## TABLE OF CONTENTS

Chapt	er 1: Introduction and literature review	
1.1 I	ntroduction	1
1.2 0	Composite:	3
1.3 Po	lymer Nanohybrids	4
1.4 Int	roduction to PET	6
1	1.4.1 Applications and demand	6
1	1.4.2 Preparation and chemistry	10
1.5 Na	nofiller	16
1	1.5.1 Zero-dimensional (0D) nanofillers (particulates)	16
1	1.5.2 One dimensional (1D) nanofillers	17
1	1.5.3 Two dimensional (2D) nanofillers (platelets)	17
1	1.5.4 Three dimensional (3D) nanofillers	17
1.6 Str	ructure and properties of layered silicate:	18
1	1.7 Structure of polymer-clay nanohybrids	22
1	1.7.1 Phase separated (tactoid formation)	23
1	1.7.2 Intercalated.	23
1	1.7.3 Exfoliated	23
1.8 Po	lymer nanoclay hybrid preparation techniques	24
1	1.8.1 Solution casting	24
1	1.8.2 In-situ intercalative polymerization	25
1	.8.3 Melt intercalation	25
1.9 Pro	oblem of e-waste	27
1.10 S	tructure and properties of ABS	28

1.11 Polyethylene (PE)	32
1.12 Low density polyethylene (LDPE) polymer	33
1.13 Polymer blends	34
1.14 Reactive extrusion	36
1.15 Benefits of polymer blending	38
1.16 Literature review	39
1.16.1 Past studies on PET/clay nanohybrids	39
1.16.2 Past studies on polymer blends utilizing ABS	51
1.17 Objectives of this work:	59
Chapter 2: Experimental Section	
2.1 Materials	61
2.1.1 Materials for nanohybrids	61
2.1.2 Materials for polymer blends	61
2.2 Nanohybrid preparation by solvent casting	61
2.3 Blend preparation by reactive extrusion	62
2.4 Injection molding	63
2.5 Compression molding	63
2.6 Transmission electron microscope (TEM)	63
2.7 Scanning electron microscopy (SEM)	64
2.8 X-ray diffraction (XRD)	65
2.9 Fourier-transform infrared spectroscopy (FTIR)	65
2.10 UV-visible spectroscopy	66
2.11 Nuclear magnetic resonance spectroscopy (NMR)	66
2.12 Atomic force microscopy (AFM)	67
2.13 Polarized optical microscopy (POM)	67

2.14 Thermogravimetric analysis (TGA)	67
2.15 Differential scanning calorimetry (DSC)	68
2.16 Mechanical properties	68
2.17 Vicker Hardness Test	69
2.18 Dynamic mechanical analysis (DMA)	
2.19 Two dimensional small angle X-ray scattering (SAXS)	
2.20 Gas barrier measurements	71
2.21 Heat distortion temperature (HDT)	
Chapter 3: Structural, mechanical and gas barrier properties of po	oly(ethylene
terephthalate) nanohybrid using nanotalc	
3.1. Introduction	73
3.2 Experimental	74
3.2.1 Materials	74
3.3 Results and discussion	74
3.3.1 Dispersion and interactions	74
3.3.2 Thermal properties and stability	78
3.3.3 Mechanical responses	79
3.3.4 Modulus prediction by micro mechanical models:	81
3.3.5 Microhardness of the nanohybrids	
3.3.6 Theoretical modeling of hardness	86
3.3.7 Temperature dependent viscoelastic properties	88
3.3.8 Effect of stretching on structure	
3.3.8.1 2D-Small angle X-ray scattering (SAXS):	
3.3.8.2 Wide-Angle X-ray diffraction (WAXD)	
3.3.9 Effect of nanotalc on gas barrier	

3.3.10 Theoretical modeling of gas permeability	97	
3.4 Conclusions	102	
Chapter 4: Effect of addition of NK75 nanoclay on properties of PET/clay nanohybrid		
4.1 Introduction	104	
4.2 Experimental	106	
4.3 Results and discussion	106	
4.3.1 Dispersion and interactions	106	
4.3.2 Thermal properties and stability	110	
4.3.3 Mechanical responses and predictions	111	
4.3.4 Microhardness of the nanohybrids and predictions	113	
4.3.5 Temperature dependent viscoelastic properties	114	
4.3.6 Effect of stretching on structure	116	
4.3.7 Effect of nanoclay on gas barrier	119	
4.3.8 Theoretical modeling of gas permeability	120	
4.4 Conclusion	121	
Chapter 5: Enhancement in properties of PET/clay nanohybrids using 30B n	anoclay	
5.1 Introduction	123	
5.2 Experimental	125	
5.3 Results and discussion	125	
5.3.1 Dispersion and interactions	125	
5.3.2 Thermal properties and stability	127	
5.3.3 Mechanical responses and predictions	129	
5.3.4 Microhardness of nanohybrids	132	
5.3.5 Analysis of stress distribution		
5.3.6 Effect of stretching on structure		

5.4 Conclusion
Chapter 6: Utilization of E-waste by single-step reactive extrusion
6.1 Introduction
6.2 Experimental
6.2.1 Materials
6.2.2 Preparation of materials146
6.2.3 Sample preparation146
6.2.4 Optimization of blends
6.2.4.1 MA concentration dependence
6.2.4.2 Composition dependence
6.2.4.3 Temperature dependence
6.2.5 Gel content by solvent extraction
6.3 Results and discussion
6.3.1 Phase morphology151
6.3.2 Gel content through solvent extraction
6.3.3 Proof of crosslinking and determination of its site
6.3.4 Thermal properties159
6.3.5 Mechanical properties162
6.3.6 Dynamic Mechanical Analysis (DMA)167
6.3.7 Heat distortion temperature (HDT)
6.4 Conclusion:
Chapter 7 Conclusions and Scope for future works
7.1 Conclusions
7.1 Scope for future work:

## LIST OF FIGURES

Figure 1.1: PET applications in different sectors
<b>Figure 1.2:</b> Global PET production capacity in different regions (Total production 30.3 million tons in the year 2017)
<b>Figure 1.3:</b> Global PET consumption in packaging sector in different forms of packaging applications (Total consumption 23.5 million tons in the year 2016)
<b>Figure 1.4:</b> Demand forecast of PET consumption market size in different application sectors in U.S. (values shown are in USD million) between the years 2014 to 2024. The packaging sector was leading segment in the year 2014 and was forecasted to grow with an estimated compound annual growth rate (CAGR) of 7% from year 2016 to 2024
Figure 1.5: Chemical structure of PET 10
Figure 1.6: Reaction mechanism of EG production
Figure 1.7: Reaction mechanism of the production of DMT using para-xylene
Figure 1.8: (a) Esterification and (b) transesterification reaction mechanisms for PET polymerization
Figure 1.9: Polycondensation reaction mechanism
Figure 1.10: Reaction of vinyl ester and hydroxyl end groups
Figure 1.11: Esterification reaction
Figure 1.12: Structure of layered silicate
<b>Figure 1.13:</b> Development of polymer clay nanohybrid ( <b>a</b> ) tactoid formation results phase separated structure; ( <b>b</b> ) intercalated structure; ( <b>c</b> ) exfoliated structure
Figure 1.14: Elements of ABS
Figure 1.15: Structures of monomer units of ABS
Figure 1. 16: polymer chain branching in various kinds of PE
Figure 2.1: Solvent casting route for the nanohybrid preparation

**Figure 3.4:** (a) Stress–strain curves of PET and its nanohybrid containing 4 wt % of filler concentration; (b) Improvement in modulus values in P–T nanohybrids for different amount of filler loading comparing pure PET. The number after P–T indicates the nanotalc content (wt %) in the hybrid; (c) variation in toughness values as a function of filler concentrations; and (d) predictions of modulus values using different micromechanical models as indicated.

**Figure 3.7:** Structural advancement in PET and its nanohybrids containing 4 wt % of filler concentration; (a) 2D SAXS images of before and after stretching of the nanohybrid (the stretching is in vertical direction and the stretched samples are denoted with "-s" in addition to pre-existed abbreviation); (b) Lorentz corrected  $I(q)q^2$  versus q plots, inset image shows plots of I(q) (scattering intensity) versus (q) (scattering vector); (c) Debye–Bueche fitting of the low value of scattering intensity to get the correlation length values of unstretched and stretched PET and its nanohybrid; (d) Linear fitting of slope values of low q values. ...... 91

**Figure 3.8:** (a)WAXD patterns of the unstretched and stretched sample of PET and its nanohybrid; (b) WAXD pattern of pure talc nanoclay (c) schematic representation of the enhancement in short-range ordering due to adherence of nanotalc particles onto the polymer chains after stretching; and (d) TEM images of the stretched P–T (4 wt %) nanohybrid...94

**Figure 3.9: (a)** Permeability of PET and its nanohybrids for different filler concentrations; **(b)** schematic representation of gas molecules path through pure PET and in nanohybrids containing nanotalc which cause the tortuous path for the gas molecules to pass through. 96

**Figure 4.1:** Structure of organic modifier which is used for modification of NK75. HT denotes hydrogenated tallow, which contains  $\sim 65\%$  C<sub>18</sub>,  $\sim 30\%$  C<sub>16</sub>,  $\sim 5\%$  C<sub>14</sub>...... 105

**Figure 4.6:** Effect of nanoclay inclusion as measured through dynamic mechanical analyzer on (a) storage modulus; (b) loss modulus; and (c) tan  $\delta$  of PET and its nanohybrids...... 115

**Figure 5.8:** (a) SAXS images of unstretched and stretched samples of PET and P-B, (b) Intensity vs. wavevector plot extracted from the SAXS images; (c) Lorentz corrected profiles of the unstretched and stretched samples; (d) Debye Bueche model fitting for calculation of correlation lengths of unstretched and stretched samples; (e) Wide angle XRD plots of unstretched and stretched samples; (f) Wide angle XRD plots of pure Cloisite 30B clay; (g) High magnification TEM images of unstretched and stretched and stretched and stretched (h)

**Figure 6.1:** POM images show effect of different MA concentrations of (**a**) 0%; (**b**) 0.75%; (**c**) 2%; (**d**) 5%; and (**e**) 10% on structures of blends containing 75% PE and 25% ABS. 147

**Figure 6.2:** POM images show the effect of varied concentration ratio of PE and ABS (shown as P/A), (**a**) and (**b**) has P/A as 75/25 without MA and with 5% MA respectively; (**c**) and (**d**) has P/A as 50/50 without MA and with 5% MA concentration respectively. ..... 148

**Figure 6.5: (a)** Photographic images of samples before and after the indicated solvent extraction, below each image, the percentage weight remained after each solvent extraction is mentioned; **(b)** Optical microscopic images in reflectance mode of the samples before and after solvent extraction; and **(c)** SEM images of samples before and after solvent extraction. 156

Figure 6.11: Heat distortion temperature of PE, its indicated blends and ABS. ..... 169

## LIST OF TABLES

<b>Table 1.1:</b> Effects of nanoparticles on polymers
Table 1.2: Details of few of surface modified MMT clay (Southern Clay Products, Inc.)    21
<b>Table 3.1:</b> Vicker hardness values for PET and P-T nanohybrids 85
<b>Table 3.2:</b> Permeability values for different concentrations of nanotalc in PET nanohybrids
<b>Table 4.1:</b> Vicker hardness values for PET and P-NK nanohybrids
<b>Table 4.2:</b> Permeability values for different concentrations of nanoclay in PET nanohybrids
<b>Table 6.1:</b> Melting temperature (T <sub>m</sub> ) and degradation temperature (T <sub>d</sub> ) obtained through DSC and TGA studies
<b>Table 6.2:</b> Mechanical properties of pure polymers and their blends