INFLUENCE OF UNMODIFIED AND MODIFIED NANOCLAY CONTENT ON MECHANICAL AND THERMAL PROPERTIES OF THE WASTE POLYOLEFIN

(KESAN KANDUNGAN NANOCLAY TIDAK TERUBAH DAN TERUBAH KE ATAS SIFAT MEKANIKAL DAN TERMAL POLIOLEFIN TERPAKAI)

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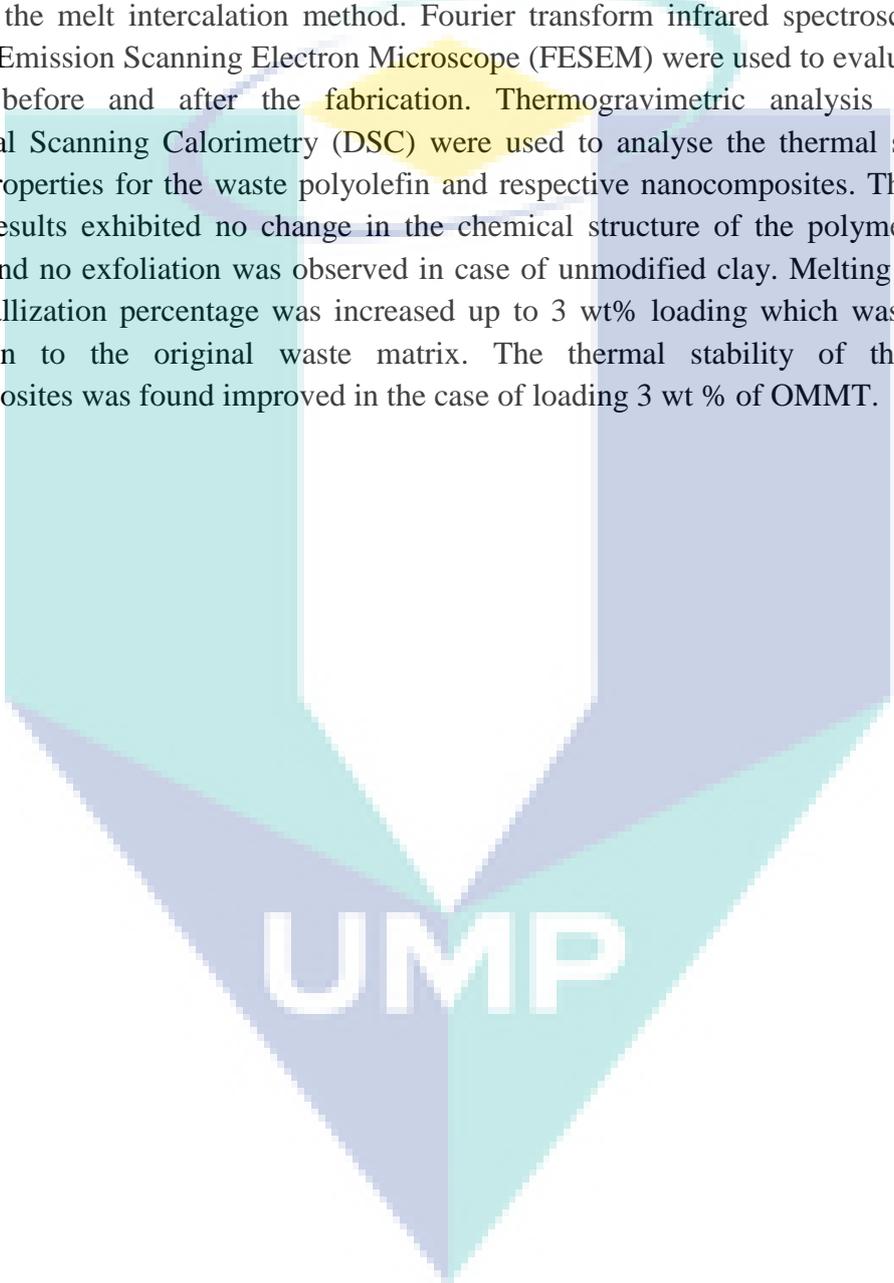
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ABSTRACT

The aim of this research (waste to wealth), is to study the improved thermal and mechanical properties of waste polypropylene (wPP) in a nanocomposite. For this purpose, Organo-modified (OMMT) and unmodified sodium montmorillonite clay (MMT) were employed to fabricate polypropylene/clay nanocomposite. Commercial grade (OMMT) and (MMT) were added in a range of 1-5 wt %, in wPP to prepare polypropylene-clay nanocomposites, following the melt intercalation method. Fourier transform infrared spectroscopy (FTIR) and Field Emission Scanning Electron Microscope (FESEM) were used to evaluate polymer structure before and after the fabrication. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were used to analyse the thermal stability and thermal properties for the waste polyolefin and respective nanocomposites. The FTIR and FESEM results exhibited no change in the chemical structure of the polymer after clay addition and no exfoliation was observed in case of unmodified clay. Melting temperature and crystallization percentage was increased up to 3 wt% loading which was the best in comparison to the original waste matrix. The thermal stability of the wPP/clay nanocomposites was found improved in the case of loading 3 wt % of OMMT.

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CHAPTER 1

General Introduction

1.1 Introduction

The produced amount of plastic solid waste is accelerating rapidly, despite the growing attempts to reduce, reuse, recycle or recover such a great amount, it is almost impossible to bring all waste to recuperate. This is primarily due to their extensive applications in the packaging industry as well as in everyday usage goods; because they do not possess any side effects that can be harmful to human beings [1].

The development of polymer nanocomposites during the past two decades has further strengthened the industrial applications of these polymers. In particular, polymer–clay nanocomposites have been a remarkable area of research interest. Various types of polymer matrices (thermoset, thermoplastics, and rubbers) packed with clays have been studied. Among the clays, montmorillonite (MMT)-based clays have been proven to be a successful nano-additive in the polymer matrices and showing superior property improvement (thermal, mechanical, and optical) even at very low concentrations of about 3–5 wt % [2-4].

Commercial and lab prepared straight low density PE (LLDPE), PE-g-MA grades were used by Wang et al., [22], where melt mixing method were used to prepare silicate nanocomposites, by lab. prepared LLDPE-g-MA and LLDPE reacted with PE-g-MA, respectively. The application of LLDPE-g-MA, as a compatibilizer for HDPE/o-MMT system was studied by [23]. Low density polyethylene (LDPE), a extensively utilized packaging matter, sounds to be especially striking for nanocomposite production, commonly because of the supposed advancement of obstacle characteristics. Nevertheless, the details concerning this nanocomposites, with PE-g-MA, as a compatibilizer, are uncommon [24].

The influences of clay exfoliation in LDPE based nanocomposite [24] were worst the HDPE based system, due to further difficult permeation of unlinear LDPE polymer molecules into clay galleries. Olewnik et al., [25], studied the creation of polyolefins/adjusted montmorillonite nanocomposites about 1.5–5 wt% clay adjusted with 4, 4'

methylenebisaniline, with an emphases on the thermal and structural properties of generated nanocomposites. The clay content effect on the structural behaviour of polypropylene (PP) and high density polyethylene (HDPE) composites, also were revised by [26].

1.2 Problem Statement

Drozdov et al., [27], studied a comparison of the result in the polymer/clay composite properties for many researcher. It was reported, "There are many experimental studies regarding the morphology and mechanical properties of inserted and exfoliated nanocomposites with HDPE matrixes. It has been reported that support of HDPE with MMT clay layers consequences in (i) an expansion in the Young's modulus, and (ii) a reduction in extending at break. The same consequences have been revealed in experiments on other polymer–clay nanocomposites, as well as on particulate microcomposites, the above-mentioned results may be considered as accurate".

Based on the previously reported research and our studies on the recycling of the polyolefin [28–32]. The following study enlightens the synthesis of waste polyolefin/ Organ-modified and unmodified sodium montmorillonite nanocomposites, by melt interaction method and exploring the effect of clay content on the waste LDPE and HDPE structural, thermal and mechanical properties. The characterization behaviour of the resulting polyolefin/clay nanocomposites are studied by XRD and FESEM, respectively. Mechanical (Tensile and nanoindentation) and the thermal behaviours were analysed by using Instron Universal testing machine, TGA, and DSC. The properties of the new waste polyolefin/clay nanocomposites were later compared with the original waste polymer nanocomposites, compatibly.

1.3 Research Objective

The objectives of this research were the following

1.3.1   To fabricate waste polyolefin nanoclay using two methods (solution intercalation and melt intercalation)

1.3.2   To characterize the new nanocomposite samples by (FTIR, TEM, and SEM)

1.3.3   To study the mechanical and thermal properties for fabricated nanocomposite and compared with the virgin.
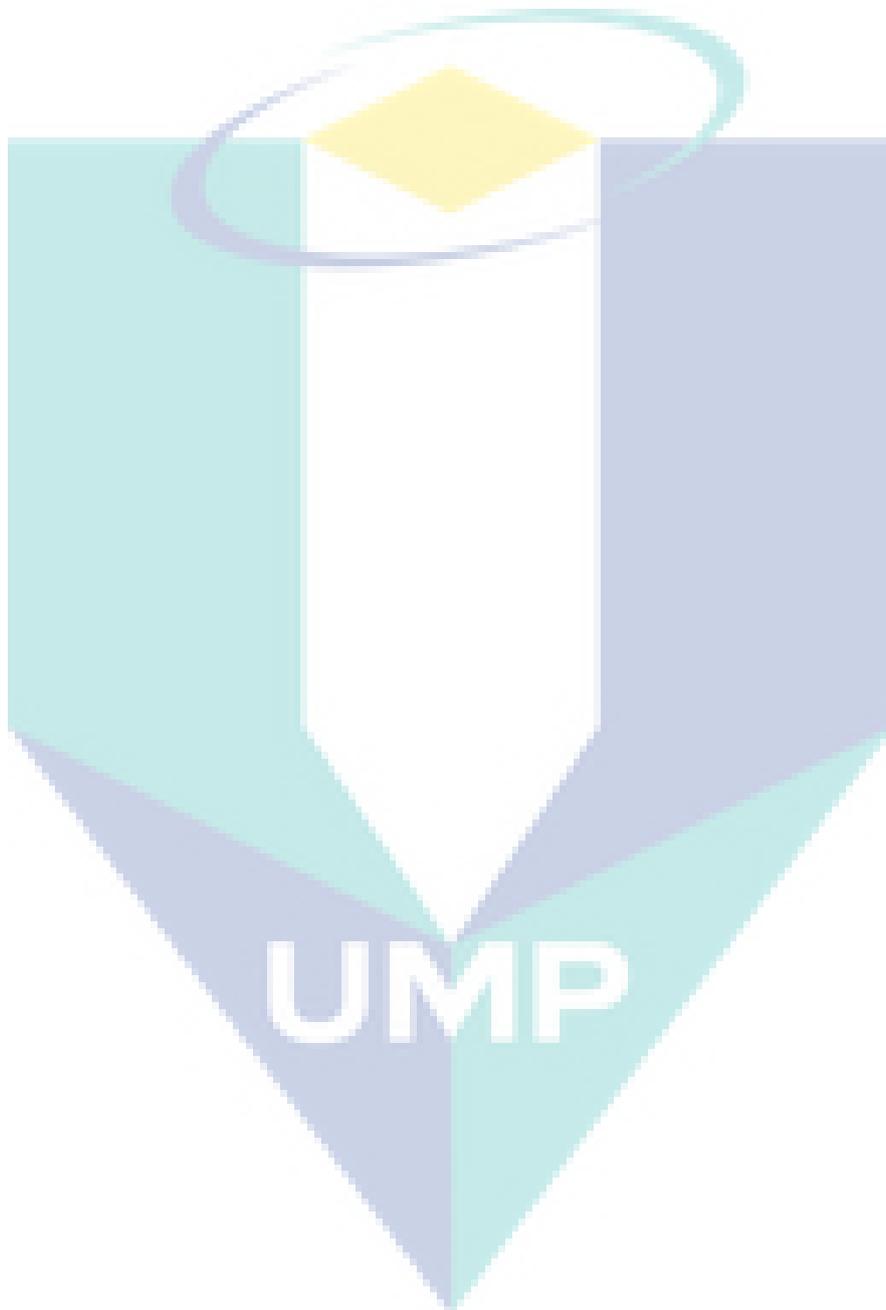
CHAPTER 2

Comparison of Organic Solvents Effect on Polyolefin Waste Materials Recycling Using Dissolution/Reprecipitation Method

2.1 Abstract

Polyolefin belong to a class of thermoplastics used globally in a wide variety of applications. The current technology of plastic waste disposal is becoming inadequate due to new regulation rules, increasing expenses and because most common polymers are not appreciably biodegradable. To achieve desirable properties in reconditioned polyolefin for any dissolution technique, the selectivity, durability and sustainability of solvents is crucial. Therefore, this study aimed to develop durable and sustainable solvents for the reconditioning of used polyethylene (PE) and polypropylene (PP) using the dissolution/reprecipitation technique. Waste polyolefins based on LDPE, HDPE and PP was reconditioned using a set of pure and blend non-polar organic solvents, at various ratios of polyolefin and solvents. The reconditioned polymer was compared with virgin polyolefin polymers. Commercial waste products (bags, detergent containers, laboratory pipettes, chemical liquid containers, some pharmaceutical materials and food retail products) and model polymers were used as raw materials. The recovery of reconditioned polymer with the proposed solvents was seen to be greater than 94% for all samples. The properties of the reconditioned polymer Using the dissolution/ reprecipitation method were characterised by FTIR, polymer density, molecular weight, thermal properties (melting point, heat of fusion and crystallinity) and mechanical properties (stress at maximum load, stress at yield, elongation at break and elastic modules), these properties were in-contrast with those of the virgin polymer.

2.2 Introduction

The dissolution/repreciptation process plays a significant role in plastics recycling, belonging to the mechanical recycling techniques [1]. Previous studies have demonstrated that the dissolution/precipitation of the thermoplastic polymers especially the polyolefin family can be set apart and reprocessed with the help of a solvent/non-solvent system. Solvent-based methods carry some phases of treating plastic waste with solvents so that the polymeric materials can be dissolved, and then separated through the process of re-precipitation. These methods are useful in a way that they are competent enough to deal with mixtures of polymers, based on the selective dissolution rule. Other than that, the dissolution/repreciptation method carries a series of advantages as follows: (i) the plastic waste is converted to the acceptable form like powder or small grains, (ii) additives and insoluble impurities can be separated via filtration, (iii) the method can survive with except heating for dissolving, and that no further degradation, due to the recycling method itself is anticipated, and (iv) the added value during the polymerization stage stays to be intact and the recycled polymers which are contaminant-free, can be used for any sorts of applications, since the final product is of competitive quality, compared with the virgin materials [1], [2]. Several researchers have already successfully examined recycling of used waste commodity polymers by the dissolution/repreciptation system [1]–[7]etc.

The aim of this study is to produce a new low-cost pure or blend solvent system to dissolve and repreciptate a waste polyolefin polymer, to enable the solvent to reducing the dissolution temperature and time, therefore the product cost will be reduced. It would be significant if the process can be applied at low, or room temperature.

2.3 Experimental

2.3.1 Materials

Three different types of polyolefins were used in this study, low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP). The virgin LDPE grade (LD N109X), HDPE (HD5403AA) and PP grade (G452), used as standards for the experiments, were donated by Petlin, Polyethylene and Polypropylene Malaysia Sdn Bhd respectively. They were used together with a number of commercial waste products made

from LDPE (general used bags, intravenous fluids containers, some laboratory materials such as pipettes), HDPE (chemical containers, liquid dish washing containers and body lotion, shampoo bottles) and PP (transparent food container, ice cream container and intravenous fluids containers). The solvents used (xylene, petroleum ether, n-hexane, toluene, turpentine, mesitylene) were of reagent grade purities form Sigma-Aldrich and Merck Germany. Three types of petroleum ether (PetE) were used, with boiling point ranges of 40-60 oC , 60-80 oC and 90-120 oC and notations A, B, and C, respectively.

2.3.2   Preparation of Used Polyolefin Sample.

The waste plastic containers were first rinsed with tap water and then cut with a plastic crusher machine into randomly pieces size between 2cm-4cm. The pieces were then cleaned with distilled water and placed in simple vacuumed oven for 3-6 hours at 50 ^{o}C.

2.3.3   Dissolution/reprecipitation technique

The experimental procedure was performed for several rates ranging from (0.5-40) % weight/ volume polymer/solvent. The solvent and pieces of waste polymer were added to the flask with three necks; the first with a vertical condenser with tap water, the second with a mercury thermometer to measure temperature and the third with a stirrer. An oil bath was used for heating with a flask immersed and a high speed stirrer doing the mixing. The system was heated for 30 minutes and brought to the desired temperature. Once the polymer pieces had dissolved completely, the flask was removed from the oil bath and left to cool for 15-30 minutes, after which the solution was carefully poured into a non-solvent. The precipitate was then washed, filtrated and dried at 70 °C in a vacuumed oven for 10-15 hrs. The resulting polymer was in granular (powder) form.

2.4 Characterization

2.4.1 Fourier transform infrared (FTIR)

FTIR was used to determine the functional group of the product, based on the peak value. The chemical structure of the standard polymers and waste sample plastics, before and after the restoration process was confirmed by recording their IR spectra. The instrument used was a Nicolet (Avatar 370 DTGS) FT-IR spectrophotometer with a resolution of 4 cm^{-1}. The recorded wave number range was from 400 to 4000 cm^{-1}. Small pieces of 1mm thickness were prepared for testing using a hand press, as specified for FTIR testing in ASTM D5477.

2.4.2 Differential Scanning Calorimetry (DSC)

DSC is widely used for examining polymers to check their composition. Besides melting point temperatures, this technique makes it possible to observe heat of fusion and crystallinity. The device used in this study was the DSC Q1000 (V9.6, Build 290) from TA instruments. The testing was performed according to ASTM D3418–03. Samples of nearly 10 mg were prefaced into a pan which is inserted in suitable position of the instrument and the heat liberated was recorded at a temperature interval 20–300 °C and a scan rate of 10 °C/min, in nitrogen atmosphere.

2.4.3 Universal Testing Machine (UTM)

The Universal Testing Machine Shimadzu AG-X, was used to measure the tensile mechanical properties of the virgin and waste polymers before and after recycling. Stress at maximum load, strain at break, stress at yield and elastic modulus were noted. Five specimens were examined for each sample and the average values reported. The testing was performed according to the standard ASTM D638-03. The speeds of the testing were 5 mm/min for LDPE and HDPE, while for PP it was 1 mm/min. A carbon steel frame was prepared according ASTM D638-03 (type I). Each specimen weighed 13-15 grams and was prepared using a hydraulic thermo press under the following conditions: temperature, 170 °C for LDPE, 200 °C for HDPE and 230 °C for PP, pressure, 10 MPa; time of heating, 15 min. The testing was done after 48-72 hrs. in room temperature and 60-65% humidity.

2.5 Results and discussion

Continuous with the previous work [8]–[12]The waste materials used in this study based on LDPE were carrier bags, laboratory pipettes, and intravenous fluids containers, which are assigned the abbreviations L1, L2 and L3, respectively. HDPE were chemical containers, liquid dish washing containers and bottles of body lotion and shampoo which are abbreviated as D1, D2 and D3, respectively. Finally for PP were transparent food containers, ice cream containers and intravenous fluids containers which are abbreviated in this study to FC, IC and IFC, respectively. Tables 1 show the solvents and non-solvents used for these systems. Ratio 1:1 by volume of blend solvents is used in this study.

Table 1: The solvents and non-solvents used in LDPE dissolution

Solvent	Non-solvent
Xylene	n-Hexane and PetE(A,B,C)
Xylene + PetE(C)[a]	n-Hexane and PetE(A,B,C)
Xylene + PetE (B)[b]	n-Hexane and PetE(A,B,C)
Toluene	n-Hexane and PetE(A,B,C)
Toluene + PetE (C)	n-Hexane and PetE(A,B,C)
Mesitylene	n-Hexane and PetE(A,B,C)
Mesitylene + PetE (C)	n-Hexane and PetE(A,B,C)
Turpentine	n-Hexane and PetE(A,B,C)
Turpentine + PetE (C)	n-Hexane and PetE(A,B,C)
Turpentine + benzene	n-Hexane and PetE(A,B,C)
PetE (C)	n-Hexane and PetE(A,B,C)

(a) PetE (C), means Petroleum ether at boiling point (90-120)°C, b petroleum ether with boiling point (60-80)°C

2.5.1 Dissolution Temperature and Recovery Percentage

Different experimental conditions were tested for each waste LDPE, HDPE and PP in order to find the optimum conditions in terms of dissolution temperature, type of solvent and/or non-solvent and initial polymer concentration. Figures 1-3 shows the dissolution temperature and figures 4-6 shows recovery percentage of the three LDPE, HDPE and PP waste products in all the solvents used at a concentration of 1g polymer and 20 ml of solvent, respectively.

Figure 1: LDPE dissolution temperature in pure and blend solvents
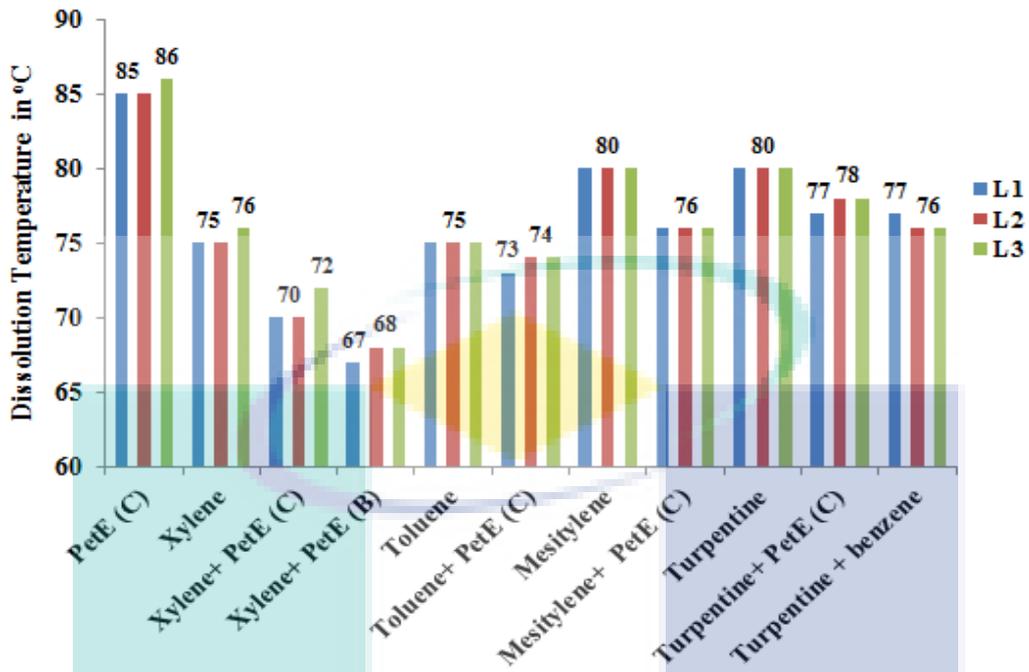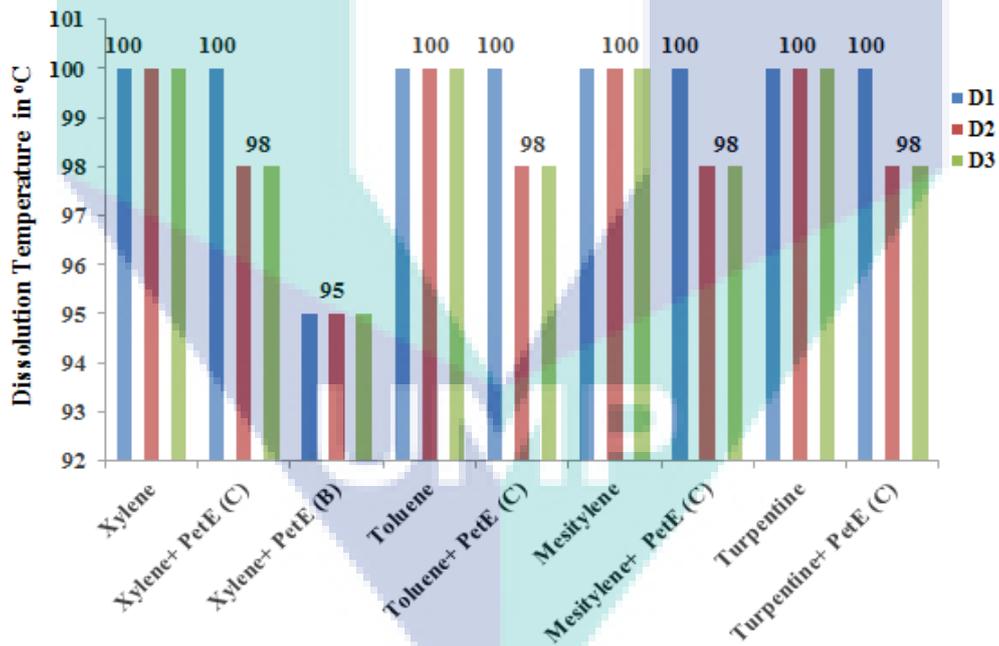

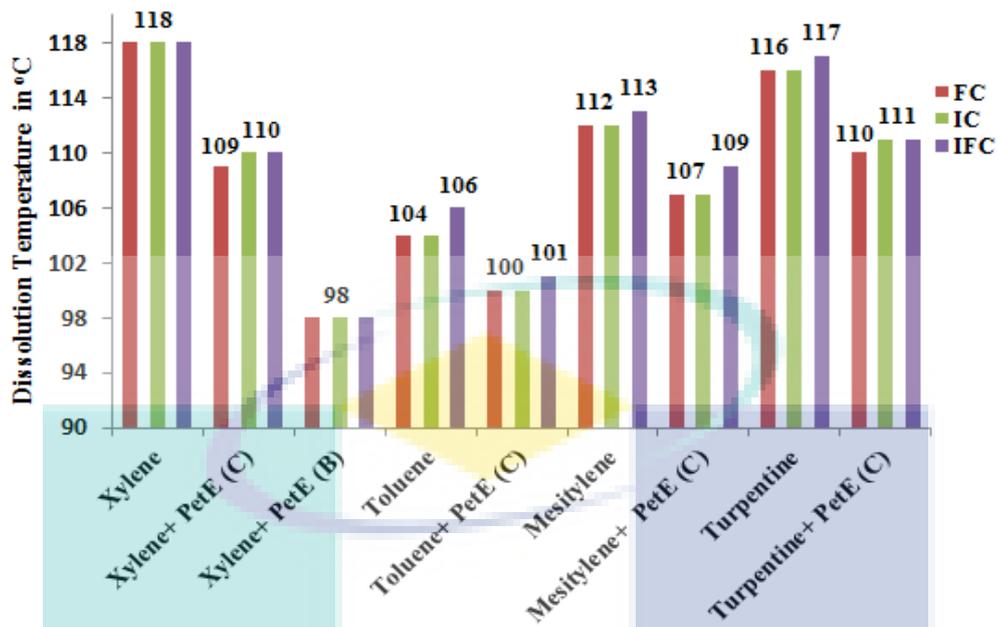**Figure 2:** HDPE dissolution temperature in pure and blend solvents.

Figure 3: PP dissolution temperature in pure and blend solvent
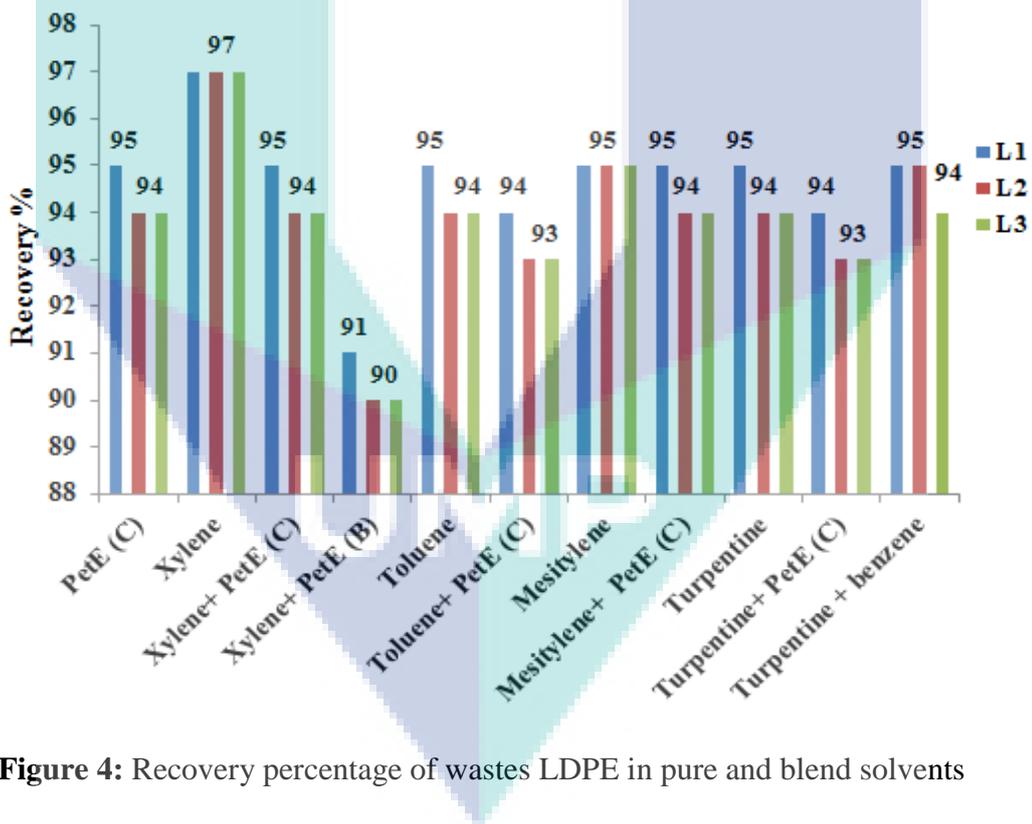

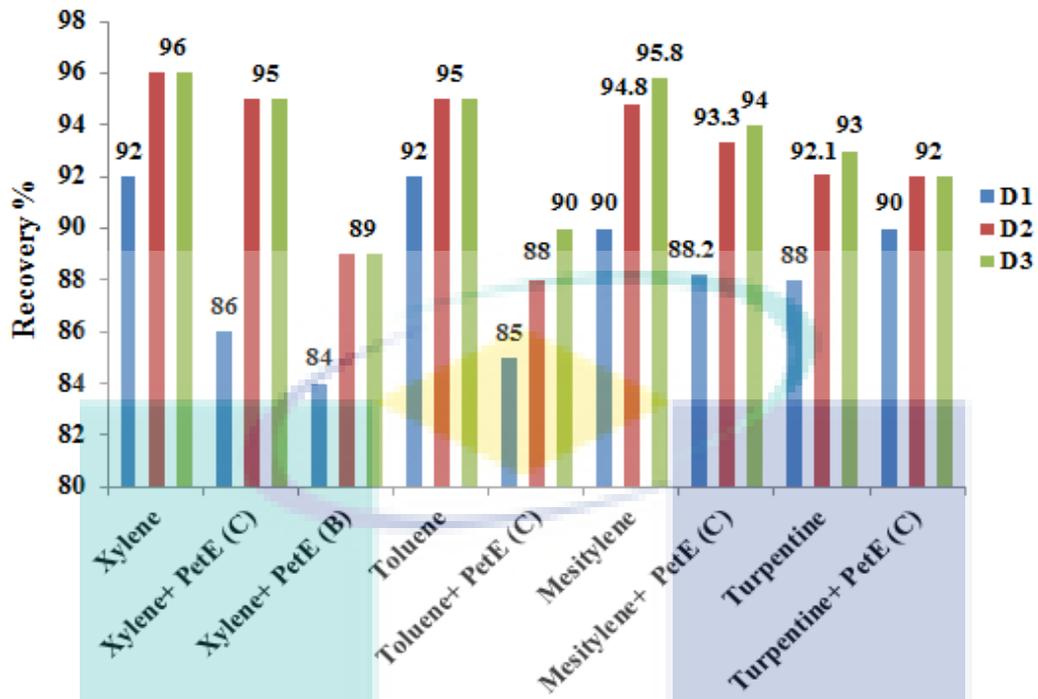**Figure 4:** Recovery percentage of wastes LDPE in pure and blend solvents

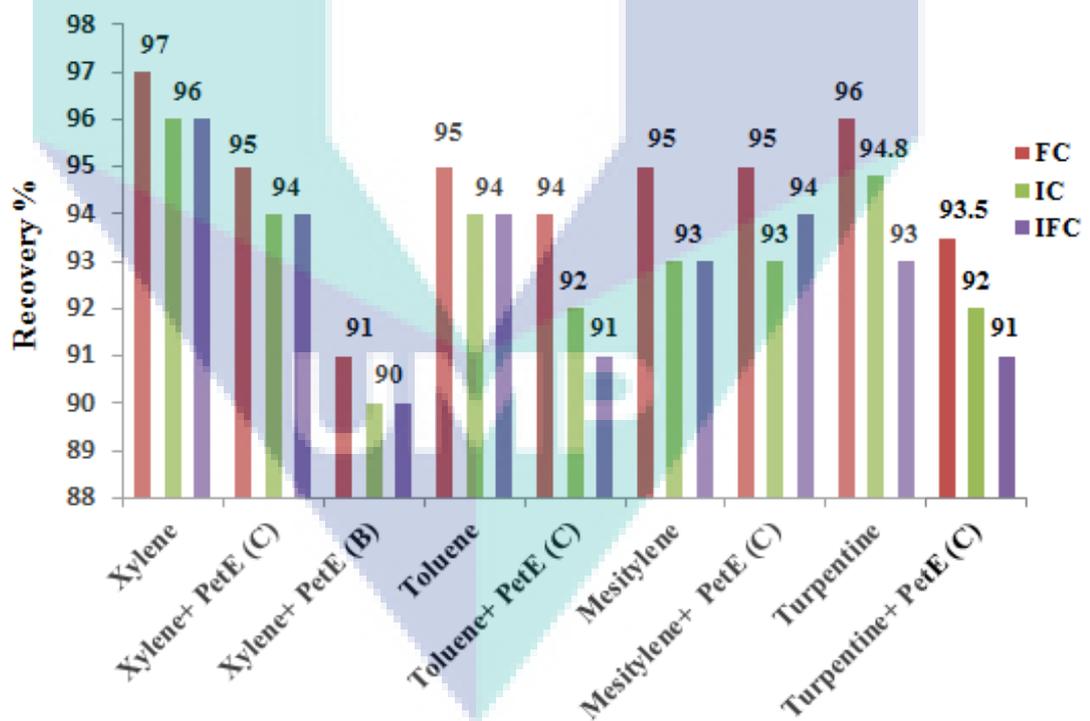**Figure 5:** HDPE recovery percentage in pure and blend solvent

Figure 6: Recovery percentage of wastes PP in pure and blend solvents

The pure and blend solvents with petroleum ether resulted in very good waste LDPE, HDPE and PP solubility. According to[13], the best recovery polymer is obtained at the dissolution temperature that is the boiling point for xylene (140 °C).The dissolution temperatures for all the wastes with the solvent mixtures containing xylene and petroleum ether were less than with pure xylene and the other solvents.

The dissolution temperatures for the mixed solvent xylene and petroleum ether (C) in a 1:1 ratio were 70°C, 100°C and 108°C for LDPE, HDPE and PP, respectively. The behaviour of PP in the solvent containing 1:1 (xylene + petroleum ether (B)) with boiling point 60-80 °C is noteworthy. Small bubbles appeared at 91°C with some dissolution. Gradually, the temperature reached 98°C with continued boiling, two minutes into which the pieces started dissolving. After 20-25 minutes, full dissolution occurred with polymer recovery of about 89-92%. The dissolution temperature for LDPE and HDPE was 67°C and 95°C, respectively. The time for all the experiments was set to 15 minutes at the required temperature. Figures1-3 shows also there is very slight effect of the waste type on the dissolution temperature.

Figure 4-6 shows the recovery percentage for all the waste products in all the solvents used in this study. The pure solvents always give product recovery higher than the blend solvent, where the range was 90-97% for LDPE wastes products. The recovery percentage for HDPE products sample was up to 95% except of D1, which was up to 90%. This can be attributed to the high degree of crystallinity of this sample. PP recovery percentages were same with the other polyolefin products, where the deference is very slight and can be neglected. For the FC the recovery percentage in all the solvent used in this system was always larger than the other two products due to the low crystillanity. However deference is slight and can be discarding.

The non- solvents used in all the experiments were n-hexane and the three grades of petroleum ether. Petroleum ether turned out to be a very good precipitator for all the polymer types, except LDPE in petroleum ether grade (C). The perfect precipitation occurred with 1:3 ratio solvent/non-solvent. With ratios of (1:1,1:2), a delay of 5-15 minutes was observed before full precipitation, except when the solution was cooled to (50-60 $^{\circ}$C) . With the blend solvents, the same grade of petroleum ether and a 1:1 solvent/non-solvent ratio yielded good precipitation.

2.5.2   Fourier-Transform Infra-Red (FTIR)

In order to conform the chemical structure of the waste polymer after reconditioning, its FTIR spectra was recorded and compared to the corresponding virgin LDPE, HDPE and PP polymer. Figures 7, 8 and 9 represent the FTIR graphs of three waste classifications in all the pure and mixed solvents used in reconditioning. Although these figures refer to the reconditioned sample using one solvent, the results were the same for all solvents used. The distinction between each polymer was made clearly. There was no significant change in the chemical structure or the characteristic bands for all kinds of wastes polyolefins used.
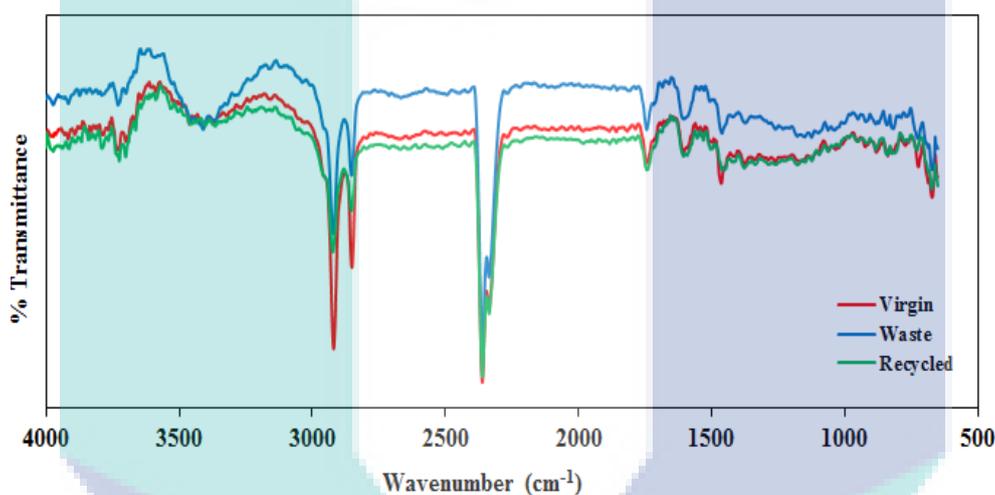
Figure 7: FTIR spectra for LDPE: virgin, waste and reconditioned
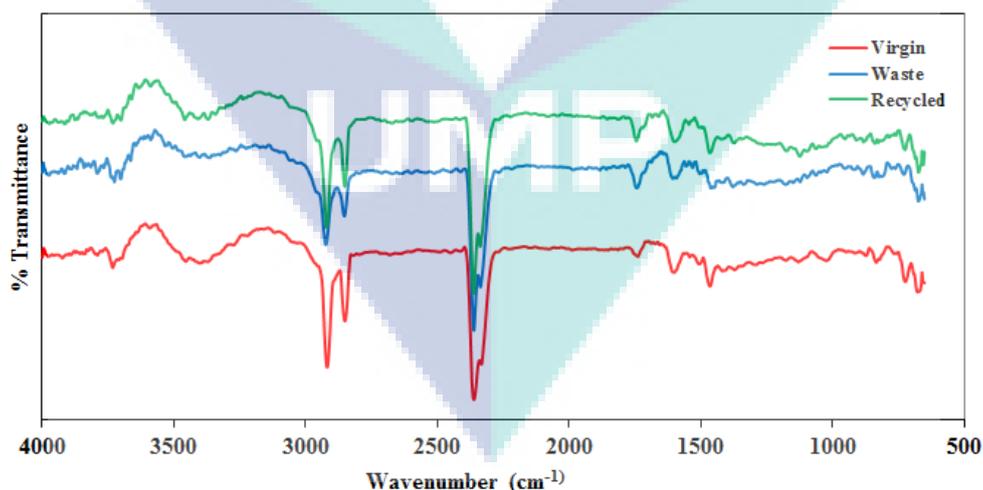
Figure 8: FTIR spectra for HDPE: virgin, waste and reconditioned
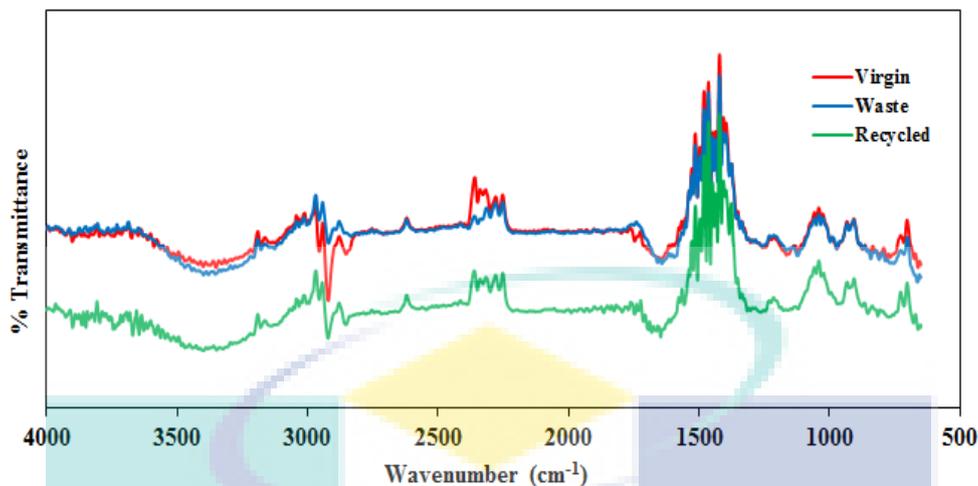
Figure 9: FTIR spectra for PP, virgin, waste and reconditioned

2.5.3 Thermal properties

The measurement of the thermal properties of the virgin polymer and waste plastic before and after recycling was done using DSC. The melting temperature remained practically unchanged by the reconditioning procedure and stayed within the permissible limits after reconditioning in all solvents used. The crystallinity of the products was also calculated, by dividing the heat of fusion at the melting point for each polymer by the reference heat of fusion, which was 293 J/g and 207 J/g for PE and PP, respectively[14], [15]. The melting points and crystallinities for some testing samples for LDPE, HDPE and PP are shown in Table 2, 3 and 4 respectively. According to[16], the melting temperature and melting range fluctuation for the waste and reconditioned grades could be attributed to plasticization and additives of the polymer due to the presence of trace amounts of the solvent that would likely remain in the polymer structure.

LDPE: The melting temperature of the waste products are (110.65, 112.8 and 109.45) °C for L1, L2 and L3 respectively. In addition, the crystallinity of the waste samples based on LDPE before the restoring process ranged between 24-27 %, while the crystallinities increased to 44.1-50 % after the reconditioning process. This could be due to the polymer precipitating during the reconditioned process from the solution under very slight cooling conditions, which indicates that the reconditioning process itself serves as a kind of annealing treatment [2], [17].

HDPE: The melting temperatures are (131 °C for D1 and 130°C for D2 and D3. In addition, the crystallinity of the virgin HDPE was 77% and for the waste samples before the reconditioning process 67 % for D1 and 31.9 %, 32 % for D2 and D3 respectively. The crystallinities increased to rang of (67.7-76) % after the reconditioning procedure.

PP: Like the LDPE and HDPE systems, the melting point remained practically unchanged by the reconditioning procedure and stayed within the permissible limits with only a 1 °C change. The melting temperature of the three waste products in all the solvents used in this system were (164.85, 164.85 and 164.05) °C for FC, IC and IFC, respectively. The crystallinities increased after the reconditioning procedure and reverted to the virgin PP value of 59 % at the range (51.6 -55) %. The results manifest the fact that the three wastes were made from the same PP virgin grade, the only difference being the additives. This observation also applies to the LDPE and HDPE wastes.

Table 2: Melting temperature, Tm, and crystallinity of virgin and three LDPE waste products before and after recycling

Sample	Tm (K)	Crystallinity %	Crystallinity % after reconditioning
virgin	106	52	-
L1	106	24.3	44.1
L2	113	26.2	49
L3	108	27.1	50

Table 2: Melting temperature, (Tm) and crystallinity of virgin and three HDPE waste products before and after recycling

Sample	Tm (K)	Crystallinity %	Crystallinity % after reconditioning
virgin	135	77	-
(D1)	131	67	76
(D2)	130	31.9	68.2
(D3)	130	32.1	67.7

Table 3: Melting temperature, (Tm), and crystallinity of virgin and three PP waste products before and after recycling

sample	Tm (K)	Crystillanity %	Crystallinity % after reconditioning
virgin	166	59	-
FC	165	24.7	51.6
IC	165	26.5	52
IFC	164	32.4	55

Figures 10,11 and 12 shows the DSC thermograms for the virgin and wastes LDPE, HDPE and PP polymers before and after recycling. Although DSC testing was done for all the samples in all the solvents used, the figures represent the optimum results. In order to compare the pure solvent with blend solvents, one system was chosen for each waste and a different solvent was used in every case. The results remained almost the same with a very slight change in the case of the blend solvent.

Figure (a) shows the thermograms for the dissolution of the sample in pure solvent whereas Figure (b) represents the dissolution in blended solvent. Promising results were seen for all the different solvents used, all the samples tested showed almost the same degree of crystallinity, which indicates the same fusion behaviour. Small deviations were observed for some HDPE samples, especially in the mixed solvents, but the results for LDPE and PP were good. The HDPE deviation is, as mentioned before, likely due to experimental conditions, sample preparation and the kind of waste materials used. The peak for the waste PP was very small comparison with the original and the recycled as well as for the LDPE and HDPE. This situation was accrued due to an initial additive and plasticizers and some more additives in waste polymers, so after the dissolution process using an organic solvent the additives and the plasticizers were removed from the original polymers molecules. A promising inference from the graphs is that good dissolution and precipitation is achieved after recycling the waste polymers with the proper solvent, besides an almost complete retention of mechanical and thermal properties.
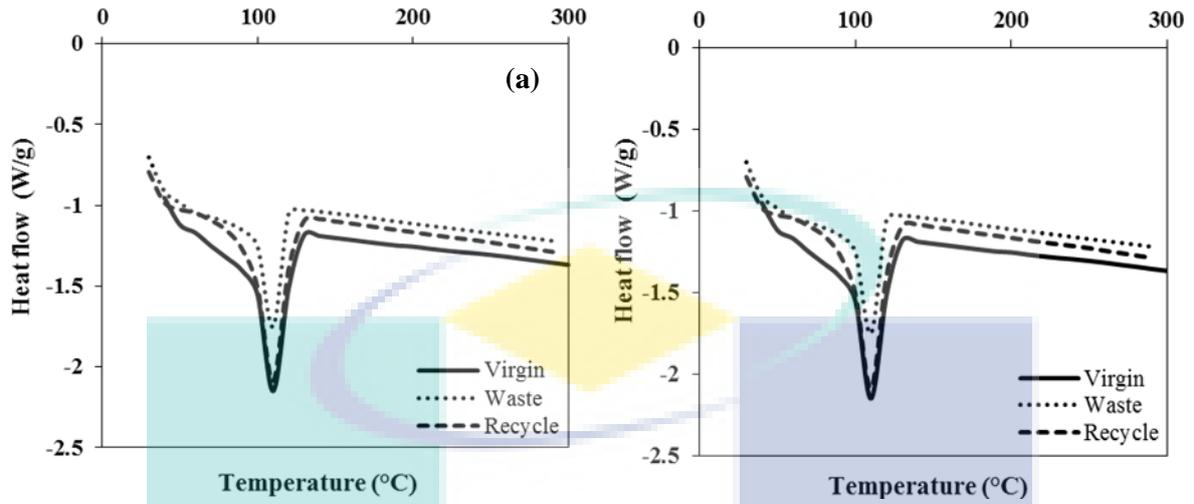
Figure 10: DSC thermograms of virgin and waste plastic before and after reconditioning based on (L1) LDPE in (a) toluene and (b) toluene/PetE(C)
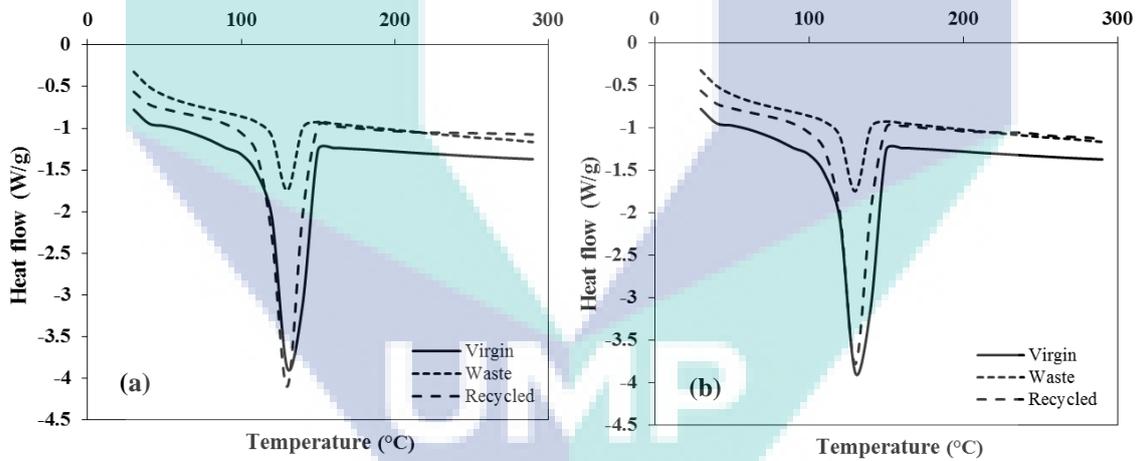
Figure 11: DSC thermograms of virgin and waste plastic before and after reconditioning based on (D2) HDPE in (a) xylene and (b) xylene/PetE(C)
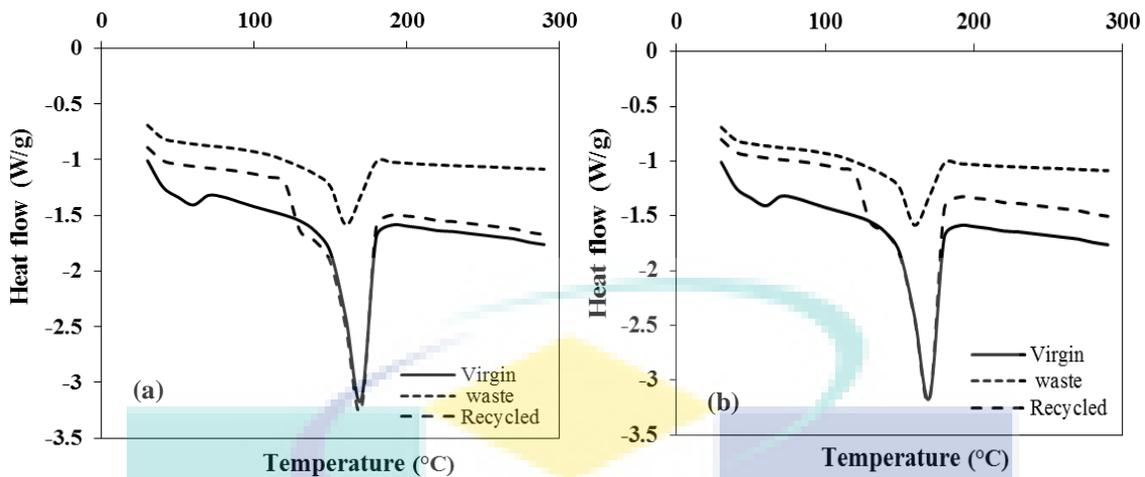
Figure 12: DSC thermograms of virgin and waste plastic before and after reconditioning based on (IFC) PP in (a) Mestylene and (b) Mestylene/PetE(C)

2.5.4 Mechanical Properties

This section presents the properties of LDPE, HDPE and PP for the virgin and the waste polymers before and after recycling (recorded using the universal testing machine Shimadzu AG-X). Two reconditioned samples were taken of each material, one with the pure solvent and the other for the blend solvent containing the pure solvent and petroleum ether. This was done in order to examine the difference in effect of the pure solvent and mixed solvent on the mechanical properties. The results are shown in Tables 5,6 and 7 respectively. The tensile stress at maximum load levels and the tensile stresses at yield measurement were seen to be very close for the virgin and reconditioned polymers. The elastic modules increased after reconditioning, possibly due to the fractionation phenomena (i.e. some lower molecular weight fractions may remain soluble in the solvents/non-solvents phase), as well as the additives initially contained in the starting material[2], [17], [18]. Due to the effects of the sample preparation methods, the tensile stress at yield for the reconditioned polymer fluctuates from the virgin polymer value, as is seen in the results.

Table 5: Tensile properties of virgin and waste LDPE before and after reconditioning

Testing type	virgin	L1			L2			L3		
		waste	rec.1	rec.2	waste	rec.1	rec.2	waste	rec.1	rec.2
Tensile stress at max. load (Mpa)	7.78	6.2	7.1	7.72	6.3	7.6	7.24	7.1	7.8	7.7
Strain at break (%)	39.788	97	70.75	74.3	102	71.6	70.35	104	68.5	69.3
Tensile stress at yield (Mpa)	4.88	4.855	5.265	4.995	4.98	5.32	5.22	5.12	5.08	4.978
Elastic modulus (Mpa)	201.4	143	174	169	150	167	172	155	180	177

rec.1 indicates to reconditioned polymer by pure solvent and rec.2 reconditioned used blend solvent.

Table 6: tensile mechanical properties of virgin and waste HDPE before and after reconditioning

Testing type	virgin	D1			D2			D3		
		waste	rec.1	rec.2	waste	rec.1	rec.2	waste	rec.1	rec.2
Tensile stress at max. load (Mpa)	18.54	17.18	18.98	18.85	14.85	18.4	18.35	15.58	18.9	18.42
Strain at break (%)	58.2	45.7	35.14	36	47	39.7	40.2	64.18	34.2	33.9
Tensile stress at yield (Mpa)	12.24	15.18	15.4	14.97	13.53	15.2	15.1	9.244	14.7	14.8
Elastic modulus (Mpa)	496.5	462	485.3	485	434.8	480	479	392.3	453	454

rec.1 indicates to reconditioned polymer by pure solvent and rec.2 reconditioned used blend solvent

Table 7: Tensile mechanical properties of virgin and waste PP before and after reconditioning

Testing type	virgin	FC			IC			IFC		
		waste	rec.1	rec.2	waste	rec.1	rec.2	waste	rec.1	rec.2
Tensile stress at max. load (Mpa)	7.86	6.76	7.4	7.1	7.1	7.92	7.55	7.4	8.11	7.9
Strain at break (%)	2.49	2.27	2.154	2.3	5.1	2.6	2.33	3.89	2.44	2.54
Tensile stress at yield (Mpa)	5.9	4.58	4.28	4.8	2.98	5.38	5.34	3.53	5.76	5.4
Elastic modulus (Mpa)	744	624.8	717	722	465	733	743.5	554	728	739

rec.1 indicates to reconditioned polymer by pure solvent and rec. reconditioned used blend solvent.

From the results presented so far, it can be concluded that the tensile properties of the three reconditioned LDPE polymers are similar in both pure and blend solvent with reference to the virgin.

2.6 Conclusion

Reconditioning of waste LDPE, HDPE and PP was examined by a dissolution/reprecipitation technique. Different concentrations of the polymer were used in this study. The highest concentration used for the dissolution of the LDPE was 40g polymer in 100 ml of solvent and 25g/100ml of HDPE, while for PP it was 30g/100 ml. Toluene, Xylene, Mestilyene, and Turpentine were used as pure solvents and the four solvents were mixed with petroleum ether (grades B and C) to obtain blend solvents in 1:1 volume ratios. The best pure solvent was xylene as the previous researcher said and the best of new pure solvent used in this study was the Mesitylene. Xylene/PetE(B) and xylene/PetE(C) were the best blend solvent which are used in this investigation, where the dissolution temperature has been decreased in the new blend solvent. It was less than the dissolution temperature in the pure solvent especially in the xylene/PetE(B). The ratio of solvent/non-solvent of 1:1 with all the grades of the petroleum ether worked very well and can be used reliably.

Good recovery was seen for almost all solvents. The chemical structure showed no significant alteration after recycling, after examination by FTIR. The mechanical properties either

remained the same or improved after recycling, as was the case with crystallinity. Thus, the technique is quite effective for the recovery of waste polymer.

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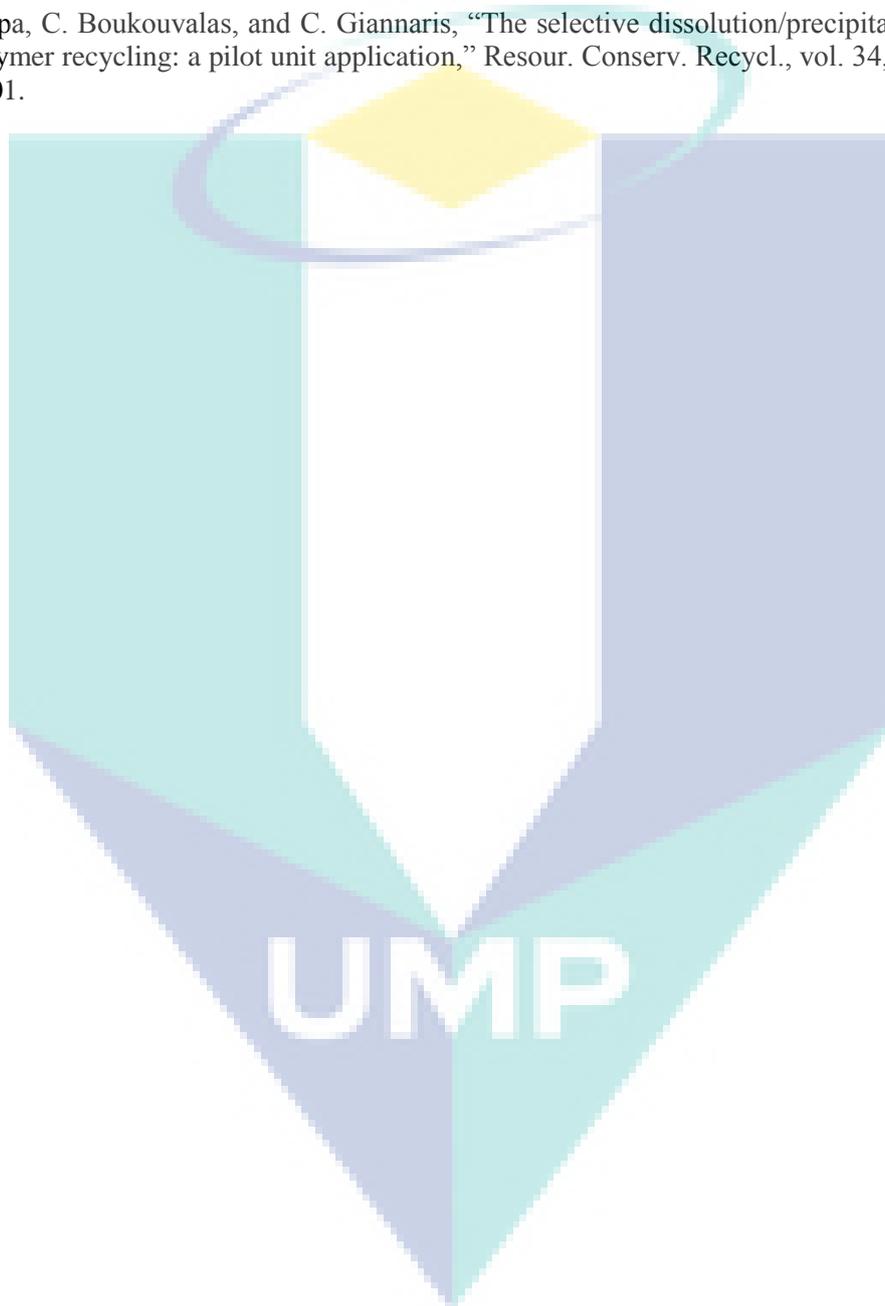
CHAPTER 3

Unmodified and Organo-modified Clay Effects on Mechanical and Thermal Properties of Waste Polypropylene.

3.1 Abstract

The aim of this research (waste to wealth), is to study the improved thermal and mechanical properties of waste polypropylene (wPP) in a nanocomposite. For this purpose, Organo-modified (OMMT) and unmodified sodium montmorillonite clay (MMT) were employed to fabricate polypropylene/clay nanocomposite. Commercial grade (OMMT) and (MMT) were added in a range of 1-5 wt %, in wPP to prepare polypropylene-clay nanocomposites, following the melt intercalation method. Fourier transform infrared spectroscopy (FTIR) and Field Emission Scanning Electron Microscope (FESEM) were used to evaluate polymer structure before and after the fabrication. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were used to analyse the thermal stability and thermal properties for the waste polyolefin and respective nanocomposites. The FTIR and FESEM results exhibited no change in the chemical structure of the polymer after clay addition and no exfoliation was observed in case of unmodified clay. Melting temperature and crystallization percentage was increased up to 3 wt% loading which was the best in comparison to the original waste matrix. The thermal stability of the wPP/clay nanocomposites was found improved in the case of loading 3 wt % of OMMT.

3.2 Introduction

The produced amount of plastic solid waste is accelerating rapidly, despite the growing attempts to reduce, reuse, recycle or recover such a great amount, it is almost impossible to bring all waste to recuperate. This is primarily due to their extensive applications in the packaging industry as well as in everyday usage goods; because they do not possess any side effects that can be harmful to human beings [1].

The development of polymer nanocomposites during the past two decades has further strengthened the industrial applications of these polymers. In particular, polymer–clay nanocomposites have been a remarkable area of research interest. Various types of polymer matrices (thermoset, thermoplastics, and rubbers) packed with clays have been studied. Among the clays, montmorillonite (MMT)-based clays have been proven to be a successful nano-additive in the polymer matrices and showing superior property improvement (thermal, mechanical, and optical) even at very low concentrations of about 3–5 wt % [2-4].

Montmorillonite, is widely employed because of its high cation exchange and swelling capacity, high surface area, and resulting strong adsorption [5]. There are two natural varieties of montmorillonite: sodium montmorillonite having a high swelling capacity in water and calcium montmorillonite with slight swelling capacity. The cation exchange ability in the interlayer space determines the most interesting property of the material which can be used as a filler for nanocomposites displaying unique mechanical properties [6]. The most desired situation occurs in nanocomposites, when the individual clay platelets disperse uniformly into the polymer (exfoliation or delamination) resulting in desired valuable properties [7].

The material properties and the paths to find isotactic polypropylene (iPP) based nanocomposites with Organo-modified montmorillonite (O-MMT), has been recently studied [8]. Hasegawa et al. [9] and Kawasumi et al. [10] have reviewed polyolefin and polypropylene /clay hybrids based on modified polyolefin and organophilic clay. Many researchers have also presented the polyethylene (PE) with O-MMT nanocomposites, using different ways for PE polymerization in the presence of layered silicate [11–14], and the application of polyethylene-grafted-maleic anhydride (PE-g-MA) as a matrix [15]. Olewnik et al. [14], studied the formation of polyolefin / modified montmorillonite nanocomposites with 1.5–5 wt % clay improved with 4, 4'-

methylenebisaniline to observe the thermal and structural properties of generated nanocomposites. It was reported that the thermal stability of the nanocomposites can be enhanced further, with a loading higher then 5 wt %.

The effect of clay content on the structure and property of polypropylene (PP)–high density polyethylene (HDPE) composites also were studied by Mohan et al., [15] and Drozdov et al. [16]. Drozdov et al., performed a comparative study on the physicochemical properties of polymer/clay composite and reported, "There are many experimental studies morphology and mechanical properties of intercalated and exfoliated nanocomposites with HDPE matrices. The reinforcement of HDPE with MMT clay platelets results in an increase in the Young's modulus, and a decrease in elongation at break, respectively."

In continuity with previous recycling work of the polyolefin using dissolution/reprecipitation technique [17-21]. Waste polypropylene/ OMMT and MMT nanocomposites are engineered by melt interaction method and the effect of clay content on the physicochemical properties of waste PP is presented in this research work. The morphology of the resulting WPP/clay nanocomposites is evaluated by mean of FTIR and FESEM. Mechanical properties are studied by using tensile machine, while thermal properties are investigated by TGA and DSC. The properties of new WPP/clay nanocomposites were also compared with the original waste polymer.
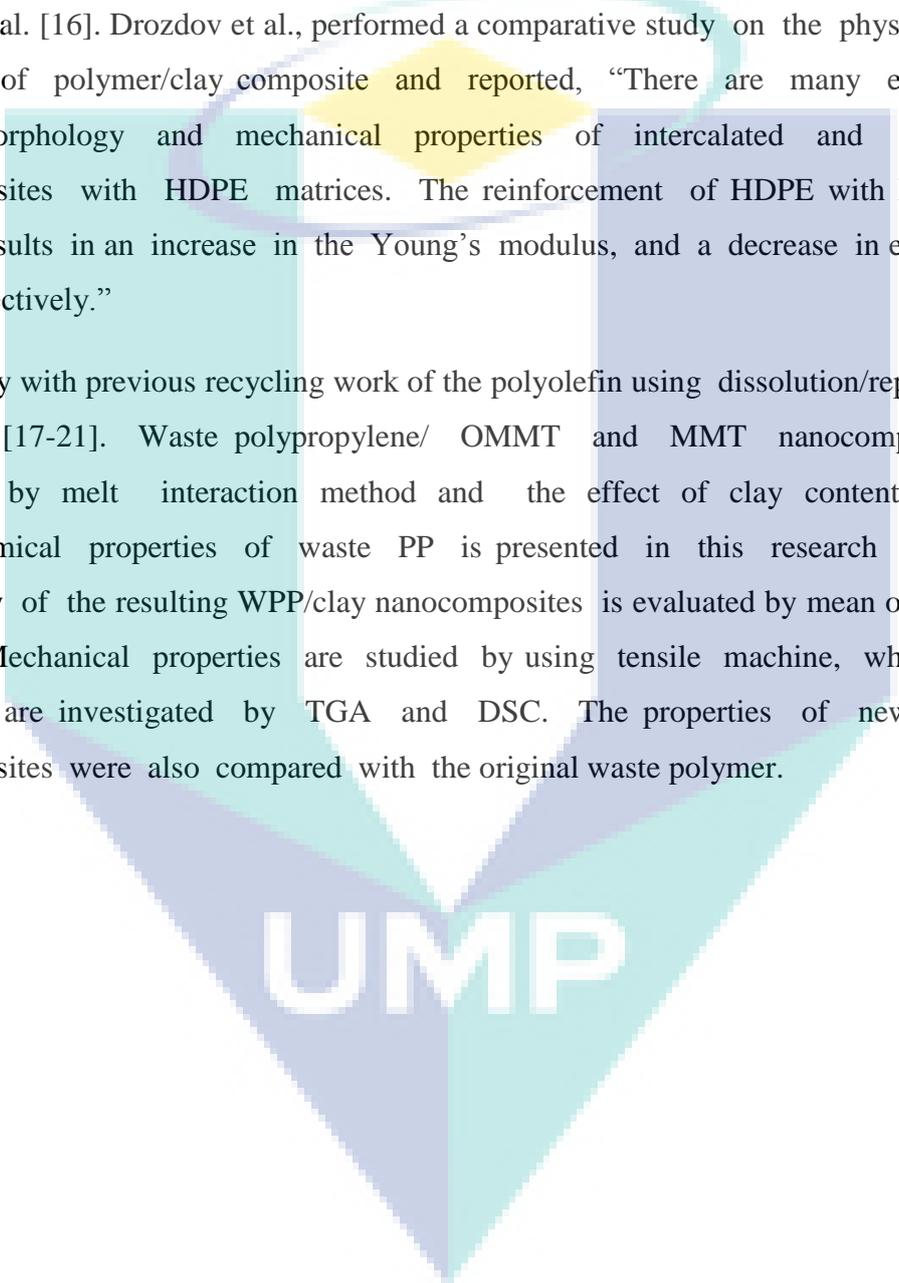
3.3 Methodology

3.3.1 Materials

The waste PP products, were collected from the trash. In this study we are focused on ice cream box with the density 0.927 g/cm-3, melt flow index 44 g/10min. The unmodified Sodium montmorillonite and Organo-modified clay (Cloisite 20A) were purchased from Southern Clay Products Inc., USA.

3.3.2 Preparation of the Nanocomposites

At first, polymer sample was prepared from ice boxes by cleaning and washing with water, then cutting into small pieces by a plastic crusher machine up to a size of range 2-4 cm. The waste polymer and clay were dried separately, in oven at 60°C for 24 hours. Clay was added in different weight percentages (1, 2, 3 and 5 wt %), then blended mechanically, in a Kitchen Aid type mixer for about 15-30 minutes. The mixture was then fed to an extruder for 20 minutes, as a blending time. Twin-screw extruder (EuroLab 16 XL), co-rotating, screw diameter 16 mm, L/D=25 was used for the nanocomposites preparation, temperature for the extruder was set at 140°C at the hopper to 180°C in the die. The screw speed was maintained at 80 rpm.

3.3.3 Characterization

FTIR study was performed by a Nicolet (Avatar 370 DTGS) FT-IR spectrophotometer with a resolution of 4 cm-1. The recorded wave number range was from 400 to 4000 cm-1. Small pieces of 1mm thickness were prepared for testing using a hand press, as specified for FTIR testing in ASTM D5477. The morphology of the nanocomposites was examined by Field emission scanning electron microscopy (FESEM; JEOL EVO-50, Japan). The fracture ends of specimens were mounted on aluminium stubs and spotter coated with a thin layer of gold to avoid electrostatic charged during examination.

Differential Scanning Calorimetry was performed by DSC Q1000 (V9.6, Build 290) from TA instrument. It was used to study melting temperature, heat of fusion and crystallinity of samples. The testing are performed according to ASTM D3418–03, with temperature interval 20–300°C and a scan rate of 10°C/min, in nitrogen atmosphere. Thermal stability for the samples before and after fabrication were determined by thermogravimetric analyser (TGA) during heating at the rate of 20°C/min from 20 to 800°C, in dry

Nitrogen. 25-30 mg samples were prepared for the testing purpose. The testing was carried out using a Universal V4.5A, TA Instruments.

The Universal Testing Machine Shimadzu AG-X, was used to measure the tensile mechanical properties. The testing was performed according to the standard ASTM D638-03 (type I), with the speed of 5 mm/min. Sample were prepared by using a hydraulic thermal press under the following conditions: temperature, 190°C, pressure, 10 MPa; time of heating, 15 min. The testing was done after 48-72 hours at room temperature with 55-60% humidity.
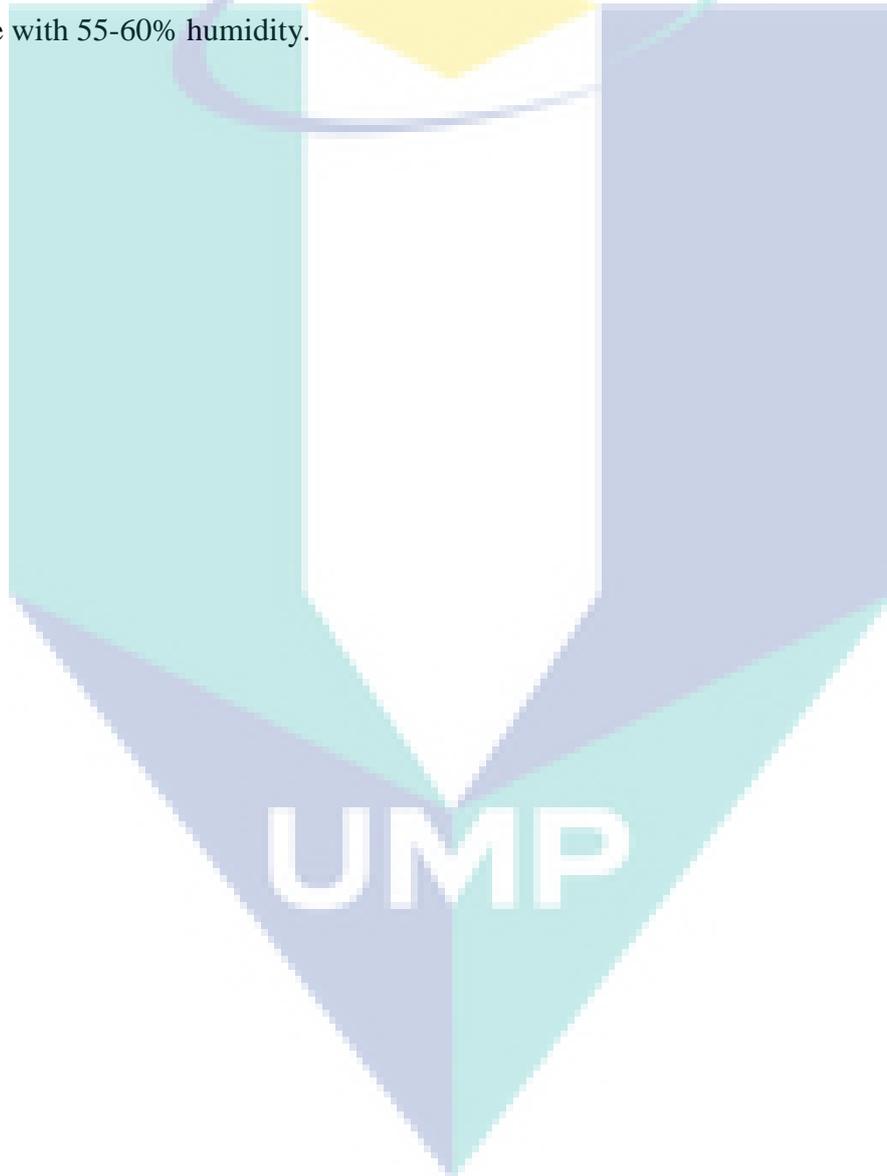
3.4 Results and Discussion.

3.4.1 FTIR Analysis

In FTIR testing, the original waste PP was compared with the fabricated nanocomposites as shown in Figure 1. No significant change was observed in the chemical structure or the characteristic bands for all the polymer samples used. Slight differences were recorded in wavenumbers, which is due to the additives present in small amounts in the waste products. However, the distinguishing peaks of the wPP/clay nanocomposites were found identical to the original wPP peaks in all the cases.
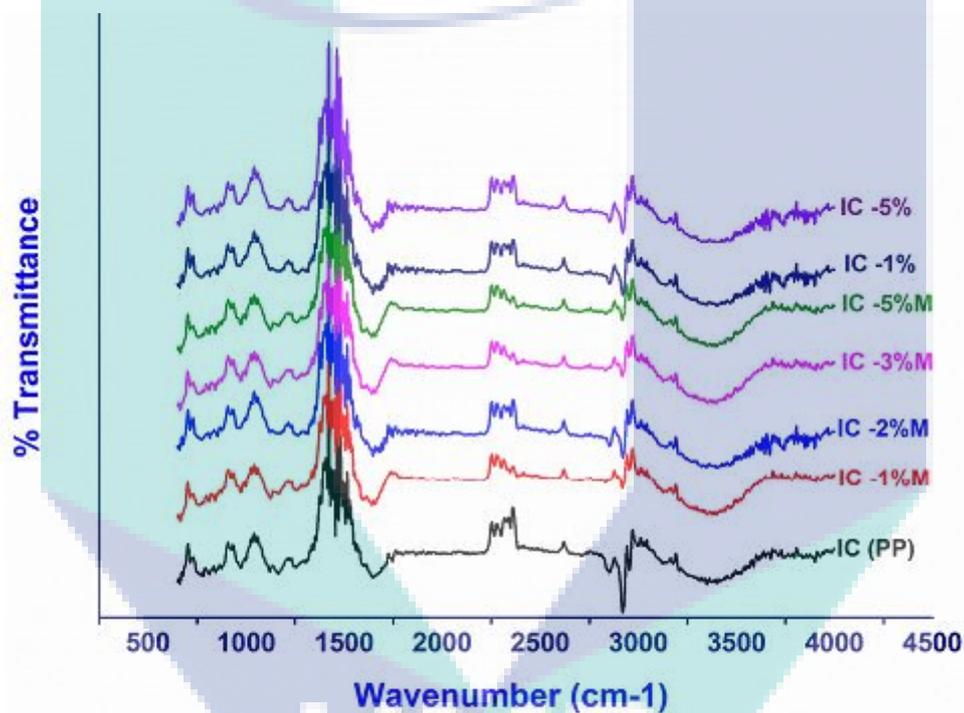
Figure 1. FTIR spectra of waste wPP (IC) and wPP/clay nanocomposites, where M is mean the modified clay.

3.4.2 FESEM Spectroscopy

FESEM images are shown in Figure 2 (wPP (2a), modified (2b) and unmodified (2c), respectively. Figure 2 b exhibits an intercalation in 2 wt % of the modified clay into the wPP. Figure 2 b shows a good compounding between the organo-modified clay and wPP, on the other hand in Figure 2 c, small exfoliation can be observed [14, 22].
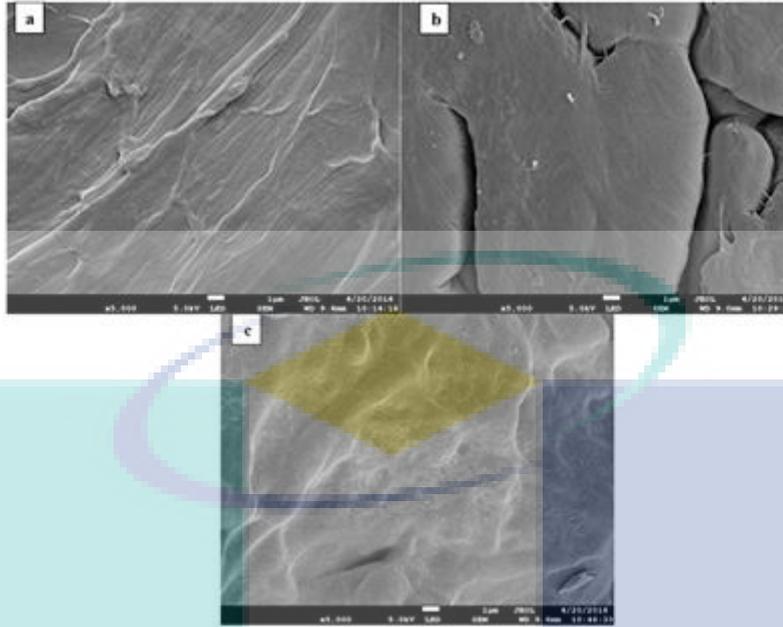
Figure 2. The FESEM images of the surfaces of a) pristine waste PP and the b) nanocomposites at 2 wt % organo-modified (Cloisite 20A) clay and c) 2 wt % unmodified clay.

3.4.3 Differential Scanning Calorimetry

DSC was used to measure the thermal properties (fusion behaviour, melting point and crystallinity) of the wPP and nanocomposite samples with varying concentration of clay, results are presented in Table 1. The percentage crystallinity C can be derived as follows:

$$C = \Delta H_{exp} / \Delta H_f$$

where, ΔH_{exp} is the experimental heat of fusion of the sample tested. ΔH_{exp} is calculated by measuring the area under the thermogram peak, while ΔH_f is taken to be 207J/g for PP which represent the heat of fusion of the 100% crystalline polymer [23, 24]. MMT addition has minimal effects on the melting temperature of wPP. The melting temperature of wPP /OMMT nanocomposite with 1 and 5 wt % OMMT slightly increases to 166.7°C, in comparison with 165°C for neat wPP. Results of DSC show that little quantity of OMMT added to the wPP matrix gives slight increasing of melting temperature. This phenomenon may be due to the efficient nucleating effects of the clay layers/ tactoids [25, 26].

Table 1. Melting temperature Tm, Heat of melting Hm, and degree of crystallinity C, of nanocomposites as a function of MMT and OMMT content.

Sample	Tm (c)		Hm/ Jg^{-1}		C (%)	
IC	165		55.9		27	
	MMT	OMMT	MMT	OMMT	MMT	OMMT
IC- 1%	164.8	166.7	60.7	65.8	29	32
IC- 2%	165	165.3	60.2	70.9	29	34
IC- 3%	164.7	164.9	55.0	72.1	27	35
IC- 5%	165.7	166.9	46.4	54.4	22	26

The heat of fusion Hm nanocomposites increases significantly, especially at a lower, 1-3 wt % concentration and decreases very slightly with further increase in clay addition, still higher value than the pure wPP. In MMT addition Hm value increased very slight in 1 and 2 wt % clay concentration and decreased less than the pure wPP with increase in clay concentration. This phenomenon may be attributed to the blockage of crystalline growth front caused by the clay platelets, dispersed in an irregular array in the nanocomposite, as it is evident in view of hot-stage microscopy studies [27].

3.4.4 Thermogravimetric Analysis

TGA is used to find the thermal degradation of the materials. Onset temperature was measured as the point in which 10% of the sample is lost, the degradation at 50% of the sample lost also are taken in respect, and the last measurement of thermal degradation is the fraction of material which is non-volatile at 873 K, known as char [28]. Figure 3 shows the TGA curves for neat wPP and wPP /clay nanocomposites containing 1, 2, 3, 5% wt of OMMT and 1, 5% wt of MMT, respectively. The temperature at weight loss 10 and 50%, while the residue at 600°C are presented in Table 2.
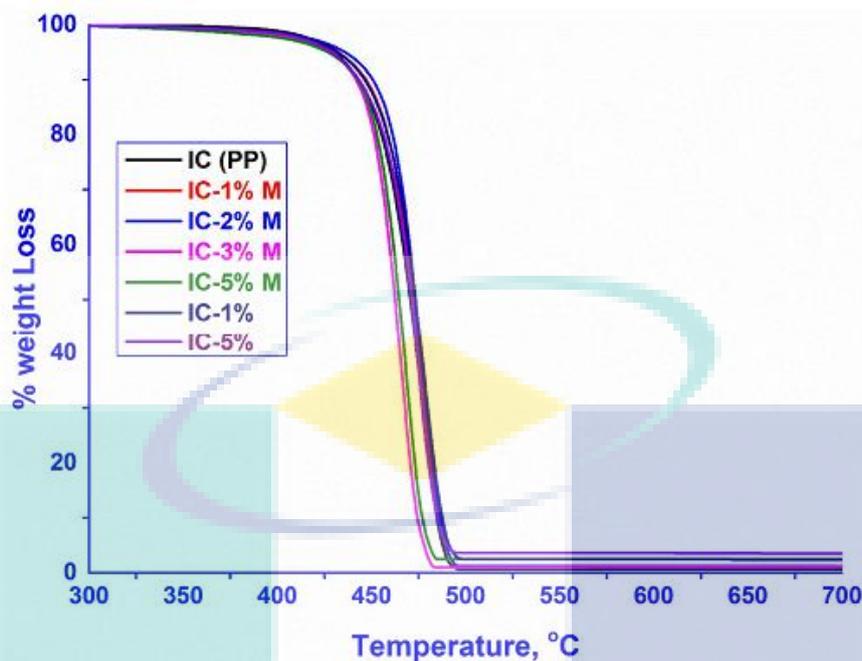
Figure 3. TGA analysis for wPP (IC) and wPP/clay nanocomposites.

wPP /OMMT nanocomposites at 1-3% wt clay show higher thermal stability as compared to neat wPP. The initial thermal stability is characterized by the temperatures at 10% weight loss. The wPP/OMMT nanocomposites show significantly enhanced initial thermal stability at 10% weight loss compared with pure wPP. The wPP/OMMT nanocomposite with 3% wt clay, shows the highest initial thermal stability. When the OMMT content is increased higher than 3% wt, the initial thermal stability decreases, but even in 4 and 5% wt is still higher than pristine wPP, but it is less than that with sample loaded with 3% wt. content. For 50% weight the thermal stability has not changed much. Comparatively lower OMMT content, the initial thermal stability increases with OMMT content. The results in wPP/MMT nanocomposites were different, the temperatures at 10 and 50% weight loss did not change as compared with pure wPP. This may be due to the aggregates of clay, which are less effective in blocking heat than the MMT layers/tactoids, increasing with clay content [26].

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Table 2. TGA data for waste PP and nanocomposites under nitrogen flow.

Sample		Temperatur/ °C at mass loss		Residue at 600 °C%
		10%	50%	
IC		443	470	0.64
IC	1% M	448	472	1.06
IC	2% M	450	473	1.24
IC	3% M	441	462	1.05
IC	5% M	442	464	2.51
IC	1%	445	473	2.46
IC	5%	443	471	3.63

3.4.5 Mechanical Properties

The mechanical properties of the matrix wPP/clay nanocomposites were measured and compared with those of the pure waste PP. Figures 4 (a, b, c, and d) show the elastic modulus, tensile stress at maximum load strain at break and tensile stress at yield, respectively.

The elastic modulus plots of samples are shown in Figure 4 a. The measured modulus of pure wPP was 465 Mpa, which increased significantly when modified clay (OMMT) was added from 1-3 wt % and were decreased at 5 wt % OMMT, even the unmodified clay (MMT) addition decreased the modulus. The maximum modulus were found as 649 MPa in wPP/ OMMT nanocomposites increase of 39% relative to pure waste PP. it has been reported that the elastic modulus increases when organo-clay is added in low content 1-3 wt %. The OMMT is dispersed in the PP matrix at nanometre scale and part of the OMMT is intercalated by PP chains. This may have narrowed the segmental movement of PP macromolecules [26, 29]. On the other hand, the other three mechanical properties, tensile stress at maximum load, strain at break and tensile stress at yield show in figure 4 b, c and d respectively, decreased with clay addition. In MMT content, it was observed that the decrease in values is higher than in the OMMT content. The significantly decreased mechanical properties at clay loading may be due to the uniformly dispersed MMT tactoid with intercalated structures [26].
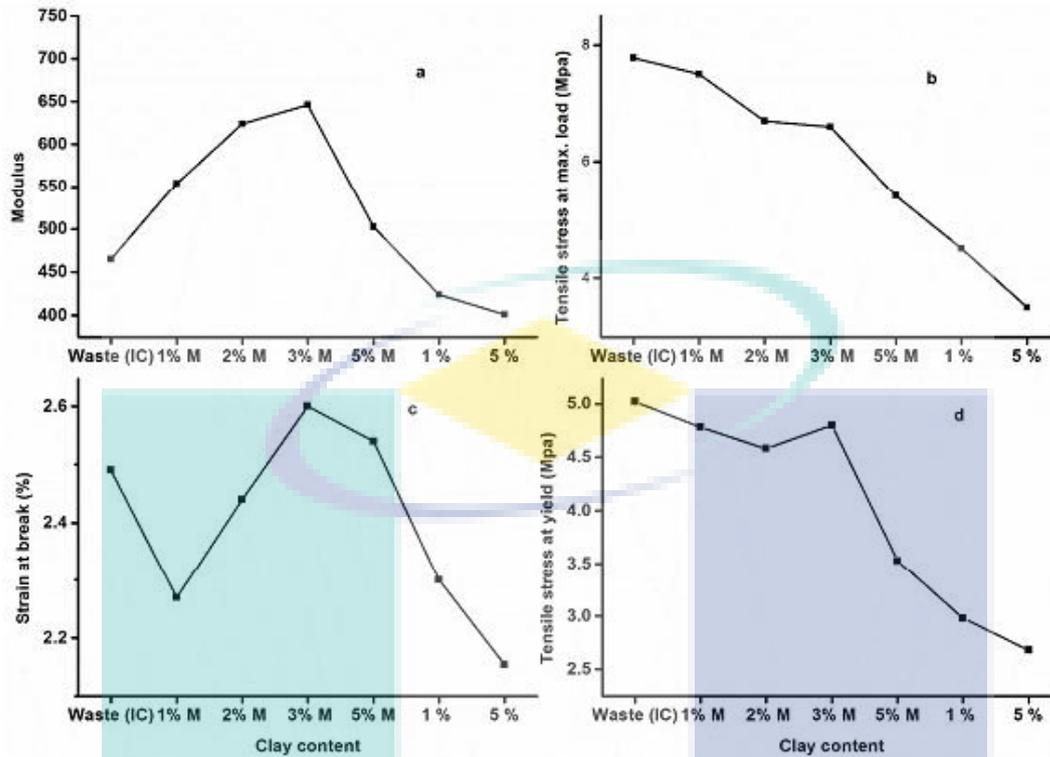
Figure 4. Effect of clay loading on tensile properties of LDPE and HDPE/clay nanocomposites.

3.5 Conclusion

The waste PP/ clay (unmodified and organo-modified) nanocomposites were fabricated using the melt intercalation method. The effects of the two types of clay on the structure and properties were studied. FTIR and FESEM testing depicts OMMT considerably affect the exfoliation, due to the interaction of OMMT with in polymer matrix. There was no intercalation observed, when MMT was added to the matrix without any modification. The DSC results revealed that in all the samples the melting temperature remains constant with a negligible change. The enthalpy of fusion was found increased in nanocomposites at low OMMT concentrations of range 1-3 wt % in comparison with the pure waste and the best was observed in 3 wt % of sample loading. Same results were observed in the thermal behaviour of the nanocomposites, with an enhancement at low OMMT percentage. The elastic modulus in the PP nanocomposites increased by 39% relative to pure waste. Tensile stress at maximum load, strain at break and tensile stress at yield were slightly decreased in the low OMMT clay content. It was concluded that by increasing the content of clay above 3% by weight a decline in the mechanical properties of the resultant composites. However, we can conclude from this study that the recycling of the waste polymer using dissolution/reprecipitation method was better

than reinforcement of the waste PP by nanocomposites fabrication in melt interaction method.

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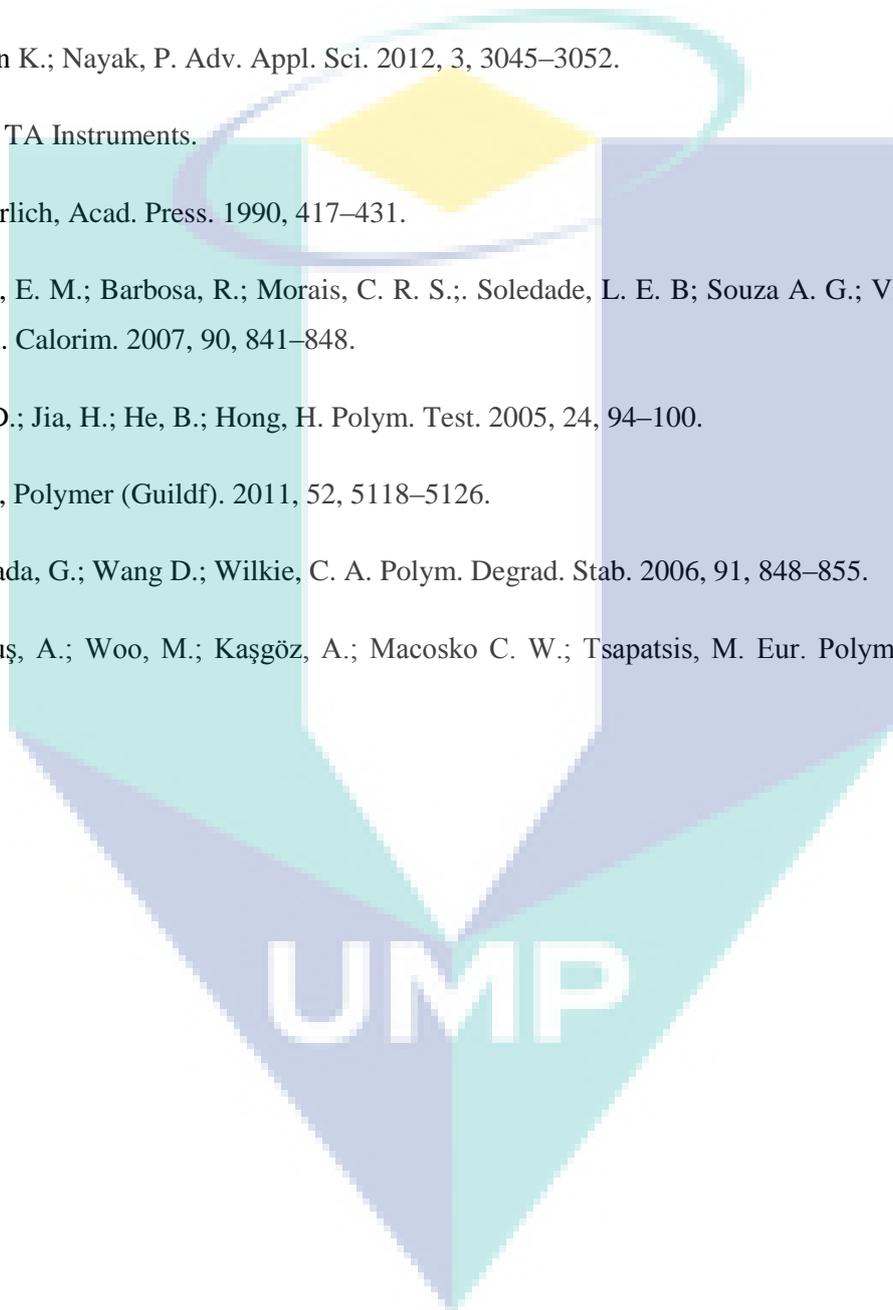
CHAPTER 4

Mechanical and Thermal Properties of the Waste Low and High Density Polyethylene-nanoclay Composites

4.1 Abstract

In extension with the previous work, recycling of the waste polyolefins by dissolution/reprecipitation method, has been investigated. The goal of study was to explore the influence of organo-modified/ unmodified sodium montmorillonite clays, on the behaviours of waste polyolefins inclusive low density polyethylene (LDPE) and high density polyethylene (HDPE). 1-5 wt % of unmodified (MMT) and Organo-modified clay (OMMT) were added to the polyolefins, to prepare polyolefin-clay nanocomposites by melt intercalation method. X-ray diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM) were used to estimate the dispersion of clay in the polymer matrices and the morphology of nanocomposites. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were used to analyse the change in the thermic properties of the waste polyolefins nanocomposites. The XRD and FESEM results showed an intercalated structure in the HDPE and LDPE with Organo-clay nanocomposites, whereas no exfoliation was observed with unmodified clay in both waste HDPE and LDPE, respectively. DSC and TGA, showed an improved thermal behaviours in the HDPE/Organo-clay nanocomposites (3 wt%) clay loading. Melting temperature and crystallization percentage were observed to increase in 1, 2, and 3 wt% loadings. In waste LDPE/ clay nanocomposites, no improvement was established in the thermal stability.

4.2 Introduction

Polymeric materials are progressing largely in recent and innovative applications, extending between bicycles to aerospace, ware to customer electronics, farming, and sporty industries. Polymeric materials are significant type of material science, which endures to be a developing field in forthcoming decades [1–3]. Recently, the demand of polymeric consumption (mostly plastic), has increased dramatically due to increasing world population and the requirements, respectively [4,5]. The manufactured amount of plastic rigid wastes escalated in no time, although the growing efforts to minimize, reuse, recycle and recover the wastes are progressive to a higher extent. The increment is predominantly due to extensive plastic applications in the packaging and food industry, and in other everyday goods simply because they do not own any side effects that can be detrimental to human kind [6].

Montmorillonite is one of the most common smectite, which has wide applications because of its higher cation exchanging and ability of puffiness, rise superficies area, and ensuing powerful adsorptions [7]. There are two normal types of montmorillonite, where sodium montmorillonite exhibited a higher ability of puffiness in water whereas calcium montmorillonite possessed low ability of puffiness. The capability to interchange cations in the interlayer area and clay particles uniform dispersion regulate the most fascinating behaviours of the substance, that can be employed as a filler for nanocomposites presenting distinctive mechanistic behaviours [8,9]. The advancement in polymer nanocomposites, during the past two decades has further reinforced the manufacturing usage of the polymeric materials.

In specific, polymer–clay nanocomposites have a fabulous region of research catching attention. Different kinds of polymeric matrixes (thermoset, thermoplastics, and rubbers), full of with clays have been investigated. Between the clays, montmorillonite (MMT)-based clays, have been assured to be a effective nano-additives in the polymeric matrixes by displaying better properties (thermic, mechanistic, and optic), at least clay concentrations of between 3–5 wt% [10–13].

Material properties description and the paths to find isotactic polypropylene (iPP) based nanocomposites with organo-modified montmorillonite (o-MMT), recently revised in [14]. Hasegawa et al., [15] and Kawasumi et al., [16] are reviewed polyolefin and polypropylene/clay mixture depend on adjusted polyolefins and organophilic clay. There are many researcher also worked on the polyethylene (PE) with o-MMT as nanocomposite using

different ways for instance PE polymerization in the existence of layered silicate [17–19] and [20,21] are used the enforcement of polyethylene-grafted-maleic anhydride (PE-g-MA) as a matrices.

Trading and lab. prepared straight low density PE (LLDPE), PE-g-MA grades were usedby Wang et al., [22], where melt mixing method were used to prepare silicate nanocomposites, by lab. prepared LLDPE-g-MA and LLDPE reacted with PE-g-MA, respectively. The application of LLDPE-g-MA, as a compatibilizer for HDPE/o-MMT system was studied by [23]. Low density polyethylene (LDPE), a extensively utilized packaging matter, sounds to be especially striking for nanocomposite production, commonly because of the supposed advancement of obstacle characteristics. Nevertheless, the details concerning this nanocomposites, with PE-g-MA, as a compatibilizer, are uncommon [24].

The influences of clay exfoliation in LDPE based nanocomposite [24] were worst the HDPE based system, due to further difficult permeation of unlinear LDPE polymer molecules into clay galleries. Olewnik et al., [25], studied the creation of polyolefins/adjusted montmorillonite nanocomposites about 1.5–5 wt% clay adjusted with 4, 4' methylenebisaniline, with an emphases on the thermal and structural properties of generated nanocomposites. The clay content effect on the structural behaviour of polypropylene (PP) and high density polyethylene (HDPE) composites, also were revised by [26].

Drozdov et al., [27], studied a comparison of the result in the polymer/clay composite properties for many researcher. It was reported, "There are many experimental studies regarding the morphology and mechanical properties of inserted and exfoliated nanocomposites with HDPE matrixes. It has been reported that support of HDPE with MMT clay layers consequences in (i) an expansion in the Young's modulus, and (ii) a reduction in extending at break. The same consequences have been revealed in experiments on other polymer–clay nanocomposites, as well as on particulate microcomposites, the above-mentioned results may be considered as accurate".

Based on the previously reported research and our studies on the recycling of the polyolefin [28–32]. The following study enlightens the synthesis of waste polyolefin/ Organ-modified and unmodified sodium montmorillonite nanocomposites, by melt interaction method and exploring the effect of clay content on the waste LDPE and HDPE structural, thermal and mechanical properties. The characterization behaviour of the resulting polyolefin/clay nanocomposites are studied by XRD and FESEM, respectively. Mechanical (Tensile and

nanoindentation) and the thermal behaviours were analysed by using Instron Universal testing machine, TGA, and DSC. The properties of the new waste polyolefin/clay nanocomposites were later compared with the original waste polymer nanocomposites, compatibly.

4.3 Experimental

4.3.1 Materials

The waste polyolefin material was collected from h trash, waste LDPE was collected from generally used bags name for an easy treatment (B), density 0.927 g/cm3, melt flow index 0.841 g/10 minutes. The waste HDPE was collected from empty chemical containers in the lab. (D), density 0.962 g/cm3, melt flow index 0.252 g/10 minutes. The unmodified sodium montmorillonite and organo-modefied clay (Cloisite 20A), were purchased from Southern Clay Products Inc., USA.

4.3.2 Method for preparing the nanocomposites

Firstly, the polymer samples were prepared by washing and cleaning up with tap water and cutting them into smaller pieces, by using plastic crusher machine to the size 2-4 cm, respectively. The clay was added (1, 2, 3 and 5) wt%, to the waste polymer. Secondly, the clay and the waste polyolefin samples were blended in a Kitchen Aid type mixer, for about 15-30 minutes. The blended mixture was oven dried at 60pC, for overnight period. The mixture was then fed to an extruder for 20 min. as blending time. Twin-screw extruder (EuroLab 16 XL), co-rotating, screw diameter 16 mm, L/D=25 was used for the nanocomposites preparation. Temperature for the extruder were set as 150pC, whereas 190pC was set at the hopper. The screw speed was fixed at 80 rpm for all the samples.

4.3.3 Characterization

X-ray diffraction (XRD) patterns between 3º - 80º were obtained with an X-ray diffractometer (Rigaku Mini FlexII, Japan) using CuKa filter radiation ($\lambda= 1$ 0.15406 nm), at 30 kV and 15 mA. The morphology of the nanocomposites was investigated by field

emission scanning electron microscopy (FESEM; JEOL EVO-50, Japan). The breaking ends of samples were mounted on aluminium stubs and spotter coated with a thin layer of gold to prevent electrostatic charged throughout testing.

Differential Scanning Calorimetry, DSC Q1000 (V9.6, Build 290) from TA instrument was used to determine melting temperature, enthalpy of fusion (ΔH^{exp}_f) and crystallinity (%C). The testing are accomplished depend on ASTM D3418–03, with temperature period 20–300 °C and a scan rate of 10 °C/min. in nitrogen atmosphere. Thermal stability for the samples before and after fabrication were determined by thermogravimetric analyser (TGA) through heating at the rate of 20°C/min. from 20-800°C, in dry N_2. 25-30 mg sample was prepared for the testing.

The testing were accomplished employing a Universal V4.5A, TA Apparatuses. The Universal Testing Machine Shimadzu AG-X, was used to measure the tensile mechanical properties. The testing was performed according to the standard ASTM D638-03 (type I) with speeds of the testing were 5 mm/minutes. The sample was prepared using a hydraulic thermo press under the following conditions of: temperature (190 °C), pressure (10MPa), time of heating (15 min.). The testing had done after 48-72 h in room temperature and 55-60% humidity.

4.4 Results & Discussion

4.4.1 X-Ray Diffraction

X-ray diffractograms of waste LDPE and HDPE and respective nanocomposites are presented in Fig. 1 and 2, respectively. The XRD patterns showed two distinct 110 at and 200 reflection peaks. The 110 and the 200 peaks are noticed at 21.76° and at 24.04°, respectively for HDPE/clay nanocomposites, and at 21.64º and at 23.94o, respectively for LDPE/clay nanocomposites, with no obvious difference between them.

In comparison with the HDPE, LDPE/Organo-modified clay and non-modified clay systems, the PE/Organoclay system has a better dispersion of Organoclay in the matrix, which may be the result of the strong interaction between organic modified clay molecules and the particular silicate layer. In weight percent clay addition, the peaks remarkably lowered, revealing proper exfoliation of clay in the polyolefin matrices, in spite of the exfoliation is

lower in HDPE/unmodified clay and LDPE/clay nanocomposites than in HDPE/Organo-modified clay. The results are consistent with the previously reported results [21,22,33].
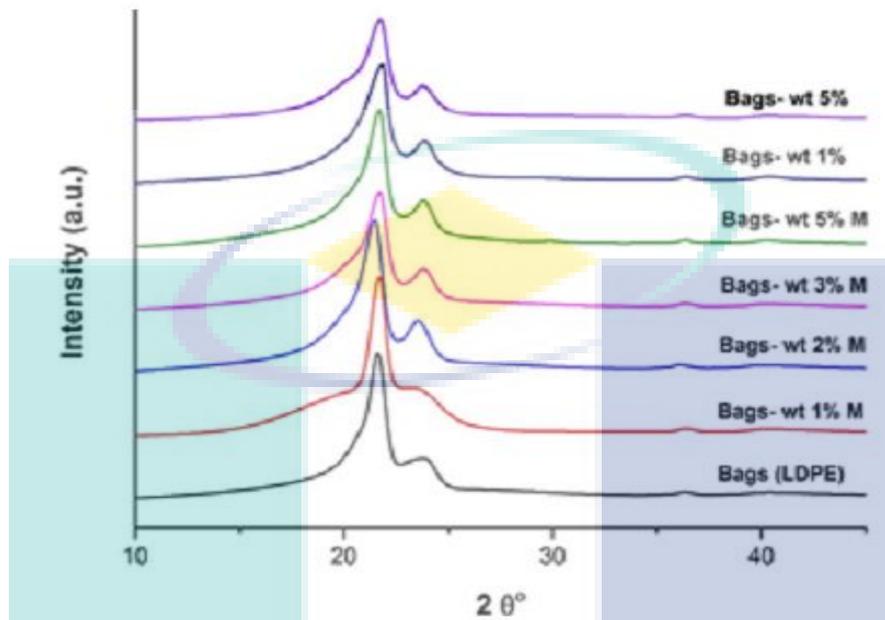

Fig. 1. X-ray diffraction curves of waste LDPE (Bags) and waste LDPE /clay nanocomposites, where M is mean the modified clay
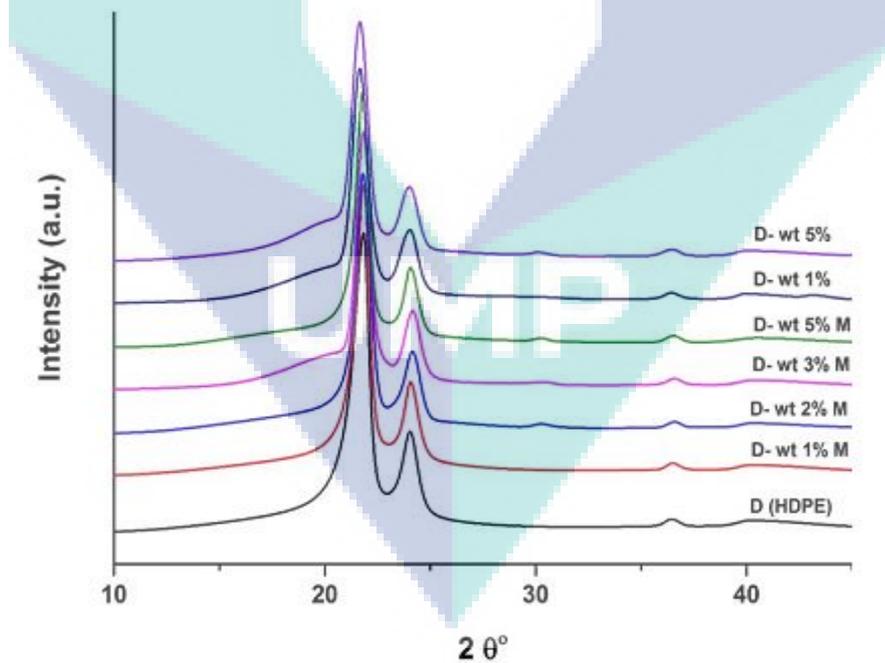

Fig. 2. X-ray diffraction curves of waste HDPE, Chemical container (D) and waste HDPE /clay nanocomposites, where M is mean the modified clay

4.4.2 Field Emission Scanning Electron Microscopy (FESEM)

FESEM testings as shown in Fig. 3 and 4 showed a good correlation with X-RD results, indicated the intercalation of 2 wt% modified and unmodified clay into the waste LDPE and HDPE, respectively. The exfoliation phenomenon of insertion and accumulation is complicated to study from FESEM definitively, that can be simply indicated with the XRD studies. Fig. 3 b showed a good compounding between the organo-modified clay, on the other hand in figure 3 c small exfoliation can be observed. In the case of waste LDPE the exfoliation in the two types of clay was very slight [34,35].
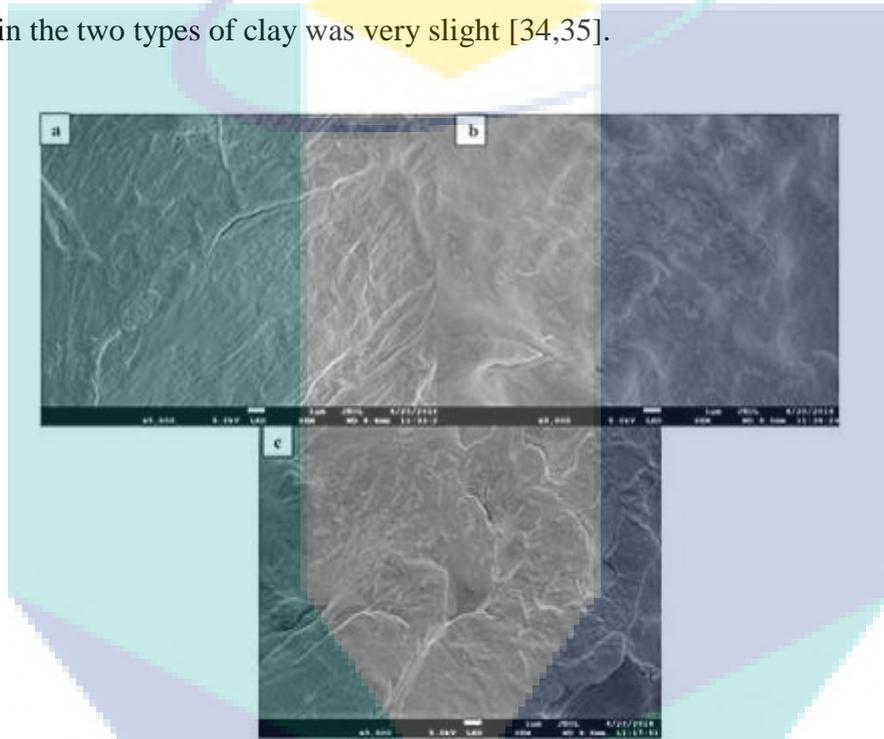
Fig. 3. The FESEM images of the surfaces of a) pristine waste LDPE and the b) nanocomposites at 2 wt % organo-modified (Cloisite 20A) clay and c) 2 wt % unmodified clay

4.4.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry Thermal properties (fusion behaviour, melting point and crystallinity), of the waste polyolefin and nanocomposites of variable clay concentration were analysed by using DSC technique (Table 1) .The percent crystallinity (%C) is then determined using the following equation:

$$\%C = [\Delta H^{exp}_f / \Delta H^0_f] \times 100\%$$

where, ΔH^{exp}_f is the experimental enthalpy of fusion of the specimen tested. ΔH^{exp}_f is calculated by measuring the area under the thermogram peak in terms of J/g, while ΔH^0_f is a standard value and represents the enthalpy of fusion if the polymer were 100% crystalline, it has been taken to be 293J/g for PE (LDPE and HDPE) [36,37]. MMT, in addition has minimal effects on the melting temperature of both the waste HDPE and LDPE, respectively. The melting temperature of waste HDPE/OMMT nanocomposite with 1 and 5 wt% OMMT, slightly increased to 137.33 ℃, when compared with 136.2 ℃, for a neat waste HDPE. In waste LDPE nanocomposites, no temperature change was observed by OMMT addition. DSC results showed that little quantity of OMMT in the HDPE matrix produced a slight increment in the melting temperature. The phenomenon may have occurred because of the effective nucleation influences of the silicate strata/ tactoids [38, 39].

Table 1: Melting temperature Tm, Heat of melting Hm, and degree of crystallinity C, of nanocomposites as a function of MMT and OMMT component

Sample	Temperatur/ °C at mass loss			Residue at 600 °C%
	5%	10%	50%	
D	430	443	470	0.64
D 1% M	431	448	472	1.06
D 2% M	436	450	473	1.24
D 3% M	427	441	462	1.05
D 5% M	427	442	464	2.51
D 1%	426	445	473	2.46
D 5 %	428	443	471	3.63
B	413	428	461	0.62
B 1% M	426	438	463	1.30
B 2% M	430	440	458	1.73
B 3% M	429	440	459	1.70
B 5% M	428	440	457	2.17
B 1%	417	432	464	1.83
B 5 %	414	429	462	3.91

The heat of fusion H_m, for waste HDPE/OMMT nanocomposites increased significantly, especially at lower loadings (1-3 wt%), and showed a little decrease in further clay addition. however still it is higher than the pure waste HDPE. In MMT addition H_m was increased very slightly in 1 and 2 wt% clay concentrations, while decreased in comparison with the pure

waste HDPE, with higher clay concentrations. Different results were observed for LDPE/clay nanocomposites, where only for 1 wt% OMMT concentration, the heat of fusion increased very slightly, while decreased was observed for all the samples. It was also observed to be lower than H_m value for neat waste LDPE, with the MMT addition.

The phenomenon may be produced by the stoppage of crystalline outgrowth, instigated by the clay layers, distributed in an uneven arrangement in the nanocomposite, as observed in some of the thermal microscopy researches [40].

4.4.4 Thermal Gravimetric Analysis

The material thermal degradation of the samples were studied by TGA analysis. The outset temperature of the degeneration are the important parameters, that is metric as that is indicated 5% - 10% weight loss of the specimen, the middle-period of the thermal degeneration, and the final calculation of thermic degeneration is the portion of substance that is non-volatile at 873 ºK, famous as charcoal, respectively [41].

Figures 5 and 6 depicts the TGA curves for neat LDPE, HDPE and LDEP, HDPE /clay nanocomposites containing 1,2,3,5 wt% of OMMT, and 1,5 wt% of MMT, respectively. The temperature weight loss 5, 10 and 50% and the residue are presented at 600 ºC in Table 2. LDPE /OMMT nanocomposites at 1-3 wt% clay showed increasing thermic constancy as equated to organized waste LDPE. The beginning of thermic constancy is distinguished by the temperatures at 5%, 10% weight loss. The LDPE/OMMT nanocomposites showed significantly enhanced initial thermal stability at 5% and 10% weight loss, when compared with the pure waste LDPE. The LDPE/OMMT nanocomposite with 3 wt% clay, display the critical initial thermic constancy. When the OMMT components is raised up more than 3 wt%, the beginning of thermic constancy decreased even in 4 and 5 wt% still higher than pristine LDPE, but it is less than that with 3 wt% content. For 50% weight loss the thermal stability has not had much change.

At comparatively lesser OMMT component, the first thermic constancy rises with OMMT component. The results in LDPE/MMT nanocomposites were different, the temperatures at 5%, 10% and 50% mass loss were not found changed when compared with pure LDPE.The reason behind that may be because of the accumulations of clay, that have low influence in stopping heat in comparison with the MMT sheets/tactoids, rising with clay component [39].
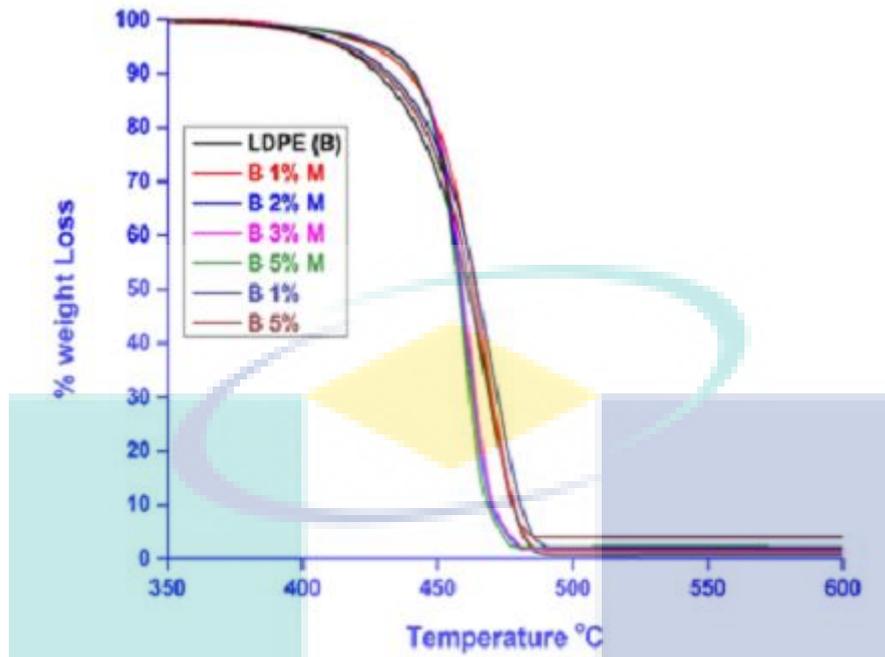
Fig. 5. TGA analysis for waste LDPE (B) and LDPE/clay nanocomposites
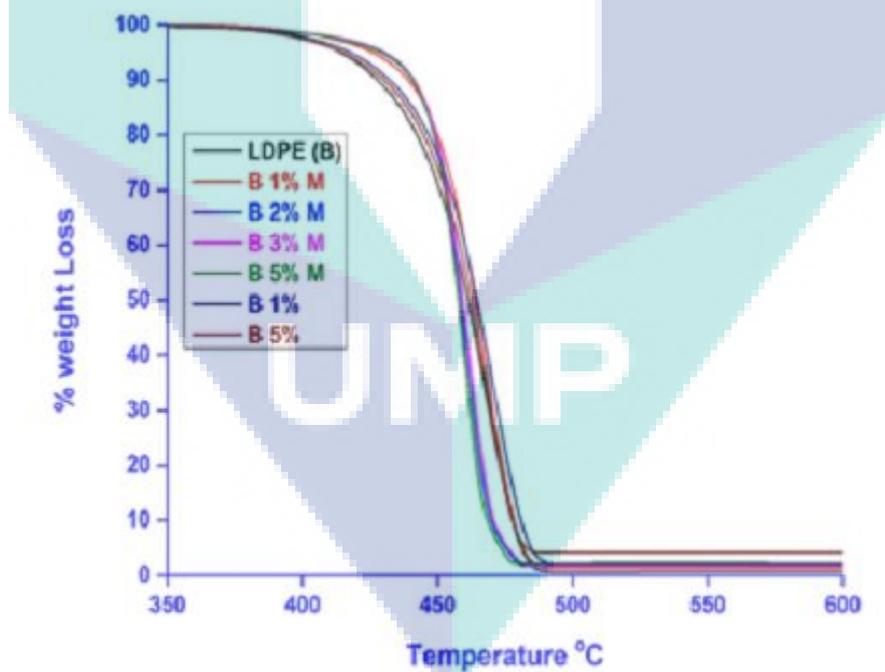

Fig. 6. TGA analysis for waste HDPE (B) and HDPE/clay nanocomposites

On the other hand in case of HDPE/clay nanocomposites, we observed almost the same results with a slight deference. The higher thermal stability was observed for the samples 1% and 2% wt OMMT content only, at the temperatures at 5%, 10% and 50% weight loss has slightly decreased in first thermic constancy if the clay content increased more than 2% wt. in the mid-point at 50% weight loss of 3% and 5 % wt OMMT were considerably decreased to 462 ℃ and 464 ℃ compared with 470 ℃ for thepure waste HDPE. The temperature at 5%, 10% and 50% weight loss of HDPE/MMT nanocomposites were very slightly changed when compared with the pure waste HDPE. That is for may be for the same reason mention in LDPE/clay nanocomposites [39].

Table 2: TGA data for waste LDPE, HDPE and their nanocomposites under nitrogen flow

Sample	Temperature / ℃ at mass loss			Residue at 600 ℃%
	5%	10%	50%	
D	430	443	470	0.64
D 1% M	431	448	472	1.06
D 2% M	436	450	473	1.24
D 3% M	427	441	462	1.05
D 5% M	427	442	464	2.51
D 1%	426	445	473	2.46
D 5 %	428	443	471	3.63
B	413	428	461	0.62
B 1% M	426	438	463	1.30
B 2% M	430	440	458	1.73
B 3% M	429	440	459	1.70
B 5% M	428	440	457	2.17
B 1%	417	432	464	1.83
B 5 %	414	429	462	3.91

4.4.5 Mechanical Properties

The mechanistic characteristics of the matrix LDPE and HDPE/clay nanocomposites were measured and compared with those of the pure waste and recycled LDPE and HDPE by dissolution/reprecipitation method. Fig. 5 shows the elastic modulus, tensile stress at maximum load strain at break and tensile stress at yield. The elastic modulus plots of samples are shown in Fig. 5 a. The measured modulus of pure LDPE and HDPE were found 150 and 462 Mpa respectively, which increased significantly when modified clay (OMMT) was added from 1-3 wt%, and were decreased at 5 wt% OMMT, even the non-modified clay (MMT), addition decreased the modulus. The highest modulus were observed as 207 MPa in LDPE/ nanocomposites , with an increase of 38% in relation with the pure waste LDPE and the highest modulus was found as 496 MPa in HDPE/ nanocomposites, 7.4% higher to the pure waste HDPE. The elastic modulus increased with the addition of org-clay in low contents of 1-3 wt%. The OMMT when dispersed in the polyolefin matrix at a nanometre scale, a part of the OMMT gets inserted by polyolefin chains. This may seize the segmental motion of polyolefin macromolecules. As a result, the modulus of the PP nanocomposites increased with the OMMT loading [39,42].
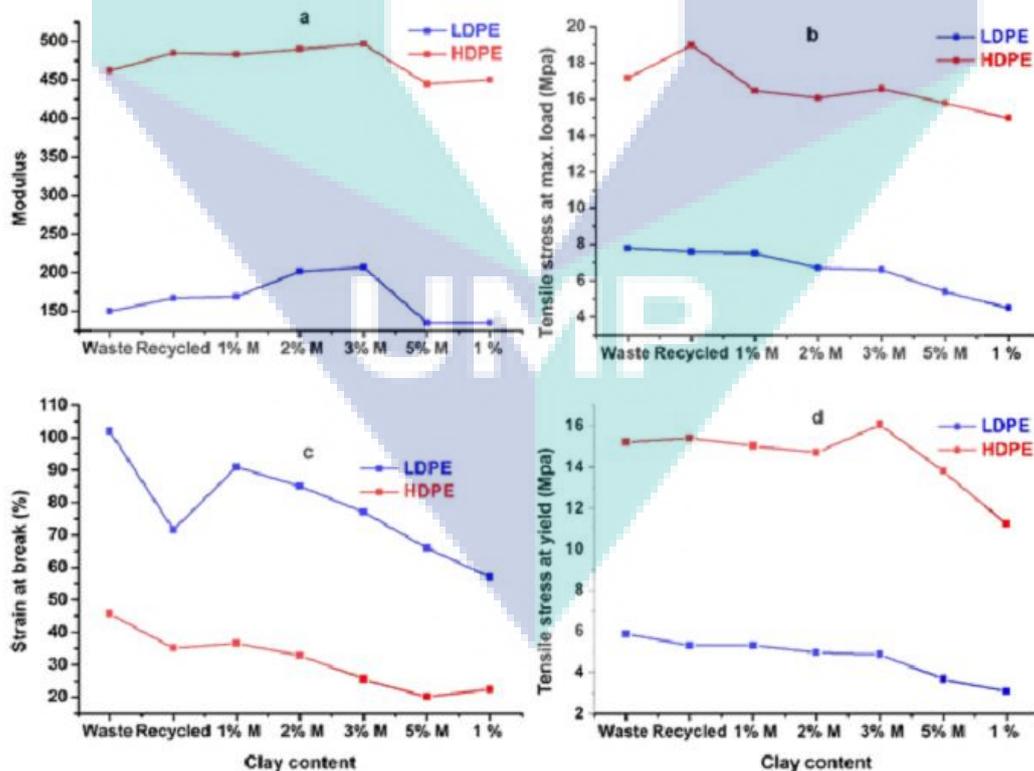

Fig. 7. Effect of clay loading on tensile properties of LDPE and HDPE/ clay nanocomposites

On the other hand, the other three mechanical properties, tensile stress at maximum load, strain at break and tensile stress at yield are showed in Fig. 5 b, c and d respectively. All the following properties were observed to decrease with the clay addition. A higher decrease in the behaviours were observed with the MMT contents addition, in comparison to the OMMT content studies. The considerable reduction in the mechanical properties, at clay loadings is because of the regularly sparse MMT tactoids with the inserted structures [37].

4.5 Conclusion

The waste polyolefin (LDPE and HDPE) /clay (unmodified and organo-modified), nanocomposites were fabricated by employing the melt intercalation method. The physicochemical effects of the two types of clay on the structure and properties were also calculated. XRD and FESEM results, exhibited a considerable effect of OMMT due to the exfoliation and interaction of OMMT within the polymer matrix, while there is no exfoliation and intercalation was observed in polymeric composite of MMT.

The DSC results showed that in almost all the samples the melting temperature remained the same with no major alterations. The enthalpy of fusion was increased in nanocomposites at low OMMT content (1-3 wt%), in comparison with the pure waste polyolefin, whereas the best behaviour was presented by 3 wt%. Same results were observed in the thermal behaviour of the nanocomposites, where enhancement in behaviours were observed at low OMMT content. The highest elastic modulus in the LDPE nanocomposites, was increased up to 34%, in relation with the pure waste LDPE, whereas increase of 7.4%, was calculated in HDPE nanocomposites. Tensile stress at maximum load, strain at break and tensile stress at yield were slightly decreased in the low OMMT clay content. Additional clay contents, resulted in a decrease in the mechanical properties of nanocomposites. However, it is concluded from the study that the recycling of the waste polymer using dissolution/reprecipitation method, showed a better reinforcement of the waste polyolefin by nanocomposites fabrication, in melt interaction method.

4.6 References

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