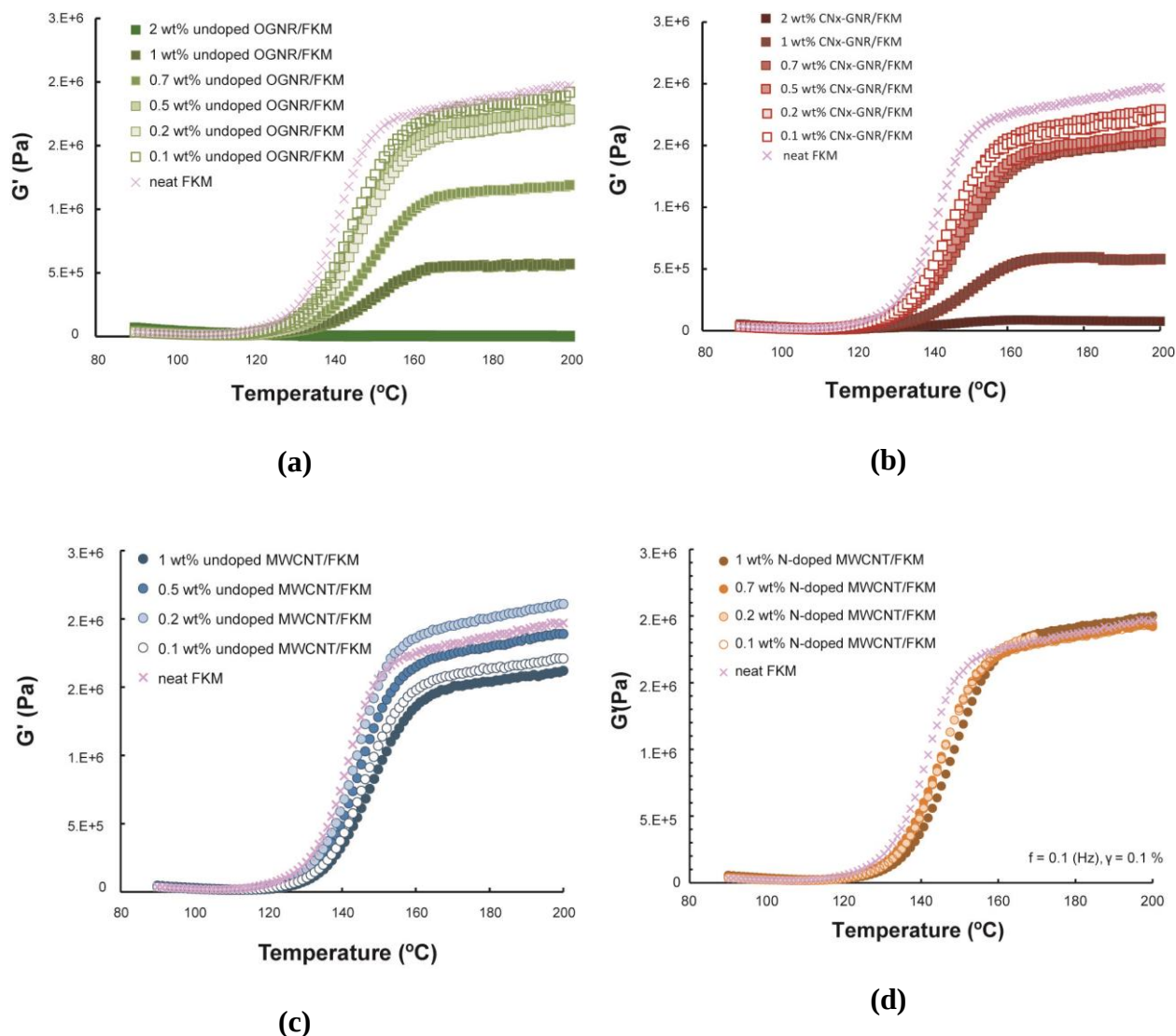


Figure 5.9. Temperature evolution of elastic modulus for (a) un-doped oxidized GNR, (b) oxidized CNx-GNR, (c) undoped MWCNT and (d) CNx- MWCNT nanocomposite samples for different concentrations

The other observed region is the substantial increase in elasticity (stiffness) due to the increase in the three dimensional network density as a result of the continued crosslinking process. As the curing process reaches its final stages, a high temperature plateau-like region is observed; however, an equilibrium value is not observable. No over-curing reversion was observed for temperatures as high as 200 °C. Based on the results presented in Figure 5.9, slower cure kinetics, and also smaller

final elasticity, were observed for oxidized GNR nanocomposite samples. A critical concentration, at which the hindrance effect of un-doped OGNR presence on crosslinking process becomes dominant, is distinguishable and an almost uncured state was reached at 2 wt% loading of undoped OGNR. For O-CN_x-GNR nanocomposite, the deleterious effect was less significant. These findings are in good agreement with non-isothermal DSC results and cured rubber glass transition temperature measurements. One may suggest that by incorporating oxidized GNRs, it is possible to limit organic peroxide efficiency and control the final topology of the cured rubber network. It can be hypothesized that these observations are correlated to oxidized GNR surface functional groups, which could either change the mechanism of the curing process or consume the organic peroxide in a non-productive manner.

In Table 5.3, cure behavior parameters of the FKM gum and nanocomposites are given. Both the gel point temperature and maximum cure temperature (T_{max} is the temperature at which $\left(\frac{\partial^2 G'}{\partial T^2}\right) = 0$) are both shifted to higher temperatures for nanocomposite samples, as compared to FKM gum. The delayed gelation process for nanocomposite samples can be partly because of the hindered mobility of the reactive species as a result of the increase in viscosity in presence of nanofillers. However, the huge decrease in maximum cure rate, $\left(\left(\frac{\partial G'}{\partial T}\right)_{T=T_{max}}\right)$, for higher concentrations of oxidized GNR/ FKM nanocomposites can be explained only in conjunction with the so-called hindered mobility. This would substantiate the hypothesis of the existence of a side reaction interfering with the crosslinking process in oxidized GNR/ FKM nanocomposites. The difference between the final elasticity G'_{∞} and minimum elasticity G'_0 revealed a descending trend for the oxidized GNR samples. This indicates the lower crosslink density and organic peroxide efficiency achieved in these samples.

Table 5.3. Cure behavior of FKM rubber compounds with different loading of the filler

Sample	Filler loading (wt %)	Gel point temperature (°C)	T_{max} (°C)	$G'_{\infty}-G'_0$ (kPa)	$\left(\frac{\partial G'}{\partial T}\right)_{T=T_{max}}$ (kPa.°C ⁻¹)
FKM rubber	0	112.1	138.0	1972	63.3
CNx-GNR/FKM	0.1	114.4	145.2	1713	91.1
	0.2	116.7	134.9	1773	59.0
	0.5	117.8	148.6	1583	90.6
	0.7	118.9	146.3	1528	53.3
	1	121.1	155.5	568	24.4
	2	115.5	150.9	52	1.8
undoped GNR/FKM	0.1	114.0	145.2	1871	75.0
	0.2	117.6	134.9	1855	32.5
	0.5	118.7	148.6	1913	59.1
	0.7	121.2	146.3	1164	44.5
	1	123.5	155.7	548	16.3
	2	120.1	153.2	-	-
CNx-MWCNT/FKM	0.1	115.0	140.6	1968	71.0
	0.2	115.5	142.9	1975	70.0
	0.7	114.4	140.6	1980	72.1
	1	117.8	145.2	1994	75.1
	3	121.5	150.9	2688	140
undoped MWCNT/FKM	0.1	118.9	142.9	1699	68.8
	0.2	116.7	141.8	2111	90.0
	0.5	117.8	140.6	1942	92.7
	1	121.0	146.3	1599	78.8

From a theoretical point of view, the final elasticity is supposed to be a direct function of the number of elastic crosslinks and trapped entanglements. Obviously, the formation of non-elastic defects would not be desirable and have no contribution to the cured rubber elastic network. As

mentioned earlier, the dominance of side reactions could lead to networks with a lower density of crosslinks and higher content of non-elastic defects [43].

Figure 5.10 compares the cure behavior of the nanocomposite based on thermally reduced CNx-GNR with those of the oxidized GNRs at a fixed concentration of 2 wt%. FKM gum results were also included for comparison. As observed, reduced graphene nanoribbons had relatively no harmful effect on the cure behavior of FKM rubber. The efficiency of organic peroxide, in the FKM/ reduced GNR nanocomposite, is comparable with FKM gum.

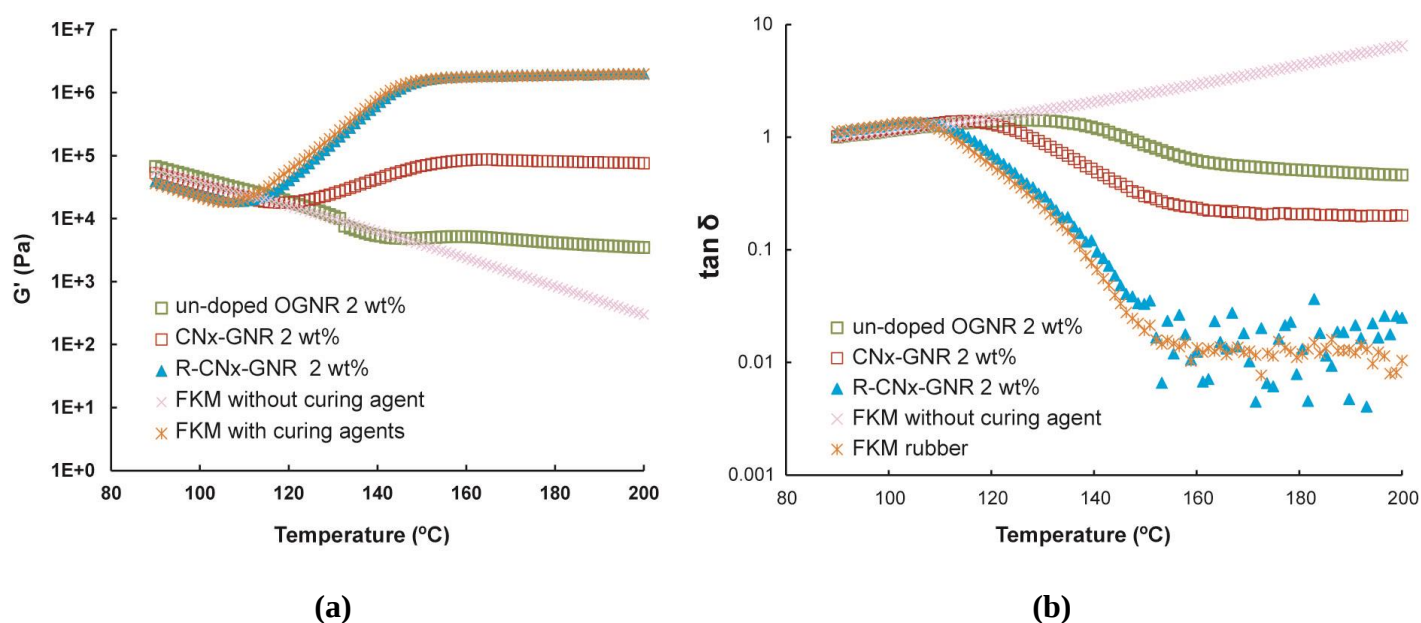


Figure 5.10. Temperature dependence of (a) elastic modulus and (b) damping factor for FKM gum and different GNR nanocomposites

The presence of the nanofiller slightly retarded the crosslinking process. This latter observation provides further evidence for the validity of our hypothesis, which considers oxygen surface functional groups as the main reason for the suppressed crosslinking process in concentrated GNR/ FKM nanocomposites.

Figure 5.11 depicts the frequency dependence of the elastic modulus for different cured GNR nanocomposites. These samples underwent the same thermal protocol as the samples in Figure 5.10 and their elastic modulus has been captured as a function of frequency at 250°C. The result for reduced GNR nanocomposite corresponds to a polymer gel far above the gel point, with solid-like behavior. Such behavior, however, is not observed for the oxidized GNR samples, which is in good agreement with our previous observations.

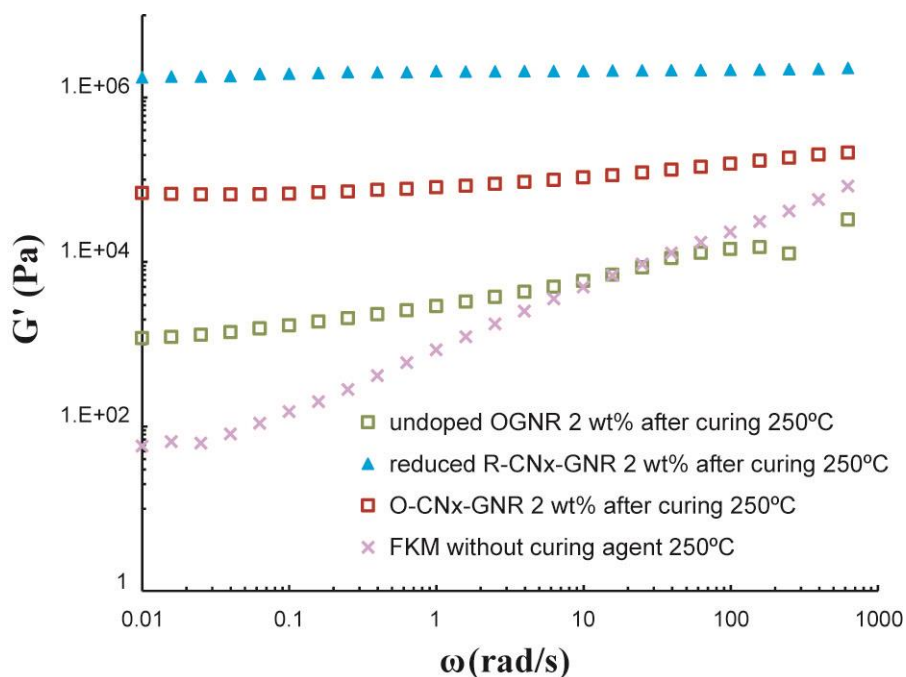


Figure 5.11. Frequency dependence of elastic modulus for cured CNR nanocomposite samples and uncured FKM, with no curative, at 250°C

5.6. Conclusion

Nitrogen doped and undoped GNRs were successfully obtained through chemical unzipping the parent MWCNTs. Then, FKM/GNR and FKM/MWCNT nanocomposites were prepared using a solution-mixing/melt-mixing protocol. The effect of MWCNT, CNx-GNR and un-doped GNR,

incorporated into FKM on the curing behavior, was studied. The importance of accounting for the effect of surface functional groups on the cure behavior of oxidized GNR/FKM nanocomposites is validated, based on the results of this work. Linear viscoelasticity, in conjunction with DSC, shows that oxygen functional groups on the GNR surface can significantly interfere with a C-C covalent bond formation; hence, an almost uncured state was achieved for concentrated samples. Conventional spectroscopy results further revealed the signature for potential side reactions explaining this behavior. The thermal reduction technique was able to efficiently suppress this deleterious effect and a similar cure behavior as FKM gum was observed for the reduced GNR/FKM samples.

5.7. References

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Chapter 6

Dielectric Properties of Multi-Walled Carbon Nanotube (MWCNT)/Clay/Polyvinylidene fluoride (PVDF) Nanocomposites: Effect of Clay Incorporation*

6.1. Presentation of the Article

In this article we investigate the effect of utilizing hybrid fillers in tuning dielectric properties of poly vinylidene fluoride (PVDF) for charge storage applications. PVDF were chosen as the matrix due to its piezoelectric properties. The main nanofiller, as for most of the electrical applications of polymer nanocomposites, was multi wall carbon nanotube (MWCNT) and the secondary filler was nanoclay. Hybrid nanocomposites of MWCNT/nanoclay/ PVDF were successfully produced through melt-mixing process with a range of MWCNT concentration (0.1 to 1.0 wt%) and different clay loadings (1.0 and 3.0 wt.%). For the specific application of charge storage, these materials need to have high dielectric permittivity and low dielectric loss. Based on the results presented, this goal could be accomplished at an optimum level of clay and MWCNT loadings. The main part of this work has been done by Maryam Khajepour, Dr. Sundarararaj has supervised the work, and Dr. Arjmand has helped with interpretation of the results.

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Dielectric Properties of Multi-Walled Carbon Nanotube (MWCNT)/Clay/Polyvinylidene fluoride (PVDF) Nanocomposites: Effect of Clay Incorporation

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6.2. Abstract

This study investigates the effect of clay addition on the broadband dielectric properties of multi-walled carbon nanotube/polyvinylidene fluoride (MWCNT/PVDF) composites, i.e. frequency range of $10^1 - 10^6$ Hz. Different loadings of MWCNT and clay were used for the preparation of three-phase (MWCNT/Clay/PVDF) nanocomposites via melt-mixing method. The crystalline structure and morphology of nanocomposites were examined by employing characterization techniques such as X-Ray diffraction, transmission electron microscopy, and differential scanning calorimetry. The dielectric spectroscopy showed that introducing clay into the MWCNT/PVDF nanocomposites at a critical MWCNT concentration improved dielectric properties tremendously. It was interestingly observed that the incorporation of a specific amount of clay, i.e. 1.0 wt%, into the (MWCNT/PVDF) nanocomposite at a critical MWCNT loading, i.e., 0.5 wt% MWCNT, resulted in a huge increase in the dielectric permittivity (670% at 100 Hz) and a considerable reduction in the dissipation factor (68% at 100 Hz).

6.3. Introduction

In the recent decade, conductive filler/polymer composites (CPCs) have gained great attention as charge storage materials due to their high flexibility combined with tunable dielectric properties. Inherent properties of polymer matrix, conductivity of filler, and conductive filler-polymer interaction play crucial roles in CPC's performance. Electroactive polymers are ideal matrices for charge storage materials, benefiting from their electromechanical properties and large dielectric permittivity [1, 2]. Among electroactive polymers, polyvinylidene fluoride (PVDF) has drawn great attention due to its applications as a polar piezoelectric material [3-6]. PVDF is a semi-crystalline polymer which has five distinct crystalline forms; among which, the polar β -phase has found the most interest because of its piezo-, pyro- and ferroelectric properties resulting in enhanced dielectric permittivity [4, 7-9]. The ferroelectric property of PVDF comes from the dipoles formed in hexagonal crystal lattice structure of β -phase [3].

In terms of conductive filler, carbon nanotubes (CNTs) are ideal conductive fillers for CPCs due to their high aspect ratio and remarkable electrical, thermal and mechanical properties [5, 10]. Moreover, it was found that CNTs contribute significantly to the formation of β -phase of PVDF, thus, enhancing ferroelectric properties [3, 4, and 6]. However, there are some challenges while using CNTs in polymer matrices. Firstly, it is critical to achieve a good dispersion of CNTs in the polymer matrix, since enhanced properties are achieved only when there is a good interfacial interaction between CNTs and polymer matrix [11, 12]. Naturally, existence of high van der Waals attraction between CNTs causes aggregation and consequently increase in the percolation threshold [10, 12]. Thus, improving dispersion of CNTs is essential with regard to the cost, flexibility and percolation threshold [10, 12].

Secondly, high dielectric permittivity and low leakage electrical current in CPCs can be obtained only at filler loadings very close to the percolation threshold (at intermediate levels of conductivity) [13]. Narrow insulator-conductor transition window around the percolation threshold is a critical challenge in manipulating CPCs for charge storage applications [4]. Accordingly, several efforts have been taken to improve the overall dispersion of CNTs into polymer matrices and to impede the insulator-conductor transition [10, 11]; (1) chemical modification of the surface of conductive fillers [10], (2) introducing secondary particles [10, 14] and (3) aligning conductive filler [15]. Unfortunately, a reduction in the dielectric permittivity was an unavoidable consequence of these techniques [15]. Also, chemical modification may weaken atomic structure of CNTs and thus lead to decrease of electrical and mechanical properties [10, 11 and 14].

Herein, we study the impact of clay, as a secondary filler, on dispersion and dielectric properties of MWCNT/PVDF nanocomposites. It has been reported that good dispersion and load transfer of clay compared to other secondary fillers lead to improved dispersion of conductive fillers without impairing electrical and mechanical properties [16]. The results showed that clay improved the MWCNT dispersion, leading to a wider insulator-conductor transition, which makes it easier to manipulate the dielectric properties of the polymer. Furthermore, enhanced β -phase crystallization of PVDF and consequently improved dielectric properties is anticipated.

6.4. Experimental

6.4.1. Materials

A semi-crystalline PVDF polymer (3M 11008/0001) was obtained in pellet form, from 3M Canada, with an average density of 1.55 g/cm³. The Cloisite 30B clay, grade 17172, was obtained from Southern Clay Products Inc. The MWCNTs (NanocylTM NC7000) were obtained from Nanocyl

S.A. (Sambreville, Belgium). According to the manufacturer, the MWCNTs were produced with catalytic carbon vapor deposition (CCVD) process and had an average diameter of 9.5 nm, a length of 1.5 μm , a surface area of 250-300 m^2/g and high aspect ratio (>150). All the materials were used as received without any pretreatment.

6.4.2. Composite preparation and molding

To obtain homogeneous distribution of MWCNTs in the polymer matrix, melt-mixing technique was used to increase the interactions between polymer and fillers via high temperature and shear forces [11]. In this work, a Haake Rheomix Series 600[®] batch mixer with Banbury blades was used at 220°C and rotor speed of 50 rpm. The PVDF was first masticated for 3 minutes and then, clay and MWCNTs were added to the PVDF and mixed for an additional 12 minutes. Samples with dimensions of 42x25x1 mm^3 were compression molded with a Carver hot press at 200°C under 35 MPa pressure for 10 min.

6.4.3. Characterization tests

Wide angle X-ray diffraction (XRD) was performed using a Geigerflex 2173 diffractometer with Co $K\alpha$ radiation at a wavelength of 0.179 nm to examine the morphology, particularly the crystalline structure of the nanocomposites. Fourier transform infrared (FTIR) spectroscopy attenuated total reflectance (ATR) was used to characterize the morphology of (MWCNT/clay/PVDF) nanocomposites. FTIR-ATR was recorded on an IL Nicolet NEXUS 470 FT-IR with Zn-Se detector, having resolution of 4 cm^{-1} and accumulation of 128 scans.

Crystallization behavior was also investigated using differential scanning calorimetry (DSC) via a Q-500 TA Instrument with second melting procedure from -90°C to 200°C and cooling/heating ramp of 10°/min. The samples were ultramicrotomed to sections of ~ 70 nm using Leica EM UC6 cryo-microtome. Transmission electron microscopy (TEM) analysis was carried out on the ultramicrotomed sample sections using a Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, Oregon, USA) at a 200 kV acceleration voltage with the standard single-tilt holder. The images were captured on a Gatan UltraScan 4000 CCD camera (Gatan, Pleasanton, California, USA) at 2048x2048 pixels.

The dielectric properties of the nanocomposites were measured with an impedance/gain-phase analyzer (Solartron SI 1260) in the frequency range of 10 Hz to 10^6 Hz. We performed three repetitions for each concentration. Prior to the measurements, the electrodes were painted on the samples using silver paste. Direct current (DC) conductivity of the samples was measured employing two different setups. For the nanocomposites with conductivities lower than 10^{-2} S m⁻¹, a Keithley 6517A electrometer connected to a Keithley 8009 test fixture (Keithley Instruments, USA) was used. For the samples with electrical conductivities more than 10^{-2} S m⁻¹, the measurements were performed with a Hiresta-UP (MCP-HT450) resistivity meter connected to a ring probe URS type. The applied voltage was 10 V for all the measurements.

6.5. Results and Discussion

6.5.1. Crystallization

The composites' crystalline structure and the amount of α and β phases were investigated by XRD, DSC, and FTIR-ATR tests. Since β phase is polar in nature, it is the most desirable crystal phase for charge storage applications. This form gives the best piezoelectric and ferroelectric

properties of PVDF which is more preferable for enhancement of the dielectric behavior of the composites. Figure 6.1 shows the effect of MWCNT incorporation on PVDF crystalline structure as determined by XRD results.

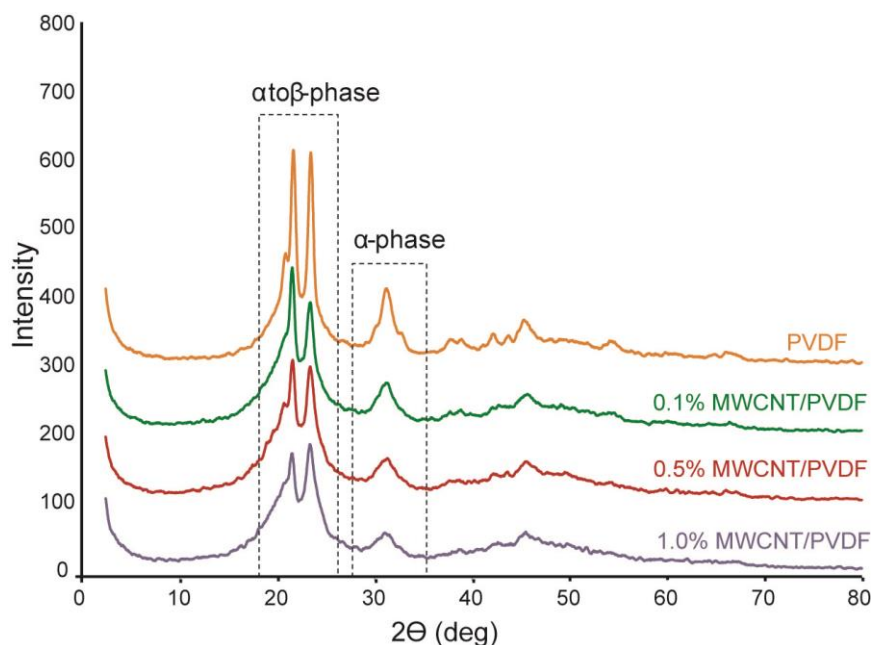


Figure 6.1. XRD results for pure PVDF and MWCNT/PVDF nanocomposite

From the peaks at $2\theta = 21.5^\circ$ and 31° , which all correspond to α phase crystals [3, 6 and 16], it can be concluded that MWCNT incorporation enhances the transformation of α into β phase. Furthermore, it has been reported that clay addition also enhances the β phase formation [3, 17]. Presence of clay restricts the polymer chain's motion and can induce the polymer lamellae to grow on the clay surface. In addition, it is believed that the crystals formed on clay have a high amount of β -phase compared to other phases, when the crystallization of PVDF occurs in a confined state [3, 17]. Therefore, we may conclude that the clay addition can result in higher tendency to beta phase crystallization in MWCNT/PVDF composite. Considering those effects, a α to β transformation in the hybrid nanocomposites of MWCNT/Clay/PVDF is anticipated. This hypothesis can be proved by XRD and FTIR results for MWCNT/Clay/PVDF nanocomposites, as will be discussed in the

following paragraphs. More β phase favors piezoelectric properties, therefore, an improvement in the dielectric behavior is expected.

The effect of clay addition on 0.5 wt% MWCNT/PVDF nanocomposite structure as presented by XRD results is provided in Figure 6.2. 0.5 wt% MWCNT/PVDF nanocomposite was used as representative in order to study the effects of clay addition on the MWCNT/PVDF nanocomposites. The intensity of the peaks at 2θ around 4.2° , which are attributed to the clay sheets basal spacing, increased confirming clay intercalation [4]. The addition of clay led to a decrease in the intensity of the peak at 21.5° and disappearance of the peak at 31° showing the transformation of α phase into β phase. Furthermore, an increase in the intensity of the peak at 23.5° (0.43 nm), which is attributed to both 110 and 200 β crystal planes is a more indication of α to β phase transformation [3, 6].

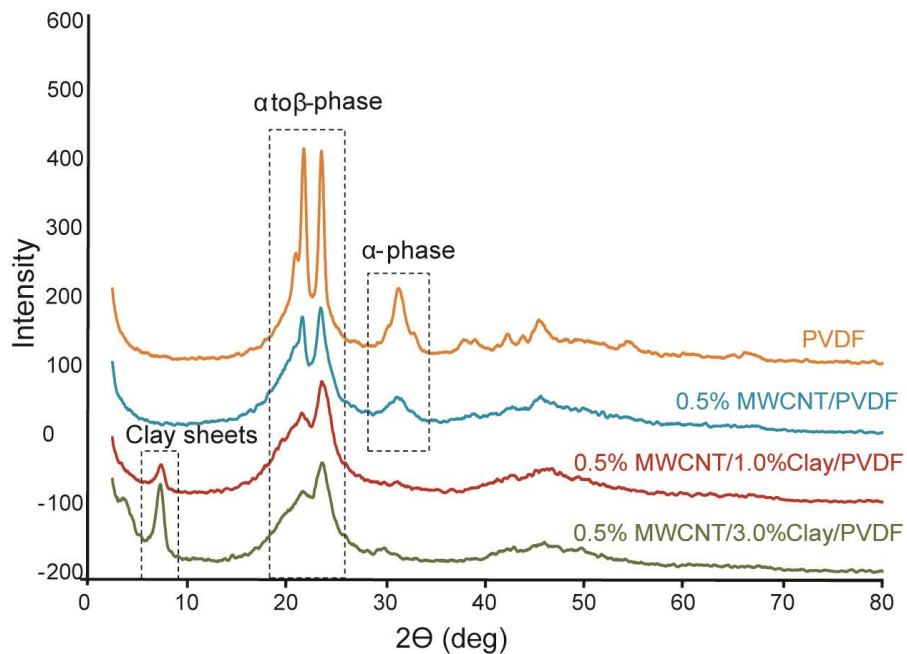


Figure 6.2. XRD results for pure PVDF, 0.5 wt% MWCNT/ PVDF, 0.5 wt% MWCNT/1.0 wt% Cloisite 30B/PVDF, and 0.5 wt% MWCNT/3.0 wt% Cloisite 30B/PVDF

The FTIR-ATR results, illustrated in Figure 6.3, show the effect of clay addition on crystal phase transformation of the 0.5 wt% MWCNT/PVDF nanocomposites. The absorbance peaks at 614, 795, and 976 cm^{-1} correspond to α phase and the peak at 840 cm^{-1} is attributed to β phase. FTIR-ATR results show that adding clay decreased the intensity of the peaks linked to α phase and increased the intensity of peak engaged with β phase.

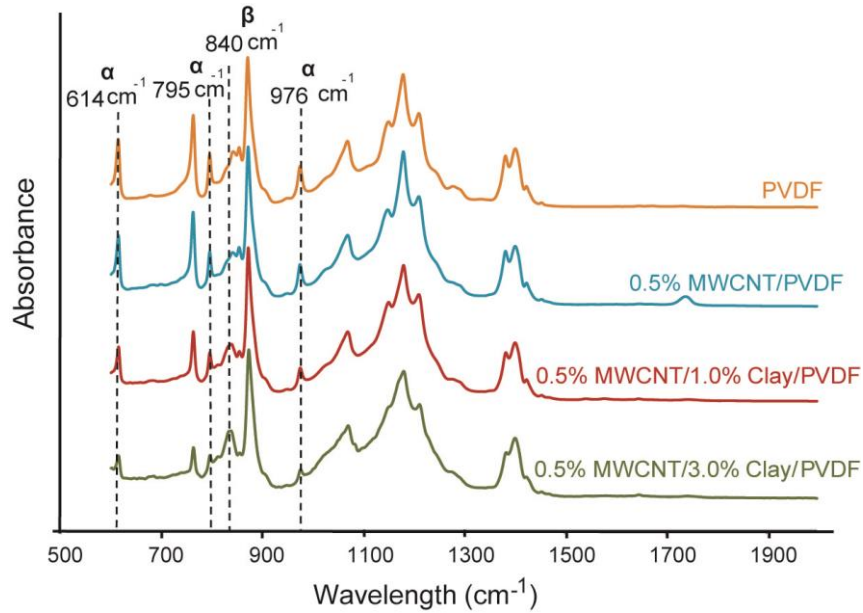


Figure 6.3. FTIR-ATR results for pure PVDF, 0.5 wt% MWCNT/PVDF, 0.5 wt% MWCNT/1.0 wt% Cloisite 30B/PVDF, and 0.5 wt% MWCNT/3.0 wt% Cloisite 30B/PVDF

The relative β phase content of the composites can be calculated according to FTIR result using Eq.6.1 [18];

$$F(\beta) = \frac{A_{\beta}}{\left(\frac{K_{\beta}}{K_{\alpha}}\right)A_{\alpha} + A_{\beta}} \quad (\text{Eq. 6.1})$$

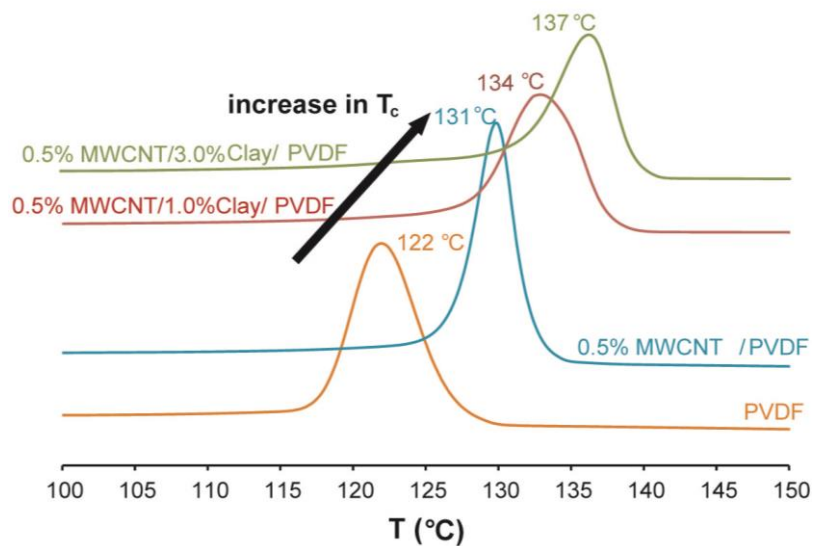
Where A_{α} and A_{β} are absorbance at 766 and 840 cm^{-1} and K_{α} and K_{β} are the absorbance coefficients (6.1×10^4 and $7.7 \times 10^4 \text{ cm}^2 \cdot \text{mol}^{-1}$) [18]. With the increase in the amount of β phase, as represented in

Table 6.1, we can conclude that embedding MWCNT and clay into the PVDF matrix led to α - β crystal phase transformation and improved dielectric behavior of the PVDF matrix.

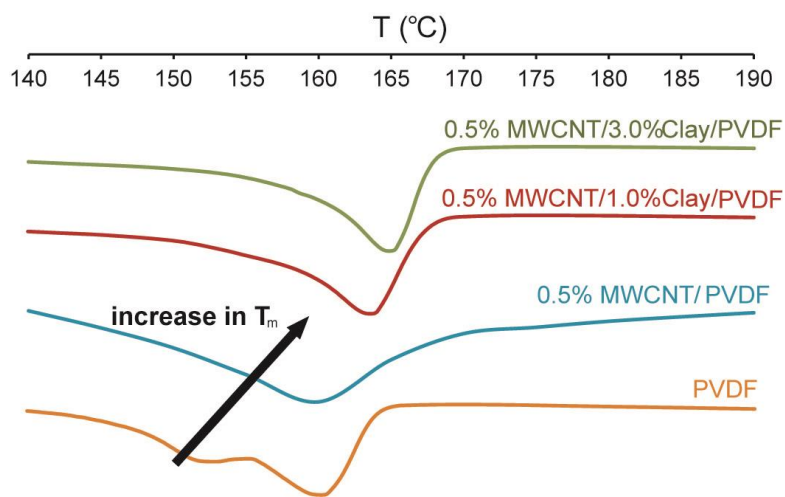
Table 6.1. β -phase content for 0.5 wt% MWCNT/PVDF composites with different clay contents

<i>Sample ID</i>	<i>β-phase content (%)</i>
<i>Pristine PVDF</i>	41.1
<i>0.5% MWCNT/PVDF</i>	41.5
<i>0.5% MWCNT/PVDF/1% C30B</i>	47
<i>0.5% MWCNT/PVDF/3% C30B</i>	55.9

Figure 6.4 depicts the DSC results, from which we can observe an increase in both the crystallization temperature (Figure 6.4-a) and melting temperature (Figure 6.4-b) as consequences of clay addition to the MWCNT/PVDF composite. These increases can be ascribed to the β -phase formation. It is reported that the tendency of PVDF to crystallize increases in the presence of nanoclay's silicate layers because of the restricted motion of PVDF molecules and good adhesion between polymer and silica particles [9, 17]. Therefore, from DSC results along with XRD and FTIR results, we conclude that clay addition increases the molecular orientation [18] and facilitates crystallization of PVDF; hence the composite would melt at higher temperature (T_m) which is an indication of more β -phase.



(a)



(b)

Figure 6.4. DSC results for pure PVDF, 0.5 wt% MWCNT/ PVDF, 0.5 wt% MWCNT/1.0 wt% Cloisite 30B/PVDF, and 0.5 wt% MWCNT/3.0 wt% Cloisite 30B/PVDF

6.5.2. Morphology

TEM images depicted in Figure 6.5 support the idea that clay addition improves the dispersion of MWCNTs into the PVDF matrix. More homogeneous dispersion of MWCNTs and less

agglomerates can be observed for the MWCNT/Clay/PVDF nanocomposites (Figure 6.5-a) compared to the MWCNT/PVDF nanocomposites without clay (Figure 6.5-b). The improvement of MWCNT dispersion and distribution upon introducing clay can be attributed to three factors: (1) increase in polymer matrix viscosity; (2) excluded volume by clay particles in the matrix; and (3) improved interaction of MWCNTs with clays [4, 10, 13, and 16]. Clay incorporation restricted the motion of polymer chains and thus led to higher viscosity of the PVDF matrix [16, 17, and 19]. The higher viscosity resulted in higher applied shear rate to MWCNT agglomerates and, hence caused better dispersion of MWCNTs. Another factor is excluded volume which is defined as the volume around a particle, i.e. clay, which other similar particles are not allowed to enter [20]. Clay particles would occupy some area in the matrix where other particles, e.g. MWCNTs, cannot get in. Consequently, MWCNTs are not able to re-aggregate and form big agglomerations in those areas in the matrix and thus will have a lower chance to form agglomerations. This will result in better distribution of MWCNTs [13]. Furthermore, it is believed that MWCNTs interact more strongly with clay than polymer matrix [16]. There is good adhesion between clay particles and polymer, and because of the better interaction of CNTs with clay, this allows for better dispersion of CNT. This synergetic effect can be ascribed to the electrophilic nature of clay and electronegativity of CNT. This attraction will contribute to an improved dispersion of CNTs in presence of clay. Thus, introducing clay into the PVDF matrix contributed possibly to improved dispersion of nanotubes. However, as illustrated in the schematic in Figure 6.6, clays also have the role of barrier as well as dispersion aid. Having much less conductivity than nanotubes, clays may introduce between the contact spots of the MWCNTs and destroy the path for electric charge carriers through the network.

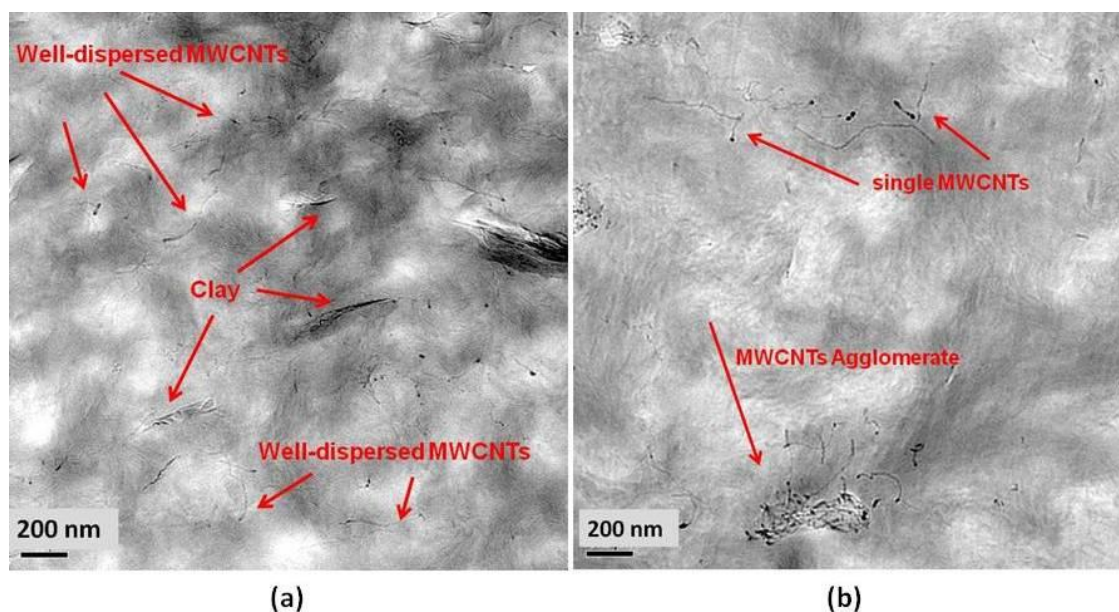


Figure 6.5. TEM images of (a) 0.5 wt% MWCNT/Clay/ PVDF and (b) 0.5 wt% MWCNT/PVDF composites. Better dispersion of MWCNT is seen when clay is added to the composite.

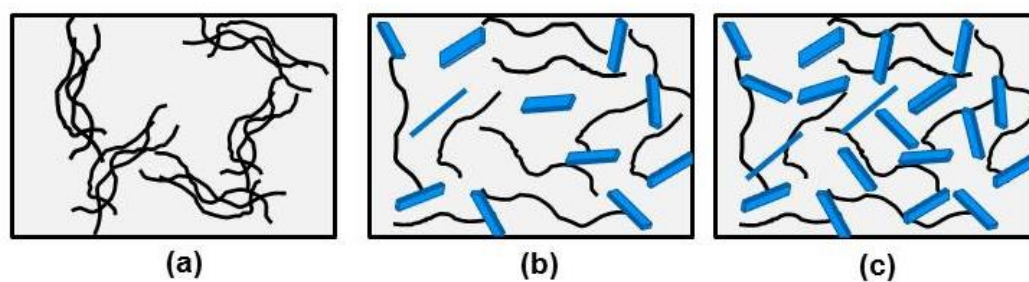


Figure 6.6. Schematic illustration of (a) MWCN/PVDF, (b) MWCNT/Clay/PVDF with moderate clay content, and (c) MWCNT/Clay/PVDF with high clay content. They black folded lines stand for MWCNTs and the blue sheets represent clays.

6.5.3. Dielectric Properties

High dielectric permittivity and low leakage current in CPCs is obtainable at filler loading close to the percolation threshold [4, 21]. Therefore, due to the insulator-conductor transition occurring at

the percolation threshold, the first step to evaluate the dielectric properties of CPCs is to determine the percolation threshold. Figure 6.7 illustrates the percolation curves of the MWCNT/Clay/PVDF nanocomposites for different clay contents. It is clear that the percolation threshold increased slightly by increasing the clay content in the MWCNT/Clay/PVDF nanocomposites. The percolation threshold for the composite without clay is around 0.3 wt% of MWCNT; however, clay addition at this concentration of MWCNT shifts the nanocomposites to the insulative region. In other words, incorporating 1.0 and 3.0 wt% clay raised the percolation threshold, i.e, around 0.5 wt% of MWCNT. The increase in the percolation threshold can be related to the deteriorated conductive network arising from the barrier role of clay sheets (Figure 6.6).

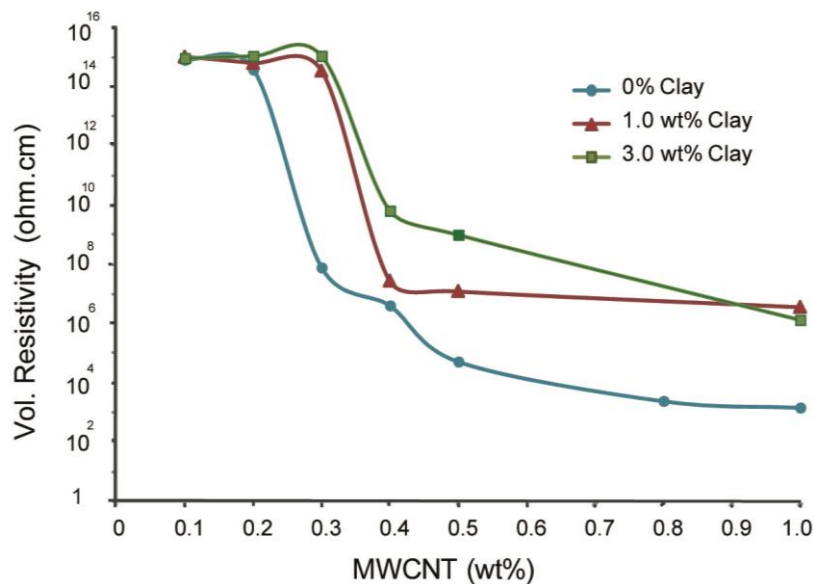


Figure 6.7. Volume resistivity as a function of MWCNT concentration for different clay contents in MWCNT/Clay/PVDF nanocomposites

Moreover, it was observed that the clay incorporation led to a smoother insulator-conductor transition. This smooth transition is a favorable dielectric behavior since it gives a wider concentration window to control the resistivity around the percolation threshold, while a sharp

insulator-conductor transition makes it extremely difficult to manipulate CPCs for charge storage applications. It is obvious that for the nanocomposites without clay a relatively sharp reduction of volume resistivity occurred, in the range of 0.2 to 0.4 wt% of MWCNT content, while the insulator-conductor transition was muted by clay incorporation. The broader concentration window of the insulator-conductor transition in the MWCNT/Clay/PVDF nanocomposites is attributed to the hindrance role of clay. This is an advantage for charge storage application like capacitors [15].

As charge storage materials should present high dielectric permittivity and low dielectric loss, the impacts of clay incorporation on the dielectric properties of MWCNT/PVDF nanocomposite were investigated. Figure 6.8 shows that dielectric permittivity increased tremendously with MWCNT content in the frequency range of study. High dielectric permittivity at high MWCNT loadings originates from nano-capacitor structures experiencing interfacial polarization [22]. Nano-capacitors in CPCs comprise conductive filler as nanoelectrodes, and insulative polymer layers between the nanofiller as nano-dielectrics [22]. Polarization moment has a magnitude equal to strength of each charge times the separation between charges. Thus, considering the scale at which charges are polarized in interfacial polarization and the presence of a large amount of nanocapacitor structures, a large dielectric permittivity was observed at high MWCNT loadings.

According to the electrical resistivity results presented in Figure 6.7, the percolation threshold is about 0.4 wt%. In order to investigate the impact of clay on dielectric properties, a MWCNT loading close to and above the percolation threshold was chosen, i.e. 0.5 wt%, where the conductive network was formed but was still unstable. The objective was to employ clay as insulating barrier to disturb unstable conductive network to reduce the leakage current. Figure 6.8 presents the impact of clay on the dielectric permittivity of the 0.5 wt% MWCNT/PVDF nanocomposites.

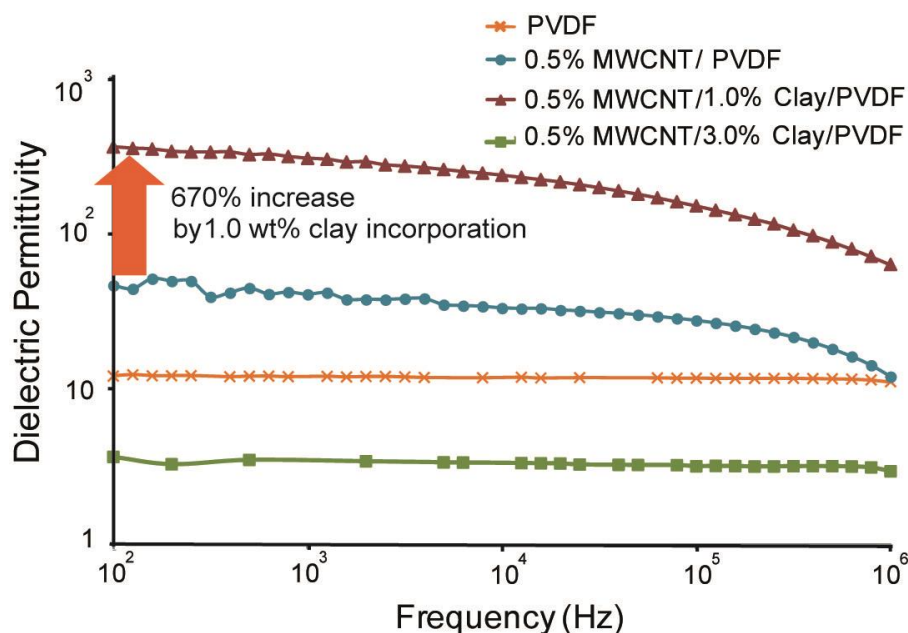


Figure 6.8. Dielectric permittivity of 0.5 wt% MWCNT/PVDF composites with different clay contents

As demonstrated in Figure 6.8, the addition of a specific amount of clay (1.0 wt %) increased the permittivity notably; that is, by 670% at 100 Hz. However, with 3.0 wt% clay content, a significant decrease was observed. This behavior can be explained by considering two counteracting parameters arising from clay addition; (1) enhanced interfacial polarization due to better MWCNT dispersion, and (2) barrier role of the clay. These roles for the incorporated clay can be simply visualized as presented in Figure 6.6. It seems that at low clay concentrations clay improved dielectric permittivity by improving dispersion; however, with increase in clay content the role of clay as barrier layer took over leading to a decay in dielectric permittivity. Therefore, it is likely that there is an optimum concentration up to which introducing clay helps to enhance dielectric permittivity. It is worth noting that incorporating clay impacted dielectric permittivity similarly for the other MWCNT contents.

As mentioned before, CPCs as charge storage materials are required to show a low dissipation factor, which is the ratio of leakage current (dielectric loss) over dielectric permittivity. The dielectric loss in CPCs originates from the movement of mobile charge carriers along conductive fillers [21]. It is also believed that at greater conductive network formation, free electrons can find more mean free paths to move in each half cycle of alternating field, and thus can dissipate more electrical energy. Given that, adding clay as insulative barrier is expected to decrease the dielectric loss by deteriorating the conductive network. Figure 6.9 presents the effect of clay addition on the dissipation factor, i.e. $\tan(\delta)$, of 0.5 wt% MWCNT/PVDF nanocomposites.

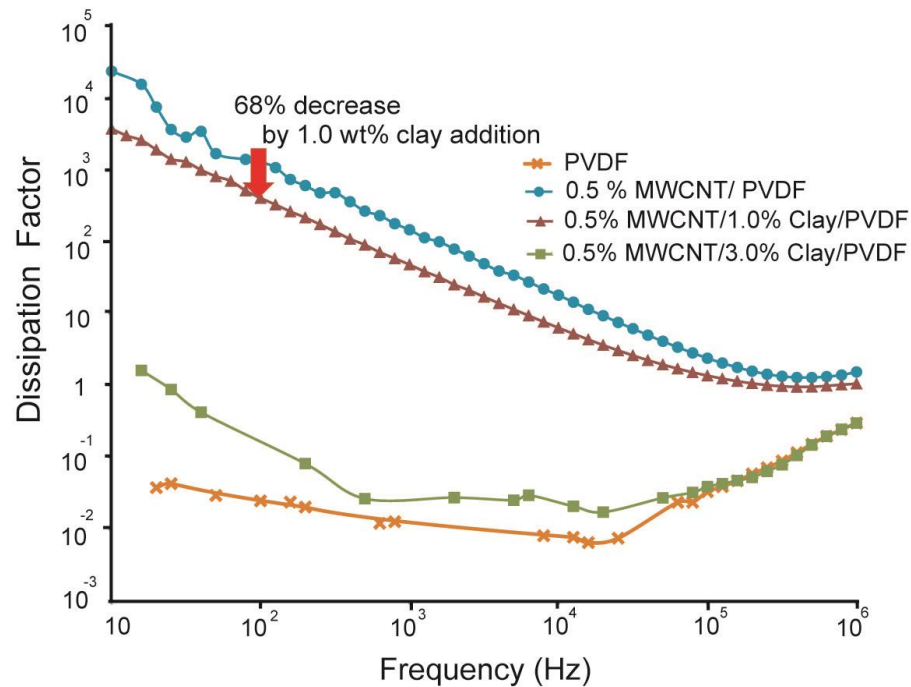


Figure 6.9. Dissipation factor, $\tan(\delta)$, of 0.5 wt% MWCNT/ PVDF composites versus frequency for different clay contents

It was observed that incorporation of clay led to a considerable reduction in dissipation factor. For instance, at 100 Hz incorporating 1.0 wt% of clay reduced the dissipation factor of 0.5 wt%

MWCNT/PVDF, 68% while adding 3.0 wt% clay reduced the dissipation factor several orders of magnitude. This can be related to the barrier effect of the clay sheets that disrupted the conductive network of MWCNTs and made it more difficult for charge carriers to move throughout the network [3]. The positive impacts of clay addition (1.0 wt%) on controlling the insulator-conductor transition, improving dielectric permittivity and reducing dissipation factor is an outstanding achievement which can potentially find industrial applications.

6.6. Conclusion

Hybrid nanocomposites of MWCNT/Clay/PVDF were produced by melt-mixing method at different concentrations of MWCNT and clay. It has been shown that introducing clay into the composite system increased the amount of β phase crystal, which is beneficial for piezoelectric, ferroelectric and dielectric properties. It was observed that adding clay to the MWCNT/PVDF nanocomposites led to a wider insulative to conductive transition window. This was ascribed to the barrier formed by clay platelets in between the MWCNTs network. Muting the sharp insulator-conductor transition through introducing clay is a significant achievement since it facilitates manipulation of CPCs around the percolation threshold.

Regarding to dielectric performance of the nanocomposites, clay showed to be effective in two ways; acting as (1) dispersion aid, and (2) barrier layer. Based on the results, clay concentration defines the controlling factor. At lower clay content (1.0 wt%), due to better dispersion of MWCNTs, improved interfacial polarization and higher dielectric permittivity were achieved. However, at higher clay content (3.0 wt%) the barrier role of clay was dominant and caused lower permittivity.

Besides the permittivity, dielectric loss also depends on the clay content. Results confirm that the dissipation factor considerably decreased by clay addition as a result of the hindrance role. Therefore, there is an optimum clay concentration to gain the desirable properties enhancement for charge storage application, which is combination of high dielectric permittivity and low dielectric loss.

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Chapter 7

Influence of Melt-Mixing Process Conditions on Mechanical Performance of Organoclay/Fluoroelastomer Nanocomposite*

7.1. Presentation of the Article

The main purpose of this article is to optimize the fabrication method and conditions for polymer nanocomposites. Melt-intercalation method for nanoclay/fluoroelastomer (FKM) production has been studied in this work. Cloisite 20A, a modified montmorillonite (Mnt) clay, was incorporated in FKM matrix via melt-mixing process using an internal Haake batch mixer. The effect of three different process conditions namely, time, temperature, and shear rate on curing behavior and mechanical performance of the nanocomposites have been investigated. Optimum combination of the process conditions led to improved crosslinking kinetics, tensile strength, elongation and modulus. The main part of this work has been done by Maryam Khajehpour and Dr. U. Sundararaj has supervised the work.

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Influence of Melt-Mixing Process Conditions on Mechanical Performance of Organoclay/Fluoroelastomer Nanocomposites

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7.2. Abstract

In this study, Cloisite 20A, an organically modified Montmorillonite (Mnt), has been incorporated into Fluoroelastomer (FKM) through melt intercalation. Since the nanocomposite preparation method and conditions, and consequently, the resulting morphology play a critical role in the final properties, the effect of different process conditions such as time, temperature, and shear rate on the vulcanization, thermal and mechanical properties have been investigated. The morphology of nanocomposites, prepared at different melt-mixing conditions, was studied using X-ray diffraction (XRD). Rheological, thermal and mechanical behaviors were investigated by moving die rheometer (MDR), thermal gravimetric analysis (TGA), and tensile strength test respectively. Also, the crosslinking density has been measured for the composites. By optimization of the melt-mixing conditions, the best mechanical performance of clay/FKM nanocomposite can be attained. We achieved the following enhancements for FKM by clay incorporation: enhancement of tensile strength up to 70%; elongation up to 94%; and modulus up to 405%.

Process temperature was found to have a critical role in the final properties of the nanocomposites, while mixing residual time and shear rate had a moderate effect. The most desirable properties and curing behaviors, including highest maximum torques, cure rates, crosslinking densities, fast crosslinking kinetics, high intercalation and best improved tensile strengths, resulted with specific combination of melt-mixing parameters.

7.3. Introduction

One well-established way to enhance the mechanical properties of polymers is adding inorganic filler to the organic polymer matrix. The incorporation of conventional fillers (e.g. carbon black or glass fiber) may cause some drawbacks, such as sloughing or brittleness; however, introducing well-dispersed nanofillers, such as nanoclay, into the polymer matrix overcomes this problem, bringing significant improvement in heat resistance and in mechanical properties, e.g. hardness, modulus, tensile and tear strength [1-4]. The significant advantage of nanofillers to the conventional micro-scale fillers is their extremely high surface area and stronger interaction with the polymer matrix [1, 2, 5, and 6]. Among nanoparticles, nanoclays are considered as ideal fillers for thermoplastic and thermoset polymer nanocomposites [1-6] due to ion exchange ability, swelling properties, active sites and high aspect ratio [7-10]. The clay's miscibility in the polymer, and its intercalation and exfoliation, determine the final properties of nanocomposites [11-14]. Different types of nanocomposites are likely, depending on the interaction between polymer and silicate layers; in each nanocomposite type, the physical properties are different [15, 16]. Studies show that nanocomposite structure - hence, mechanical properties - depend on both the processing conditions and the chemical nature of the clay and polymer [2, 4, 14, 17, and 18]. Therefore, to

obtain optimized properties, different methods of compounding and process conditions must be studied. While the agglomeration of nanoparticles seriously impairs the final performance of composites [12], several routes have been developed to improve the dispersion of nanoclays in polymer [19].

Direct melt intercalation is the most industrially appropriate technique for clay/polymer nanocomposites' preparation [1, 2, 14, 20, and 21] in which molten polymer penetrates the galleries between dispersed silicate platelets [4, 16]. Different compounding parameters, such as mixing time, temperature, and shear rate can affect the final nanocomposite's morphology [4, 22]. The addition of compatibilizer and/or accelerators has been shown to lead to better mixing [2, 18, and 23]. Based on previous studies, it could be concluded that: (a) a higher temperature (below degradation temperature) enhances exfoliation [3, 4, and 24]; (b) increased mixing time facilitates dispersion of clay layers [6, 14, 18, and 24]; (c) increased shear stress, up to a moderate level, yields better dispersion [18]; (d) excessive shear stress reduces exfoliation [4]; (e) using compatibilizer improves the intercalation and exfoliation but may also induce clay agglomeration [18]; and (f) a minimum mixing residence time is required to obtain a well-intercalated or exfoliated state [4].

Less attention has been paid to the nanoclay/elastomer nanocomposites compared to thermoplastics and thermosets [20, 22]. Reinforcement of elastomers by nanoclay incorporation can lead to a wide range of applications due to their light weight and processability, compared to metals [25], and enhanced mechanical properties, compared to unreinforced elastomers and traditional elastomer composites [25, 26]. Studies show that both tensile strength and modulus could be improved by a clay addition to rubber [24]. It is well known that the nanocomposite

structure, or the dispersion of nanofiller, significantly impacts the final mechanical properties. Thus, there is significant need to find an industrially viable way to disperse clay well in rubbers [23]. Some issues with processing and blending clay into elastomer occur. First, the extremely high van der Waals attraction at the nanoscale, coupled with high surface contact area, make it very difficult to disperse clay. Second, even if polymer intercalates into the clay during blending of the composite, during cross-linking, the polymer molecules are pulled out of the clay galleries.

Fluoroelastomer (FKM) is a special type of rubber that shows excellent performance when high thermal and chemical resistance are required [22, 27, and 28]. These materials are proposed in applications where elastic behavior is needed for severe environments, such as oil-well completion and production [24]. Specifically, their superior oil and water swelling resistance and low flammability make them desirable for many oil and gas industry applications [27].

In this work, montmorillonite clay/FKM nanocomposites were synthesized and their curing behavior, mechanical and thermal properties investigated. Clay/FKM nanocomposites were produced via melt intercalation by different conditions to study the effect of temperature, time, and shear stress on the final morphology and mechanical properties. We showed that an optimized combination of different process conditions leads to the composite's most desirable properties.

7.4. Experimental

7.4.1. Materials

Organically modified Montmorillonite, Cloisite 20A was obtained from Southern Clay Products Inc. Viton[®] Fluoroelastomer grade GF-200S (copolymer of hexafluoropropylene, vinylidene fluoride, and tetra fluoroethylene) was supplied by Dupont. Triallyl Isocyanurate

(TAIC), ZnO, and 2,5-dimethyl-2,5-di(t-butylperoxy) hexane were obtained from Cray Valley, U.S. ZINC, and VAROX[®] respectively.

7.4.2. Clay/ FKM Nanocomposite preparation

Clay/FKM nanocomposites, with a clay concentration of 10 phr, were prepared by the melt-mixing process using an internal batch mixer (Thermo-Fisher Haake Rheomix Series 600[®]) with Banbury blades. The clay is a commercial Montmorillonite, modified with dimethyl, dihydrogenated tallow quaternary ammonium, named as Cloisite 20A. Degradation starts at about 285°C for Cloisite 20A, which is due to thermal stability of the tallow surfactant modifier that have been used in the structure of the clay. The half-life time for the specific peroxide is 10 hours for the temperature up to 120°C which will be reduced to 1 hour at 142°C. Considering degradation temperature of Cloisite 20A, activation temperature of the peroxide, onset degradation for the pure FKM at 390°C, and also taking into account that the curing temperature for this type of clay/FKM composite is around 160°C, the processing temperature and time should be such that neither degradation nor scorching happens for the composites. The effect of three different factors, including process temperature, residual time, and the shear rate (i.e. rotor speed), were studied, each at two or three different levels. The mixing temperature was set at three values of 50, 75, and 100°C; the process residual times at two levels of 15 and 30 minutes; and the rotor speeds at 45 and 100 rpm. The experiments were designed based on the factorial design method. Considering the negative effect of co-existence of the high level of temperature and the shear rate, which leads to sample scorching, some of conditions were omitted from the design. We end up, therefore, with a set of conditions as summarized in Table 7.1.

It is worth mentioning that the melting temperature increases during the mixing procedure as a result of viscous heating due to shear applied to the composite. Thus, the maximum melting process temperature is higher than the set temperature. This maximum temperature has been also reported in Table 7.1 to show how the mixing time and rotor speed affect the temperature. Records show that the combination of high rotor speed and longer mixing time caused a relatively large rise in temperature that probably leads to composite samples scorching. This incident is noticeable for sample # 6, with a rotor speed of 100 rpm and a mixing residual time of 30 minutes.

Table 7.1. Experimental design of melt-mixing process conditions

Sample No.	Sample ID	Process Factors (High, Low, Medium)			Process Output
		T _{set} (°C)	Mixing residual time (min)	Rotor speed (rpm)	Max melt T (°C)
1	TL/tL/RH	50	15	100	91
2	TL/tH/RL	50	30	45	72
3	TM/tL/RL	75	15	45	91
4	TM/tH/RL	75	30	45	90
5	TM/tL/RH	75	15	100	115
6	TM/tH/RH	75	30	100	135
7	TH/tL/RL	100	15	45	113
8	TH/tH/RL	100	30	45	113

Vulcanization is essential to provide sufficient mechanical strength for rubbers, as un-crosslinked matrices show poor mechanical performance [26]. It is well-known that contributions of clay and vulcanization agents have equally important effects on improving curing behavior and that vulcanization affects the intercalation/exfoliation process [20, 26]. Some common curing agents were added to the Clay/FKM nanocomposites during the melt-mixing procedure. The curing additives and their concentrations were constant for all the composites: 3 phr of ZnO, 2 phr of peroxide (2,5-dimethyl-2,5-di(t-butylperoxy)hexane) and 2 phr of TAIC . After compounding FKM and the clay at the conditions of Table 7.1, the vulcanization agents were added at the same

temperature and rotor speed and mixed for another 15 minutes. Then, the samples were cured via compression molding at 160 °C and 5000 psia pressure for 20 minutes.

7.4.3. Nanocomposite Characterization

Thermal gravimetric analysis (TGA) TA instruments Q500 series was used to determine the thermal stability of nanocomposites. The TGA test was done under N₂ atmosphere at a 10°C/min heating rate, from 30°C to 800°C. An X-Ray Diffraction (Rigaku Multiflex X-ray Diffractometer) test, with Cu K α X-ray tube at a voltage of 40 kV and a current of 20 mA, was conducted to evaluate the basal spacing of clay layers in nanocomposites. The XRD tests were conducted on 18mmx20mmx2mm cured compression molded samples. Tensile strength was tested using a TensiTech machine, following the ASTM D412 standard for dumbbell specimens with the dimensions according to the standard and thickness of 2mm. Vulcanization and rheological behavior of the composites were studied using a TechPro Moving Die Rheometer (MDR⁺), which was performed at 160°C and at an oscillating frequency of 1.66 Hz, with 0.5 deg arc (ASTM D5289), for 20 min. The rheological characterization samples were disks with a 25 mm diameter and 2 mm thickness which were prepared by compression molding at 90°C and 10 MPa for 2 minutes.

7.4.4. Cross-linking Density Measurement

Three 1cmx1cmx2mm compression molded samples of each composite were exposed to methyl ethyl ketone (MEK) for 72 hours at room temperature and then dried for 24 hours at 60°C

under vacuum. The weights before and after swelling were recorded for crosslinking density calculation.

7.5. Results and Discussion

7.5.1. Thermal Stability

From the TGA and differential TGA (D-TGA) results, presented in Table 7.2, we can discern no significant difference between the thermal stability of the composites prepared at different melt-mixing conditions. The degradation onset (corresponding to 5.0% weight loss) and the total weight loss are almost the same for all composites. The only exception is sample # 6, which starts to degrade at a lower temperature compared to the other composites. This was anticipated for sample # 6 since it experienced very high melt temperature and probably was scorched.

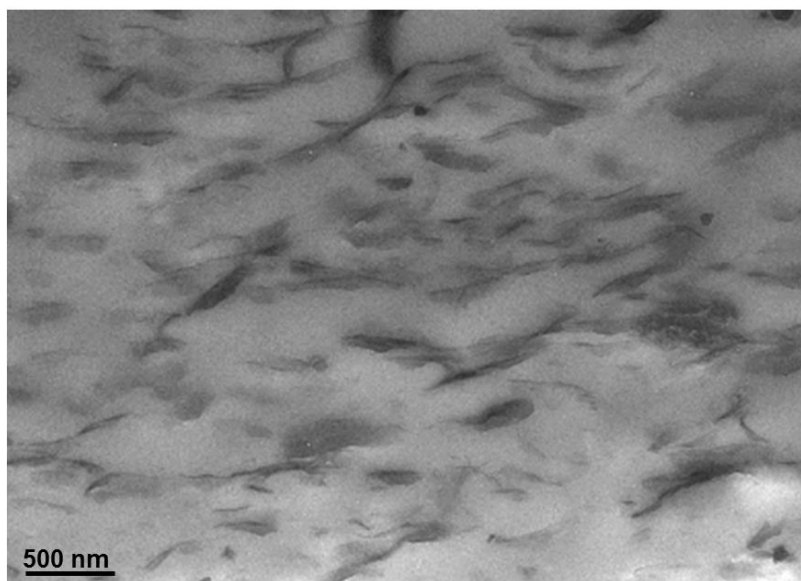
Table 7.2. 5.0% weight degradation start point for Clay/FKM composites

Sample No.	Sample ID	5% weight loss T (°C)	D-TGA peak (°C)
1	TL/tL/RH	310	345
2	TL/tH/RL	310	350
3	TM/tL/RL	305	345
4	TM/tH/RL	305	345
5	TM/tL/RH	310	345
6	TM/tH/RH	290	340
7	TH/tL/RL	310	345
8	TH/tH/RL	310	345

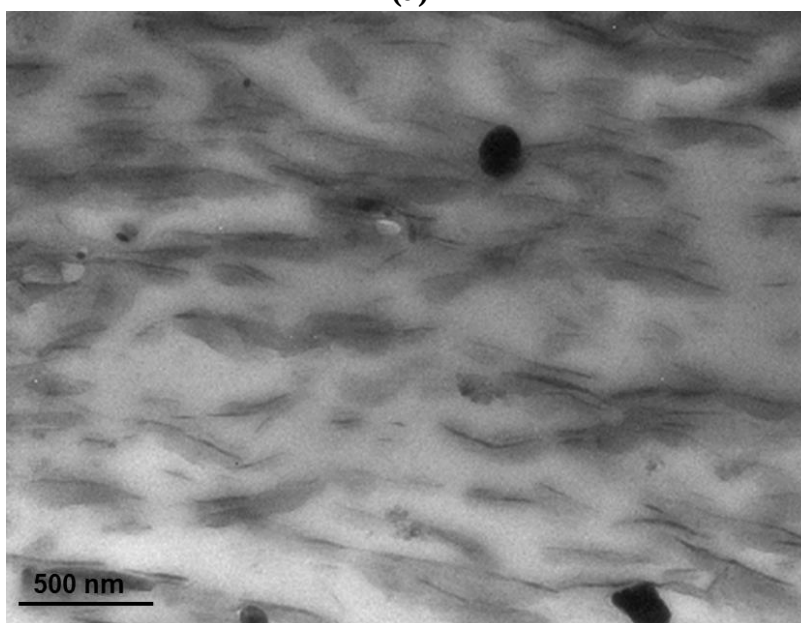
7.5.2. Morphology

A fairly good dispersion and intercalation of the nanoclay sheets in FKM matrix, for two of the samples can be observed from TEM images in Figure 7.1. These TEM images are

representative of all the samples. More exact quantitative data about the level of intercalation were obtained from X-ray diffraction (XRD) test.



(a)



(b)

Figure 7.1. TEM images of Cloisite 20A/FKM composites; (a) sample 2, (b)* sample 8.

*: dark spots are agglomeration of curing agents.

The XRD was carried out to study the effect of process conditions on the intercalation of clay sheets. Focusing on the XRD graphs demonstrated in Figure 7.2, a peak shift to the left is clearly visible for all the composites relative to pristine Cloisite 20A. The shift to lower angles and broadening of the peaks are evidence of polymer intercalation into the clay interlayers and partial exfoliation of clay sheets in the matrix. Moreover, a comparison of the final morphology for the different samples is possible in accordance to the d-spacing measured from XRD results.

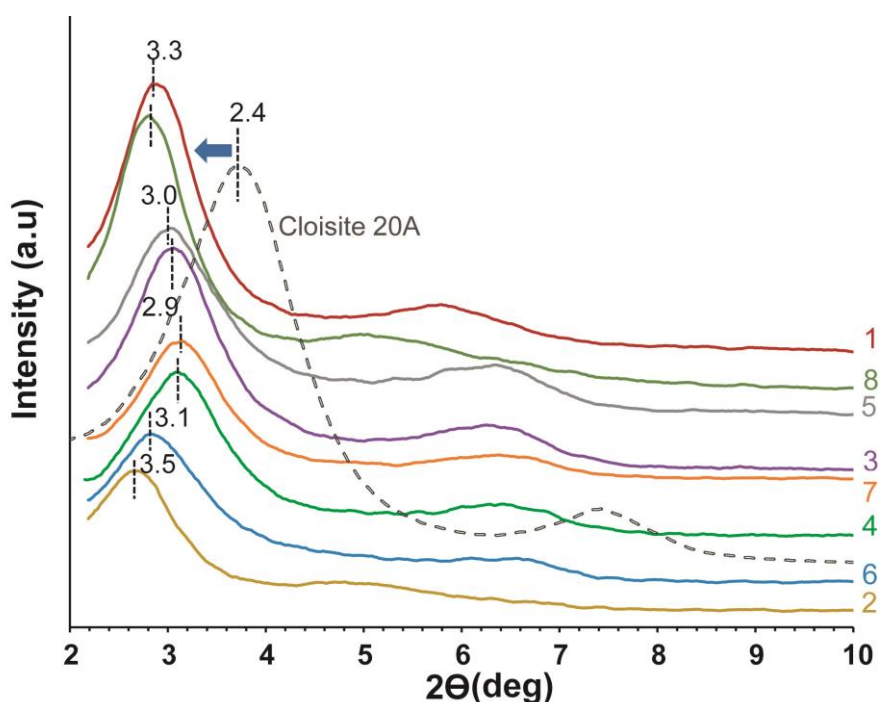


Figure 7.2. XRD results of Cloisite 20A/ FKM composites made at different mixing conditions.

According to the peak positions, which are summarized in Table 7.3, the highest d-spacing, hence most intercalation, correspond to samples 1, 2, and 8. In these three samples, only one of the melt-mixing times or shear rates assumes its highest value, while the other parameters take its lowest one. One major conclusion is that each and every one of the studied process parameters has an effect on the intercalation of clay. Furthermore, the interactions of the factors were found to

have considerable effect on the intercalation. Our observations showed that a simultaneous increase in time and shear rate has a negative effect on the intercalation.

Table 7.3. Basal spacing of clay layers in the composites according to the XRD peaks

Sample No.	Sample ID	Peak position (deg)	d ₀₀₁ (nm)
1	TL/tL/RH	2.700	3.268
2	TL/tH/RL	2.513	3.511
3	TM/tL/RL	2.978	2.963
4	TM/tH/RL	3.029	2.913
5	TM/tL/RH	2.943	2.998
6	TM/tH/RH	2.823	3.126
7	TH/tL/RL	3.064	2.880
8	TH/tH/RL	2.703	3.265
Cloisite 20A	Cloisite 20A	3.640	2.424

7.5.3. Rheometry and Crosslinking Measurement

The rheological behavior of polymer composites depends on their viscoelastic characteristics, which are affected by both filler type and concentration and the process parameters [22]. The effect of process conditions on some rheological properties are studied in this paper. Rheometry results, via MDR rheometer, represent the curing behavior and vulcanization characteristics of the composites at 160°C. From the cure curve (i.e. torque against cure time), some significant parameters - namely, minimum torque (M_L), maximum torque (M_H), induction time (t_{S2}), and optimum cure time (t_{C90}) - are determined. The curing rate (CR), which is defined as $CR = 100/(t_{C90} - t_{S2})$ is calculated and indicates the rate of crosslinking and stiffness after the scorch time [29].

As the compound is heated under pressure, the viscosity decreases and consequently, torque falls [29]. When the vulcanization process starts, the torque increases and after a while, it attains a

maximum value (M_H) [29]. M_H is the maximum torque exerted on the elastomer during crosslinking and is the measure of stiffness or shear modulus of the fully vulcanized specimen which indicates the level of curing [30]. M_L , the measure of stiffness or shear modulus of the unvulcanized specimen [30], is proportional to the viscosity of the uncured compound. The t_{s2} value is the time at which scorch occurred. t_{s2} is being recorded when viscosity of the specimen rises 2 units above M_L , therefore “s” stands for scorch and 2 stands for the viscosity. t_{C90} , is the time when 90% of the maximum torque is achieved during curing; these times give us an estimate of the vulcanization kinetics.

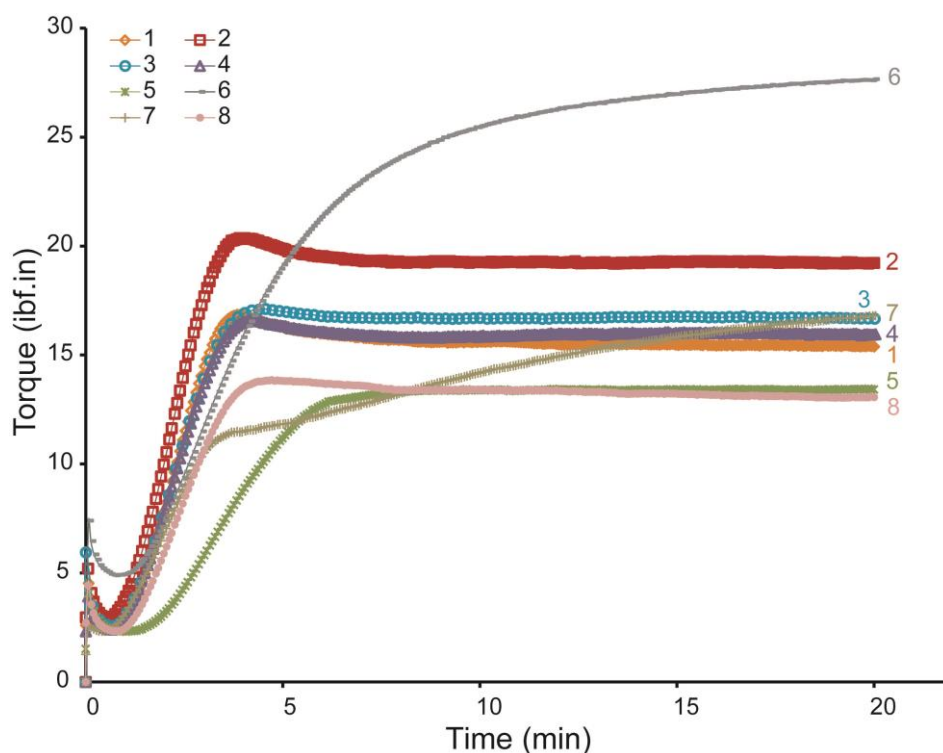


Figure 7.3. MDR Rheographs for clay/FKM composites

The rheometry test results are reported in Table 7.4 and the corresponding rheographs are illustrated in Figure 7.3. Generally, we can say that the kinetics are similar for all composites

except sample # 6, which shows unusual behavior, including scorching of the composite. Therefore, we excluded sample # 6 from comparisons and discussion. However, all data for this sample are included in the results to show that not all process conditions result in good properties, particularly in this case, when the composite is scorched.

Table 7.4. MDR rheology results for clay/FKM composites: maximum and minimum torques, t_{C90} , t_{S2} , and cure rate

Sample No.	Sample ID	M_H (lb _f .in)	M_L (lb _f .in)	t_{C90} (min)	t_{S2} (min)	CR
1	TL/tL/RH	16.72	2.25	3.2	1.41	55.87
2	TL/tH/RL	20.23	2.54	3.18	1.22	51.02
3	TM/tL/RL	16.98	2.2	3.38	1.38	50.00
4	TM/tH/RL	16.48	2.03	3.36	1.37	50.25
5	TM/tL/RH	13.32	1.96	5.64	2.45	31.35
6	TM/tH/RH	27.56	4.59	9.79	1.82	12.55
7	TH/tL/RL	16.57	1.94	13.26	1.32	8.38
8	TH/tH/RL	13.71	1.95	3.57	1.6	50.76

Based on the results, we can conclude that both the highest maximum torque (M_H) and fastest crosslinking kinetics (low t_{C90}) correspond to the composites such as samples # 1 and 2 that were prepared at conditions with either high shear rate or longer mixing residual time, while the rest of mixing parameters take their lowest levels. Sample # 1 was produced at a high shear rate but low mixing temperature and residual time, while sample # 2 was produced at a low shear rate and temperature but longer mixing time. Considering that these samples have the lowest increase in melt-mixing temperature in comparison to the others, it can be postulated that high temperature impairs the crosslinking performance.

The mechanical performance and crosslinking density were also measured. The experiments for the crosslinking measurements were done at room temperature. The chemical crosslink density of the composites can be calculated by the Flory-Rehner equation (Equation 7.1) [31].

$$\mu = \frac{-[\ln(1-V_2)+V_2+\chi_1 V_2^2]}{\bar{V}_1[V_2^{\frac{1}{3}}-V_2/2]} \quad Eq. 7.1$$

$$V_2 = \frac{m_1 \rho_s}{m_1(\rho_s - \rho_{FKM}) + m_2 \rho_{FKM}} \quad Eq. 7.2$$

Where V_2 is the volume fraction of rubber in the swollen gel (Equation 7.2 is taken from reference [32]). $\bar{V}_1$ is the molar volume of the solvent. χ_1 is the Flory-Huggins interaction parameter of the rubber with the solvent. m_1 is the mass of polymer before swelling and m_2 is the mass after swelling. Using the weights before and after swelling, the volume fraction has been calculated. The χ_1 value for FKM and MEK system at 25 °C is taken to be -1.0 [33].

Crosslinking results, given in Table 7.5, confirm that introducing clay in the FKM matrix improves crosslinking up to 87.8% (for sample # 2) compared to the neat cured FKM. Moreover, results indicate that the process conditions for samples # 1 and 2 lead to the highest crosslinking densities. These results match the calculated cure rates (Table 7.4), since the maximum CR values correspond to the same samples with the highest degree of crosslinking. In addition to having the highest M_H and lowest t_{C90} values, samples # 1 and 2 also showed the highest clay intercalation in the composite, according to the XRD test results (Table 7.3). This is additional evidence that the most promising condition is when only one of the processing parameters is at the high level while the two other factors are kept at their lower level.

Table 7.5. Crosslinking density for FKM/clay composites prepared at different process conditions

Sample No.	Sample ID	Crosslinking density (mol/cm ³) x10 ³
1	TL/tL/RH	4.92
2	TL/tH/RL	4.62
3	TM/tL/RL	4.59
4	TM/tH/RL	4.47
5	TM/tL/RH	3.86
6	TM/tH/RH	4.47
7	TH/tL/RL	4.32
8	TH/tH/RL	4.13
FKM (cured)	FKM	2.62

7.5.4. Mechanical Properties

Tensile tests were performed to examine the mechanical performance of the composites. At least three individual specimens were tested for each composite. Figure 7.4 shows the tensile curves for the different materials. The average values of the tensile strength (TS), elongation at break, modulus of the composites and their standard deviations are reported in Table 7.6. The mechanical properties of pure FKM are also reported. It is well-known that the interaction of fillers and the polymer in the composites contributes to enhancing macroscopic properties, such as tensile properties [34]. The comparison of FKM properties, with and without filler from the tensile test results shows that introducing clay in the FKM matrix significantly improves mechanical properties. Particularly surprising was the increase in elongation at break for several samples. Typically, fillers tend to lead to lower elongations for polymer composites. Our results, however, indicate a stronger bond between polymer chains and clay layers than typically found, and this is the reason for the unexpected increase in the elongation [34]. As expected, sample # 6 is the exception due to the scorching that occurred during mixing process and its tensile strength is even

less than pristine FKM. When the process temperature is close to the curing temperature, the composite starts to be cured and scorched; hence, the tensile, elongation, and modulus values will be noticeably decreased. Process conditions, therefore, should be set such that scorching is avoided.

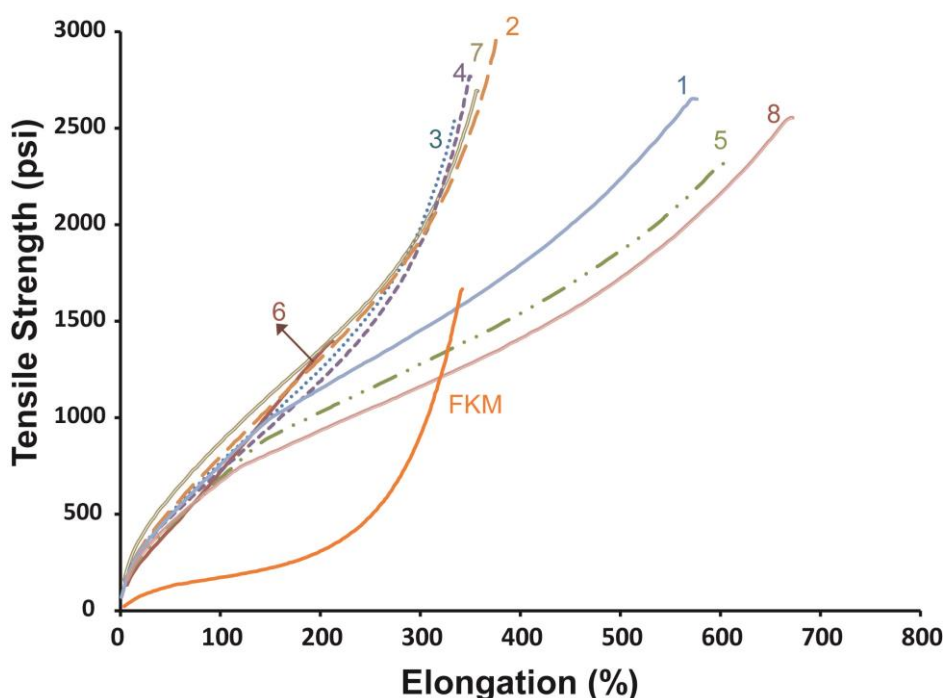


Figure 7.4. Tensile test results for FKM/clay composites prepared at different process conditions

First, by comparing the results with previous work on the same nanocomposite (i.e. 10 phr Cloisite 20A/FKM) with the same recipe and preparation method [35], we observe improvements in both tensile strength and elongation for all of our nanocomposites compared to their composites with slightly different mixing conditions. This indicates the significance of the effect of process conditions on the final properties of the composites. Studying the mechanical test results, several conclusions can be made. From the results, the highest tensile strength corresponded to Sample #2, which also exhibited the maximum torque in the rheo-curves and the most intercalation per the XRD results. With the specific conditions of low temperature, low shear and long residence time,

the tensile strength was improved by 70% for Sample #2 compared to pure FKM. These results support the idea that the conditions which lead to better crosslinking are closely related to the increase in tensile strength.

Table 7.6. Tensile test results for FKM/clay composites prepared at different process conditions

No.	Sample ID	TS		Elongation at break		Young's Modulus	
		TS (psi)	St Dev.	Elongation (%)	St Dev.	100% Modulus	St Dev.
1	TL/tL/RH	2512.9	94.3	568.4	11.5	765	6
2	TL/tH/RL	2902.9	96.6	362.4	11.3	789	8.6
3	TM/tL/RL	2475.5	75.4	329.1	12.2	816	19.7
4	TM/tH/RL	2641.9	159.6	345.6	4.4	753	18.6
5	TM/tL/RH	2305.7	10.0	598.4	7.8	703	13.4
6	TM/tH/RH	1403.1	99.6	191.2	18.1	763	31.5
7	TH/tL/RL	2544.1	130.6	336.4	25.5	869	30.2
8	TH/tH/RL	2444.1	107.7	662.1	16.3	661	6.4
FKM	FKM	1709.3	60.3	342.5	0.6	172	0.7

The elongation at break was increased up to 94% (Sample #8) and the 100% Young's modulus value was increased up to 405% (Sample #7). Considering the effect of excessive shear on the elongation and tensile strength of the composite, we can conclude that to achieve the best combination of mechanical properties of a composite, the three parameters of mixing conditions (temperature, time and shear rate) should not all be set to their highest level. Results prove that by optimization of mixing parameters the elongation could be improved as a result of good interaction between clay and polymer. Most of the previous research literature, however, shows poor elongation values since components of the nanocomposites are not able to achieve good adhesion [34]. The highest elongations correspond to samples # 8, 5 and 1, in rank order. According to their

mixing conditions, we may conclude that time, shear rate and their interaction significantly alter the elongation. For instance, in order to get a higher elongation at high shear rate it is better to have a shorter mixing time, which were the conditions for samples # 1 and 5. Also, when the mixing time is at the higher level, the best results for elongation are achieved with lower shear rate, as seen in sample # 8. Another conclusion from the comparison of samples # 5 and 3 is that we can assume that higher shear rate, with other mixing parameters kept at fixed values, causes more elongation and intercalation; however, tensile strength and modulus reduce slightly at the same time. Moreover, it could be concluded that the effect of residual mixing time on the mechanical properties depends on the temperature of the process: a longer mixing time at the relatively high melt temperature close to curing temperature (above 100°C) has a negative effect on the tensile strength, while at a relatively low melt temperature (~90°C), a longer mixing time helps to improve mechanical performance. At a fixed temperature and shear rate, longer residual time results in higher tensile strength, provided that the final process temperature is below the scorching temperature. On the whole, we need to consider the final desired mechanical performance of nanocomposites to optimize the processing conditions.

7.6. Conclusion

Organoclay (Montmorillonite Cloisite 20A)/Fluoroelastomer (FKM) nanocomposites were prepared via melt-intercalation using different process conditions. The effect of process conditions on thermal stability, curing behavior, crosslinking density, and mechanical performance of the composites were studied. The thermal stability of the composites does not seem to be significantly affected by the process conditions. The composites, however, exhibited different curing behavior

and different mechanical properties. All of the most desirable properties and behaviors, including highest maximum torques, cure rates, crosslinking densities, fast crosslinking kinetics, high intercalation and best improved tensile strengths, corresponded to the samples for which only one of the melt-mixing parameters assumes its highest value and the rest take their lowest ones. The most favorable combination of process conditions is long mixing residual time at the lowest level of temperature and shear rate (i.e., sample # 2). Results confirm that increasing either shear rate or residual time, up to a specific level at which the composite is still thermally stable, increases the maximum torque of the corresponding composite, resulting in more crosslinking and enhanced mechanical strength. It should be noted that using a high level of all mixing parameters (i.e., temperature, mixing residual time and shear rate) leads to an undesirably high melt temperature which has adverse effects and hampers the crosslinking process.

7.7. References

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Chapter 8

Summary, Conclusion, and Future Work

8.1. Summary

The main objective of this PhD thesis was to improve different physical properties of polymer nanocomposites (PNC), i.e. mechanical, thermal, and electrical properties, for different applications. This objective has been met using various strategies for nanofiller modification or process optimization. The summary of different stages of the studies that have been accomplished in this research work follows:

- ✓ Modifying Montmorillonite clay (Mnt) via edge and surface chemical treatment with the purpose of (1) compatibilizing the clay with fluoroelastomer (FKM) matrix, (2) improving nanoclay dispersion in FKM, (3) and enhancing the thermal stability of the nanoclay and the resulting PNC.
- ✓ Optimizing the melt mixing process conditions to achieve the best swelling resistance, as well as thermal and mechanical performance of nanoclay/FKM nanocomposite.

- ✓ Finding the optimum combination of hybrid fillers, namely nanoclay and multi wall carbon nanotube (MWCNT), for manipulating dielectric properties of the PNC for charge storage applications.
- ✓ Studying the influence of the nanoclay loading amount on the conductive network and nano-capacitors in MWCNT/PVDF nanocomposites.
- ✓ Investigating the effect of the nanoclay addition to the crystalline structure of poly vinylidene fluoride (PVDF) in MWCNT/PVDF nanocomposite. The crystalline structure defines the piezoelectricity of the polymer and affects the dielectric properties.
- ✓ Synthesizing a novel nanofiller - graphene nano ribbon (GNR) - by chemical unzipping our custom synthesized MWCNTs.
- ✓ Investigating the effect of GNR and MWCNT, in their modified and original form when compounding with FKM, on the curing behavior of the elastomer matrix.

8.2. Conclusion

General conclusion of this PhD thesis is that different strategies could be successfully employed in order to improve and optimize PNC properties. These strategies depend on the inherent properties of PNC constituents and the final application of the nanocomposites. Improved curing behavior, thermal, mechanical, and electrical properties of different types of PNC achieved using different methods. The main findings from the implementation of strategies for PNC modification, discussed in chapters 3 to 6 of this dissertation, are briefly presented in this section.

8.2.1. Montmorillonite modification for clay/FKM nanocomposite

The chemical modification of nanoclay was the main focus of Chapter 4. Different chemical modifiers were employed for the modification of clay via solution reaction. Then, the modified clay was compounded with FKM, through the melt mixing process. The morphology and thermal properties of PNCs were investigated. Noticeable improvements in properties of Mnt were successfully achieved by both organo-silane grafting and intercalation of surfactant in clay by ion-exchange reactions. The modifications led to: (1) increased basal spacing of the clay up to ~ 170%, (2) enhanced interaction between the clay and FKM, (3) improved dispersion of the clay in the polymer matrix, (4) advanced thermal stability of the modified clay compared to commercially available products. Among different clay modification methods, surfactant treatment prior to silane grafting resulted in the best intercalation and exfoliation of the clay nanolayers in FKM.

8.2.2. Tuning the curing behavior of FKM by incorporation of Nitrogen-doped Graphene Nano Ribbon (CNx-GNR)

The nanofillers' effect on the crosslinking density of crosslinked polymers, such as elastomers and rubbers, is an important issue that has been addressed in Chapter 5. The target nanofiller here was GNR which were synthesized from MWCNT. FKM was chosen as the crosslinked matrix. The effect of GNR on crosslinking process of FKM was investigated. Based on our results, the concentration and type of GNR surface functional groups exhibited noticeable effect on the curing behavior of GNR/FKM nanocomposites.

In this study, un-doped and nitrogen-doped GNRs were synthesized from unzipping custom synthesized un-doped and nitrogen-doped MWCNTs via chemical oxidation protocol. The GNR's surface would be oxidized as a consequence of the oxidation reaction for unzipping. A thermal reduction process was performed to eliminate the oxygen groups and produce a new GNR for GNR/FKM nanocomposite. The GNR/FKM and MWCNT/FKM nanocomposites were prepared through a solution-mixing/melt-mixing protocol. The curing process data showed that while reduced nitrogen-doped GNRs (R-CN_x-GNR) had a similar cure behavior as neat FKM, oxidized GNRs had relatively slower cure kinetics. Rheology results, in conjunction with DSC results, support the idea that the oxygen functional groups on the GNR surface can significantly hinder the curing process of FKM composites. Our hypothesis for such behavior is that potential side reactions occur due to the presence of hydroxyl functional groups on the surface of the oxidized GNRs. The effect of reduced GNR on the curing behavior of FKM validates this hypothesis, while the reduced GNR/FKM nanocomposites exhibit a similar cure behavior as that of neat FKM.

Considering all the effects and hypotheses, we conclude that the crosslinking density can be tuned using different types of nanofillers. GNR, because of its high aspect ratio and possibility to modify through surface functional groups, is an ideal nanofiller for this purpose. Using GNR as for property enhancement of the crosslinked polymers is a significant advantage for the curing process.

8.2.3. Hybrid fillers/PVDF nanocomposites

The strategy of using a secondary filler to manipulate dielectric properties was investigated in Chapter 6. Herein, a specific application for MWCNT/poly vinylidene fluoride (PVDF) as charge

storage was investigated. These properties could be accomplished by adding an optimum level of nanoclay into the MWCNT/PVDF nanocomposite. The hybrid nanocomposites of MWCNT/Clay/PVDF, with different concentrations of MWCNT and nanoclay, were produced by melt-mixing.

For the particular charge storage application of conductive polymer composites (CPCs), high dielectric permittivity and low dielectric loss are desired. Accordingly, in this work, an interesting combination of a ~670% increase in the dielectric permittivity, combined with a ~ 68% reduction in dissipation factor - the relative dielectric loss - was achieved. In conclusion, we can assume two roles for clay when it is incorporated into the MWCNT/PVDF nanocomposite: (1) dispersion aid, and (2) barrier layer. By examining the effect of clays at two different loading levels - 1.0 wt% and 3.0 wt% - we observed that at a low clay concentration (around 1.0%), they would act as dispersion aids and improve the interfacial polarization and, in turn, the dielectric permittivity. At a higher concentration (3.0 wt.%), however, their barrier role is the most dominant factor, which leads to deterioration in permittivity. Moreover, the clay incorporation also muted the sharp insulator-conductor transition. This would help us to manipulate the CPC close to the percolation threshold, which is significant when the desired dielectric properties are achievable close to the percolation region.

From another perspective, PVDF is a semi-crystalline polymer with piezoelectric properties which vary for different crystalline forms of the polymer. Since the best piezoelectric behavior has been seen for β phase crystal, as compared to other possible crystal phases in PVDF, the effect of nanoclay incorporation on the amount of the β phase were discussed in Chapter 5. It was observed

that as a consequence of the clay incorporation, the amount of β phase crystal increased. Therefore, better piezoelectric, ferroelectric and dielectric properties are expected for this hybrid composite.

8.2.4. Melt-mixing process conditions optimization for clay/FKM nanocomposite mechanical performance

One important factor that determines the properties of nanocomposite is the processing method for the PNC production. Chapter 6 delves into the melt intercalation technique as a means of PNC production. In this project, the melt-mixing process conditions were studied with the goal of attaining the best curing behavior and mechanical performance for the clay/FKM nanocomposite. Cloisite 20A, an organically modified Mnt, was incorporated into the FKM using an internal batch mixer with different shear rates, temperatures and mixing times. An experimental design methodology was used to study the influence of any of these three processing parameters, alone and in combination, on the final properties of the nanocomposites. The enhancement in mechanical properties up to 70%, 94%, and 405% for tensile strength, elongation at break and modulus, respectively, could be achieved through optimizing the process parameters.

Considering thermal, mechanical and rheological properties of the nanocomposites prepared in different conditions, the main conclusions are: (1) the most desirable properties and behaviors, including highest maximum torques, cure rates, crosslinking densities, fast crosslinking kinetics, high intercalation and best improved tensile strengths, were achieved when only one of the melt-mixing parameters assumes its highest value and the rest take their lowest ones, (2) the consequence of increasing either the shear rate or residual time causes an increase in the maximum

torque, resulting in more crosslinking and enhanced mechanical strength, (3) the best combination of results corresponded to the conditions where the mixing residual time is comparatively longer, and both the temperature and shear rate are at their lower level, and (4) the thermal stability of the composites does not seem to be significantly affected by the process conditions unless we approach or exceed the scorching temperature.

8.3. Recommendations for future work

According to the work accomplished in this thesis and the literature from previous and current studies on this research area, opportunities to continue the study are apparent. Future work and recommendations related to this dissertation are summarized in this section, and split into three areas: (1) mathematical modeling, (2) hybrid fillers, and (3) GNR/FKM nanocomposites.

8.3.1. Mathematical modeling

One recommended method to acquire a more comprehensive understanding about the structure–processing–property relationships of PNCs is via mathematical models. Mathematical modeling can be used to determine a rough estimation about the microstructure and intermolecular forces between the polymer matrix and nanofillers. Moreover, modeling may help in the development of material processing [1]. In addition, some properties and characteristics of the material, such as mechanical properties and elastic behavior of polymers, can be predicted theoretically using micromechanics relationships in mathematical methods [2]. This helps enhance

the interpretation of the materials' behavior and manipulating properties by considering the value of different coefficients and factors of PNC constituents. Two examples of mathematical modeling including interfacial interaction calculation and mechanical properties, i.e. modulus calculation for PNCs are introduced in the following sections.

8.3.1.1. Interfacial interaction between polymer and nanofillers in PNCs

Having a comprehensive understanding of interfacial interactions, optimum filler/polymer nanocomposites with highest level of dispersion thus better properties can be attained with less trial and error experiments. This is due to possibility of prediction of the desired properties based on the interaction between filler and polymer. The interfacial structure and intermolecular forces can be evaluated based on the interfacial tension [3]. The interfacial tension originates from polymers' molecular conformational restriction on the interface and the difference in polarities and intermolecular forces of the two phases [3, 4].

The surface tension of each phase, γ_i , is composed of two components: polar tension, γ_i^P and non-polar (dispersion) tension, γ_i^d [4].

$$\gamma_i = \gamma_i^P + \gamma_i^d \quad \text{Eq. 8.1}$$

Knowing the surface energies of each of the phases - filler and the polymer - the interfacial tension can be estimated:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\phi^P - 2\phi^d \quad \text{Eq. 8.2}$$

$$\left\{ \begin{array}{l} \emptyset^d = \frac{2\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} \text{ or } (\gamma_1^d \gamma_2^d)^{1/2} \\ \emptyset^p = \frac{2\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \end{array} \right.$$

Where γ_{12} is the interfacial tension, and $\emptyset^p$ and $\emptyset^d$ are the interaction terms for dispersion and polar energies, respectively. Therefore, using the surface energy of the fillers (e.g. carbon nanotube or clay), the interfacial tension for filler/polymer composites can be calculated with the Equation 8.3 [5].

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad \text{Eq. 8.3}$$

8.3.1.2. Mechanical performance of PNCs

Some mathematical models have been studied to predict PNCs' properties based on the properties of the pure components and the morphology of the composite. For instance, the Halpin-Tsai model is a well-known composite theory [1, 2, 6, and 7] that can be used for this purpose. The Halpin-Tsai model was applied to calculate the modulus of the clay/polymer nanocomposite as a function of the clay concentration and aspect ratio. This model evaluates the elasticity of the composite material based on the geometry and orientation of the filler and the elastic properties of the filler and matrix. Different parameters, including the stiffness of the clay and polymer, as well as the clay's volume fraction and aspect ratio, are considered in this model [1, 2].

The overall composite moduli (E_c) can be predicted by the Equation 8.4. [1, 2]

$$\frac{E_c}{E_m} = \frac{1 + \varepsilon \eta \phi_f}{1 - \eta \phi_f} \quad Eq. 8.4$$

$$\eta = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \varepsilon} \quad Eq. 8.5$$

Where E_f , and E_m are overall Young's modulus of the filler and matrix, respectively; ϕ_f is the volume fraction of the filler; and ε is a shape parameter which is a function of the geometry of the filler and the loading direction which itself is a function of the aspect ratio.

$$\varepsilon = f\left(\frac{L}{t}\right) \quad Eq. 8.6$$

Using the above mathematical modeling, the optimum amount and type of filler in the PNC, improved mechanical performance can be achieved. In order to get to this point, first validation of the mathematical modelling should be performed and then PNC production based on the properties of filler and polymer can be accomplished.

8.3.2. Hybrid fillers

As shown in Chapter 6, the existence of a secondary filler can tune some properties of the nanocomposites as a consequence of benefitting from superior properties of both fillers with a combination of their optimum amount. For instance, using the electrical conductivity of CNTs

beside the barrier role of nanoclays, tuning the electric and dielectric properties was shown to be possible.

It is proposed that the addition of a second filler in clay/polymer composite reduces the clay platelets' movement, while simultaneously increasing the viscosity of the composite [8]. Further studies are recommended to determine the effect of the second filler in the clay/FKM nanocomposites' properties. The ratio and nature of the second filler should be considered. Carbon black, one of the common fillers for elastomer composites, may be used as the second filler, as it is supposed to reduce the de-intercalation. Finally, thermal and mechanical properties of the dual filler composites should be considered to decide the optimum combinations.

The other interesting hybrid filler composite could be a combination of GNR and CNT. CNT has a higher stiffness and electrical conductivity and GNR has a much higher available surface area. The hybrid's possibility of altering surface functional groups to manipulate compatibilities of fillers and polymer matrix is worth exploring. This has not been purposed previously and would be an original contribution to the area.

8.3.3. GNR/FKM nanocomposites

8.3.3.1. Mechanical and electrical properties

The main purpose of incorporating modified or un-modified nanofillers into polymers is to enhance the materials' properties for different applications. Measuring the nanocomposites' properties is significant to evaluate the effectiveness of each nanofiller in the polymer matrix. Graphene nanoribbon (GNR) is a novel nanofiller which has been synthesized, modified, and

utilized in fluoroelastomer in this work. After fully comprehending the role of GNR and its effect on the structure and curing behavior of the fluoroelastomer, the next step is to study the electrical and mechanical properties of the GNR/FKM nanocomposites.

Generally, graphene-based fillers are attractive for nanocomposites due to their stiffness, strength, and thermal conductivity, combined with an impermeability to gases [9-12]. Note that nitrogen-doping is supposed to positively affect morphology, electrical and thermal conductivity [13-16]. It is expected that the proper dispersion of GNR in the FKM matrix leads to reinforcement of the nanocomposite [17]. Also, the change in the electrical properties, as compared to the CNT/FKM nanocomposites, is anticipated. To the best of our knowledge, to date there is no reports on the properties of GNR/FKM nanocomposites.

8.3.3.2. Improve compounding protocol

In this work, the mixing protocol for the GNR/FKM nanocomposite production was solution mixing and several steps of ultra-sonication, followed by melt-intercalation. The microscopic imaging results show that the GNRs lengths were broken. This leads to deterioration in the electrical and mechanical properties of GNR-based nanocomposites. It is essential to find out a more efficient method of mixing without harming the properties of GNRs during the mixing process.

8.3.4.3. Different curing system for GNR/FKM nanocomposites

Although the reactions are not clearly defined, it is essential to consider the possibility of side-reactions between the functional groups on the GNRs' surface with the curing agents, as well as the effect of residue acids on the peroxide curing mechanism. Other curing mechanisms, such as sulfur curing, are worth examining for GNR/FKM nanocomposites to determine the role of GNRs as crosslinking hinderer.

8.4. References

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