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Araştırma Makalesi / Research Article

Effect of Montmorillonite Clay on Physical Properties of HDPE/ HGS Composites

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Keywords
Nanoclay; Hollow glass spheres; High-density polyethylene; Physical properties

Abstract

Recently, there has been an increasing interest in enhancing the physical properties of polymer nanocomposites. In the present study, the effect of montmorillonite (MMT) clay ratio (0, 1, 5, 10 and 15 wt.%) on the physical properties of the high-density polyethylene (HDPE)/ hollow glass spheres (HGS) composites were investigated. The hollow glass spheres ratio is 20% by weight. After the mixture obtained from the extruder was granulated, test specimens were produced using an injection molding machine. Physical tests were applied such as melt flow index (MFI), moisture content (MC), Vicat softening point (VSP), heat deflection temperature (HDT), Limit oxygen index (LOI). The nanoclay dispersion was examined by X-ray diffraction (XRD). Images of HDPE/HGS/MMT-clay composites were taken with Scanning electron microscopy (SEM). The results obtained show that heat deflection temperature, Vicat softening point, and melt flow index decreased gradually as the MMT-clay content increased. The LOI decreased with increase in the MMT-clay content from 0 to 15wt. %. MC increased with increase in the MMT-clay content from 0 to 1 wt. %. MC didn't change with further increasing of MMT-nanoclay content to 10 percent by weight. Then, MC increased with increase in the MMT-clay content from 10 to 15 wt. %.

Montmorillonite Kilinin HDPE/ HGS Kompozitlerinin Fiziksel Özellikleri Üzerindeki Etkisi

Anahtar kelimeler
Nanokil; Cam küreler; Yüksek yoğunluklu polietilen; Fiziksel özellikler

Öz

Son zamanlarda, polimer nanokompozitlerin fiziksel özelliklerinin geliştirilmesine yönelik artan bir ilgi vardır. Bu çalışmada, montmorillonit (MMT) kil oranının (ağırlıkça% 0, 1, 5, 10 ve 15) yüksek yoğunluklu polietilen (HDPE) / içi boş cam küreler (HGS) kompozitlerinin fiziksel özellikleri üzerindeki etkisi araştırıldı. İçi boş cam küre oranı ağırlıkça % 20'dir. Ekstrüderden elde edilen karışım granüle edildikten sonra, bir enjeksiyon kalıplama makinesi kullanılarak test numuneleri üretildi. Erime akış indeksi belirleme testi (MFI), nem miktarı belirleme testi (MC), Vicat yumuşama noktası belirleme testi (VSP), yük altında eğilme sıcaklığı belirleme testi (HDT), sınırlayıcı oksijen indeksi belirleme testi (LOI) gibi fiziksel testler uygulandı. Nanokil dispersiyonu, X-ışını kırınımı (XRD) ile incelendi. HDPE / HGS / MMT-kil kompozitlerinin görüntüleri Taramalı elektron mikroskobu (SEM) ile alınmıştır. Elde edilen sonuçlar, MMT-kil içeriği arttıkça ısıl çarpılma sıcaklığının, Vicat yumuşama noktasının ve erime akış indeksinin kademeli olarak azaldığını göstermektedir. LOI, MMT-kil içeriğinin ağırlıkça yüzde 0'dan 15'e yükselmesiyle azaldı. MC, MMT-kil içeriğinin ağırlıkça yüzde 0'dan 1'e artmasıyla artmıştır. MC, MMT-kil içeriğinin ağırlıkça yüzde 10'a yükseltilmesiyle değişmedi. Daha sonra, MC, MMT-kil içeriğinin ağırlıkça % 10'dan% 15'e yükselmesiyle arttı.

1.Introduction

Nanocomposites have been attractive in the past three decades owing to the improvement of their properties. Clay platelets are convenient for polymers in order to develop new composites with enhanced properties. Modified Montmorillonite-clay has been the most popular nanoclay type in the application of composites. The Incorporation of nanoclay into polymers provides superior physical properties and flame resistance. The loading level is usually in the range of 3-6 wt. % for physical improvements. Hollow glass spheres (HGS) have been advantageous among the inorganic fillers for reinforcing polymer composites due to their lightweight property and sufficient strength. For this purpose, nanoclay, and HGS have been used to enhance the poor characteristics of polymers.

Firstly, Toyota Automobile Company used nano-clay in the polymer matrix in 1989. Since then, reinforcing polymers with nanoclay is extensive research in nanocomposites (El-Sheikhy and Al-Shamrani 2015, Turaev *et al*. 2009, Lei *et al*., 2007, Kotal and Bhowmick 2015). The majority of previous studies revealed that the optimum ratio of nanoclay was about 3-10 percent by weight.

HDPE can be reinforced with reinforcements, such as nanoclay, hollow glass spheres to enhance the properties of HDPE (Yung *et al*. 2009, Liang and Li 2007, Patankar and Kranov 2009, Liu and Xu 2011). For instance, HGS addition can provide lightweight, high stiffness, high strength and insulation property, chemical stability and the addition of MMT can provide improved thermos-mechanical properties.

Singh *et al*. investigated the influence of different amounts of Sepiolite (1–10 wt. %) and compatibilizer (0–10 wt. %), i.e., PE-graft-maleic anhydride (PE-g-MA) on HDT values of HDPE based nanocomposites. In their laboratory study, they reported the HDT values of neat HDPE increased with increasing Sepiolite content. They also found out that storage modulus and loss modulus were lower than uncompatibilized nanocomposites at the same Sepiolite loading (Singh *et al*. 2017).

Kaştan *et al*. investigated the effect of modified MMT on PA6/HDPE/PE-g-MA (80/20/5). They reported that the MMT weight percent 3wt. % had the best result in the HDT test. They also reported that the Vicat softening point of composites decreased as the MMT content increased (Kaştan *et al*. 2017).

Mohan and Kanny developed hybrid HDPE composites consisting of a three-phase material system, namely, matrix (polymer), clay filler (0–3 wt. %) (as secondary reinforcement), and glass fiber GF (0–20 wt. %) (as a primary reinforcement) with and without polyethylene-grafted maleic anhydride gMA (0–3 wt. %) (as a compatibilizer). They also found out that the compatibilizer improved the dispersion of clay particles in the polymer matrix and nanoclay addition in HDPE reduced the melt flow rate in part of their study (Mohan and Kanny 2012).

Sepet *et al*. investigated that Vicat softening temperature values decreased with increasing the wt. % of nanoclay content from 0 to 5. In work, 1.0, 2.0, 3.0, 4.0, and 5.0 wt. % of nanoclay as reinforcement and HDPE as polymer matrix were used to manufacture the nanoclay/HDPE nanocomposite. In their study, XRD patterns of the nanocomposites showed that the characteristic peak of the nanoclay was not detectable (Sepet *et al*., 2016).

In the present study, the hollow glass spheres ratio was fixed 20% by weight taking into account the results of previous studies with respect to HDPE/HGS composites (Taşdemir and Yerşeşen 2015). According to their study, HDPE polymer composites containing 5, 10, 15 and 20 wt. % hollow glass spheres were produced, and the properties of the composites were investigated. Taşdemir and Yerleşen found out that addition of HGS 20% by weight into HDPE matrix enhanced some mechanical properties such as higher elasticity modulus. Best mechanical properties were gained by the addition of HGS 20% by weight. The aim of this research is to find out the effect of MMT ratio on the properties of the HDPE/ HGS/ MMT composites. It was noticed that the physical properties of HDPE/ HGS/ MMT composites were affected by increasing clay content. Although some studies have been conducted on the reinforcement effect of MMT in thermoplastics such as polypropylene (PP) and polyethylene (PE), there have not been any studies reporting a comparison by reinforcing HDPE/ HGS composites with MMT.

2. Experimental Procedure

2.1 Materials and Composition

HDPE-based composites were produced. HDPE, known as Petilen YY (I 668 UV), was provided from Petkim, Petrokimya Holding A.S., Turkey. Its density is 0.970 g/cm^3, melt flow index is 5.2 g/10 min at 190 ^oC-2.16 kg, yield strength is 28.0 MPa and notched Izod impact is 50 J/m. Hollow glass spheres were supplied from 3M Inc., USA. The average diameter and the density of hollow glass spheres are 20 microns and 0.46 g/cc respectively. Onium Ion Modified Montmorillonite Clay (CAS No. 1318-93-0 Montmorillonite clay 61789-80-8 Dimethyl Dialkyl, Ammonium) procured from Nanocor Inc., USA. This Surface Modified Clay consists of 55 ~ 65 wt% Dimethyl dialkyl(C14-18), Ammonium 35 ~ 45 wt%. Nanomer 1.44 P nanoclay is used for this study. The mean particle sizes are in the range of 15-20 μm.

Compositions of HDPE/HGS/MMT composites are given in Table 1.

Table 1. Compositions of the composites

Groups	HDPE (wt%)	HGS (wt%)	MMT (wt%)
1	80	20	0
2	79	20	1
3	75	20	5
4	70	20	10
5	65	20	15

Table 2 shows extrusion and injection conditions. Extrusion temperature was between 190-220 ^oC at 32-37 bar pressure, and the rotation rate was 25-35 rpm. Figure 1 shows the production steps of samples.

Table 2. Production conditions of the composites

Process	Unit	Extrusion	Injection
Temperature	^0C	190-220	190-220
Pressure	bar	32-37	130-150
Screw speed	rpm	25-35	25

Sample Preparation Step 1	
	Densi DS-05 laboratory balance (Capacity: 5kg) was used to measure the contents of mixture.
(a) Densi DS-05 laboratory balance	
Sample Preparation Step 2	
	Mechanical premixing of solid compositions was done using a LB-5601 liquid-solids blender (The Patterson-Kelley Co., Inc. east Stroudsburg, PA - USA). **The brand batch blender was used to premix solid compositions for 15 min.**
(b) LB-5601 liquid-solids blender	
Sample Preparation Step 3	
	Samples with various proportions of HDPE/HGS/MMT composites granules were produced between 190-220 ^{o}C at 32-37 bar pressure, and a rotation rate of 25-35 rpm, with a Microsan co- rotating twin-screw extruder (Microsan Instrument Inc., Turkey).
(c) Microsan co- rotating twin-screw extruder (L/D ratio is 30, ∅25 mm)	
Sample Preparation Step 4	
	After extrusion, polymer composites were also dried in Binder vacuum oven (Binder, Germany) at 105 ^{o}C for 24 hours.
(d) Binder vacuum oven	

Sample Preparation Step 5	
	Subsequently, test samples were molded in injection molding machine. Injection temperature was between 190-220^{o}C and pressure was 130-150 bar.
(e) Injection molding machine (Yonca Makine, Turkey)	

Figure 1. Production steps of samples

2.2 Test Procedure

X-ray diffraction (XRD) analysis was carried out in a X-ray diffractometer Panalytical X'PERT PRO with CuKá radiation (45 kV, 40 mA) at room temperature. Heat deflection temperature (HDT) tests and Vicat softening temperature tests were carried out following ISO 75 standard and ISO 307 standard using CEAST 6521 HDT-Vicat tester. Melt flow index tests were done at 190 0C under 2.16 kg load according to ISO 1133 standard with Zwick 4100 MFI equipment. Moisture testing (MOI) was conducted as per ASTM D 6980 standard using Kern DBS 60-3 equipment. Limit oxygen index (LOI) values were measured as per ISO 4589 standard test method using Devotrans LOI equipment. SEM (Zeiss EVO LS 10; Carl Zeiss NTS, Germany) was used at 7.5 kV in order to investigate the distribution of microstructure

3. Results and Discussion

3.1 Morphology of HDPE/HGS/MMT Composites

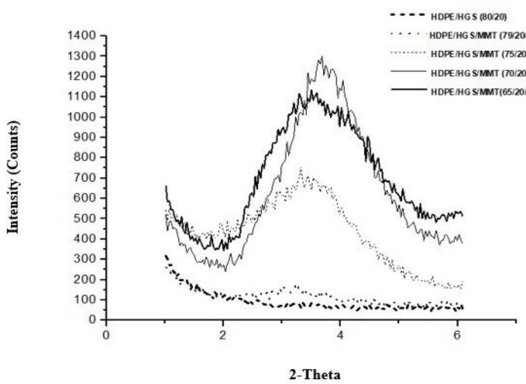


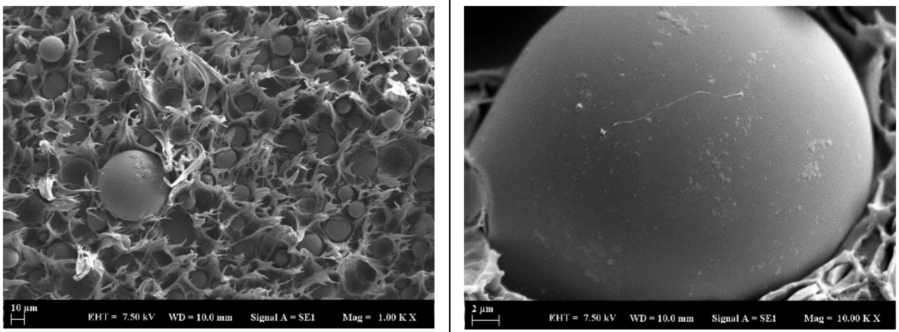
Figure 2. XRD patterns of HDPE/HGS/MMT composites

Table 3. Diffraction peak at 2θ and d-spacing

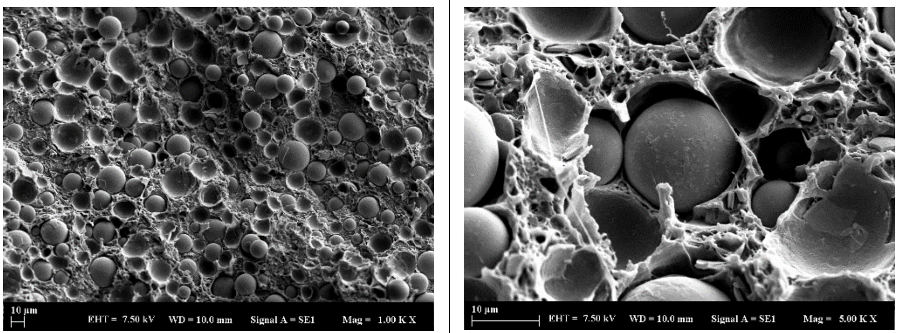
Groups	Clay Loading	Angle 2θ (Angle of Diffraction)	d-Spacing Å
2	1%	3.26°	27.06
3	5%	3.30°	26.74
4	10%	3.67°	24.08
5	15%	3.52°	25.06

Figure 2 shows the XRD pattern for the samples scanned over the range 2θ=1 to 60. There is no significant shift to the left in loading 5 wt. % MMT or more. It is understood that optimum exfoliation of nano fillers was obtained when 1 wt. % MMT was loaded to the system.

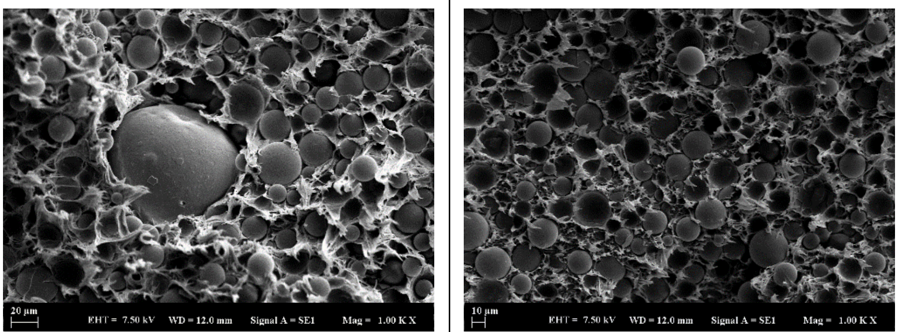
2θ = 3.26° was observed in the case of loading 1 wt. % MMT, but loading 15 wt. % MMT peak shifted to the right, which means agglomeration increases in the matrix. The diffraction peak at 2θ and d-spacing of all composites were summarized in Table 3.



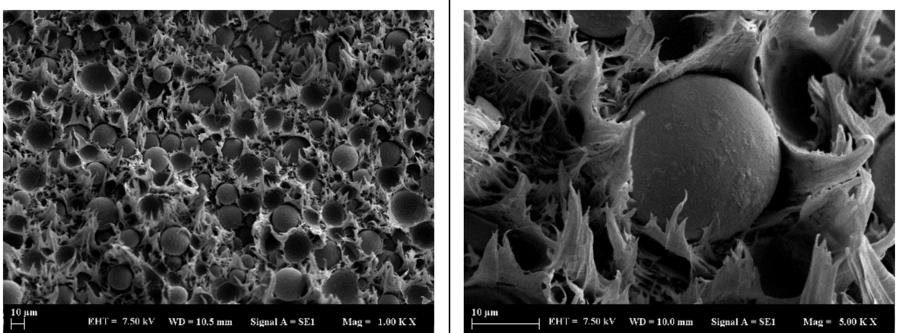
(a) HDPE/HGS/MMT (75/20/0)



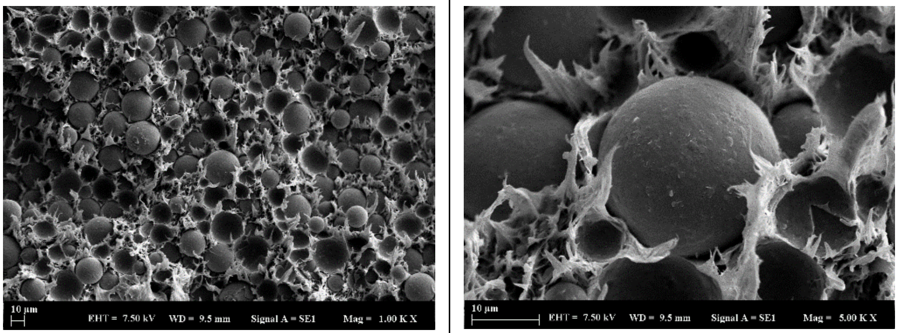
(b) HDPE/HGS/MMT (75/20/1)



(c) HDPE/HGS/MMT (75/20/5)



(d) HDPE/HGS/MMT (75/20/10)



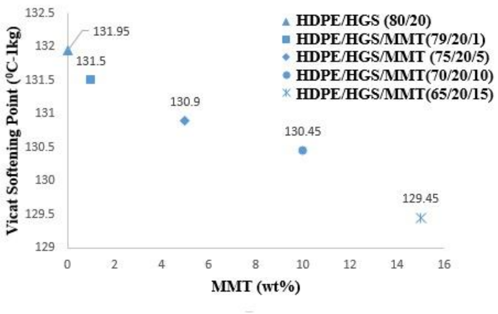
(e) HDPE/HGS/MMT (75/20/15)

Figure 3. SEM images of (a) HDPE/HGS/MMT (75/20/0), (b) HDPE/HGS/MMT (75/20/1), (c) HDPE/HGS/MMT (75/20/5), (d) HDPE/HGS/MMT (75/20/10), (e) HDPE/HGS/MMT (75/20/15)

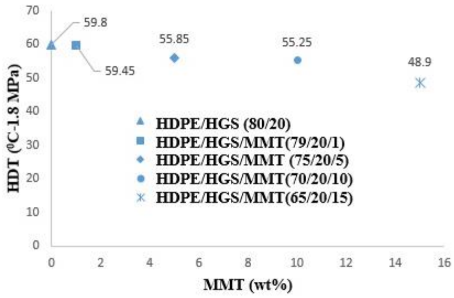
Figure 3 shows SEM images of HDPE/HGS/MMT composites with different percentages of MMT. The contrast and the boundaries can be seen clearly. The micrographs indicate that the HGS and MMT are homogeneously dispersed. The surfaces of hollow glass spheres are clean and smooth, and they are not broken because of the weak interfacial bonding between HGS and polymer matrix in the absence of a compatibilizer.

As can be seen from Figure 3, the adhesion between HGS and polymer matrix isn't strong. SEM images prove that as the MMT concentration increases, the interface between HGS and HDPE matrix aided by MMT presence. Noteworthy is the nanofilled polymer covers HGS more tightly.

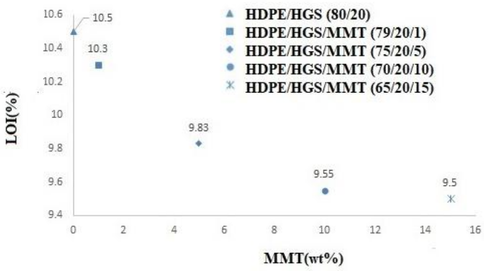
3.2 Physical properties of HDPE/HGS/MMT composites:



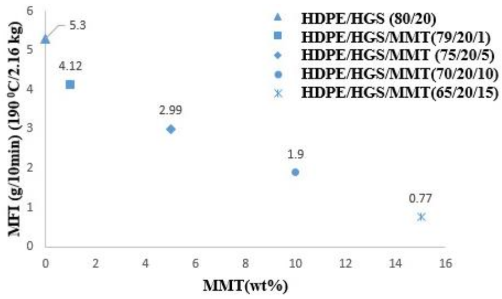
(a)



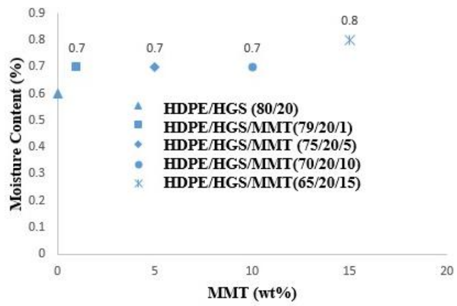
(b)



(c)



(d)



(e)

Figure 4. Physical properties of HDPE/HGS/MMT composites

VSP is useful in quality control, development, characterization of materials and comparing the heat softening qualities of thermoplastic materials. The relation between the Vicat softening point and the weight percent of MMT is shown in Figure 4a. As seen from Figure 4a, the Vicat softening point of composites without MMT has the highest value (131.95). The Vicat softening point of the three different samples (with 1, 5, and 10 wt.% of MMT) is measured as 131.5, 130.9 and 130.45oC respectively. Vicat softening temperature of composites with 15 wt. % MMT is lowest at 129.45 oC. Vicat softening temperature of HDPE/HGS/MMT composites decreases slightly compared with HDPE/HGS. Compared with the VSP of HDPE/HGS, the VSP decreased by 1.9% for the composites with 15 wt% MMT.

Heat deflection temperature is the temperature at which a thermoplastic sample deforms under a specific load. HDT test is commonly used for quality control and screening and ranking materials for short-term heat resistance. This property is helpful in the product design, engineering and manufacturing of thermoplastic components. The relation between the HDT and the weight percent of MMT of composites is shown in Figure 4b. The HDT of the composites decreases as the MMT amount increases from 0 to 15 wt %. The HDT of the three different samples (with 1, 5 and 10 wt% of MMT) are measured as 59.45, 55.85 and 55.25 oC respectively. The maximum HDT is observed at Group1 (HDPE/HGS) as 59.80 oC. Comparing with the HDT of HDPE/HGS, the HDT decreased by 18% for the composites with 15 wt % MMT.

Surface spreading of flame, fuel penetration, and oxygen index are the variables that fire performance of any polymer depends on. The limiting oxygen index (LOI) is the minimum amount of oxygen that will support combustion (Chawla 2012). Matrix type and amount, the quantity of fire-retardant additives, type and amount of reinforcement (if any) are the parameters that affect the degree of flammability of a polymer.

LOI is used to evaluate the flame retardancy of polymer composites. The oxygen index indicates the minimum concentration of oxygen that must be present in the air in order to support flaming combustion of a plastic (after ignition). Highly flammable polymer composites have a low oxygen index, and less flammable polymer composites have high values. Figure 4c shows the relation between the LOI and the weight percent of the MMT. The LOI of HDPE/HGS/MMT composites decreases as the MMT amount increases from 0 to 10 wt. %. However, LOI does not change with further increase of MMT content to 15 % by weight. The LOI of the three different samples (with 1, 5 and 10 wt% of MMT) are measured as 10.3, 9.83 and 9.55 % respectively. The LOI of HDPE/HGS is 10.5 %. The minimum LOI is observed at 15 wt% of MMT amounts as % 9.5. Comparing with the LOI of HDPE/HGS, the LOI decreased by 9.52 % for the composites with a 15 wt % MMT.

The melt flow index is- also known as the melt flow rate. MFI measures the flow rate of thermoplastic material in its molten state through a die under prescribed temperature /load conditions (Shah 1998). MFI is a measure for- material viscosity and an inverse measure of molecular weight. When comparing the same class polymers, a lower melt flow rate -corresponds to a higher molecular weight and/or less branching. The melt flow rate test is a quality control tool in manufacturing to verify incoming material and assess its processability in terms of processing techniques. It is globally used in the polymer industry product development for comparing new materials. The relation between MFI and the percent of the MMT is shown in Figure 4d. As shown in Figure 4d, the melt flow index values of composites decrease while the MMT amount increases from 0 to 15 wt %. The MFI of the three different samples (with 1, 5 and 10 wt% of MMT) are measured as 4.12, 2.99, and 1.90 g/10 min respectively. The MFI of HDPE/HGS (80/20) is 5.30 g/10 min. The minimum melt flow index is 0.77 g/10 min observed for HDPE/HGS/MMT (65/20/15). Comparing with the MFI of HDPE/HGS (80/20), the MFI decreased by 85% for the HDPE/HGS/MMT (65/20/15) composites. Mohan and Kanny observed similar results with melt flow index of glass fiber and MMT reinforced HDPE composites. The addition of clay reduced melt flow rate of the composites (Mohan and Kanny 2012).

In polymer composites, the moisture content is essential for manufacturing these materials and assuring their process quality. Moisture affects the process ability of almost all polymer composites. The amount of moisture content was calculated in terms of loss in weight of the specimens. As seen from Figure 4e, the moisture content of HDPE/HGS (80/20) composites increases as the MMT amount increases from 0 to 1 wt %. The moisture content of the three different samples (with 1, 5, and 10 wt% of MMT) is measured as 0.7 %. The moisture content of HDPE/HGS is 0.6 %. The maximum moisture content is observed at the 15 wt % of MMT amount as 0.8%. Comparing with the moisture content of HDPE/HGS, the moisture content increased by 33 % for HDPE/HGS/MMT (65/20/15).

Although the incorporation of nanoclay into polymers improves physical performance and flame resistance, significant improvement of the properties is not observed in this study.

4. Conclusions

Physical tests were applied such as melt flow index, moisture content, Vicat softening point, heat deflection temperature, limit oxygen index. The nanoclay dispersion was examined by X-ray diffraction. Also, SEM examination was conducted to evaluate the microstructure of hollow glasss spheres and nanoclay as well as material distribution in these experiments.

The following results were obtained:

It is understood from the XRD data that optimum exfoliation of nanofillers was obtained when 1 wt.% MMT was loaded to the system. VSP, HDT, MFI of HDPE/HGS/MMT composites decreased as the MMT content increased.

Vicat softening point reflects VSP is used for comparing the heat softening qualities of HDPE/HGS/MMT composites. The VSP reflects the softening point to be expected when a material is used in an elevated temperature application. The data obtained from this test showed VSP of HDPE/HGS/MMT composites decreased as the MMT content increased. There was not a significant change among VSP values of the composites.

HDT indicates at what temperature materials start to "soften" when exposed to a fixed load at elevated temperatures. HDT of HDPE/HGS/MMT composites decreased slightly as the MMT content increased.

The limited oxygen index test is the most useful flammability tests in order to select thermoplastics in terms of flammability. The limit oxygen index of HDPE/HGS/MMT composites decreased as the MMT concentration increased from 0 wt. % to 15 wt. %. This means that lower oxygen density is required to initiate and sustain combustion of the composites after the addition of MMT into HDPE/HGS composites.

MFI of the HDPE/HGS composites decreased with the nanoclay loading. In HDPE/HGS/MMT composites, MFI varied as a function of nanoclay content. The result showed that the MFI of the HDPE/HGS composites was higher than that of the nanoclay-reinforced HDPE/HGS composites.

The moisture content of HDPE/HGS polymer composites increased by the addition of 1 wt. % MMT. More MMT content from 1 wt. % to 10 wt. % by weight did not change the moisture content but 15 wt. % MMT addition increased the moisture content values of the composites.

Loading MMT into HDPE/HGS composites was expected to enhance the physical properties of composites. Nevertheless, as a result of experiments, it is observed that there was not any significantly enhanced property. This result may have revealed because compatibilizer was not used in this study. The compatibilizers such as MA-g-PE (maleic anhydride- graft- polyethylene) can provide solid interfacial bonding among MMT, HGS, and polymer matrix and more homogenous dispersion of additives. As a result of this, enhanced properties can be obtained with a compatibilizer. Further studies are needed to clarify this point. The composites will be examined after the addition of a compatibilizer such as polyethylene-grafted maleic anhydride.

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