HIGH-DENSITY POLYETHYLENE/RED MUD POLYMER COMPOSITES: EFFECT OF UV ANNEALING

MUNIR TAŞDEMIR

Marmara University, Engineering Faculty, Metallurgy and Materials Engineering Department, Istanbul, 34722, Turkey, munir@marmara.edu.tr

An investigation was carried out on the effects of red mud ratio and UV annealing treatment on the mechanical, thermal and morphological properties of high-density polyethylene (HDPE)/red mud (RM) polymer composites. Red mud, in six different concentrations (0, 10, 20, 30, 40, and 50 wt %), was added to HDPE to produce composites. The annealing UV treatment was carried out at 100°C for three different holding times: 100, 200 and 300 h. The mechanical properties, including the elastic modulus, tensile strengths, strain at tensile strength, Izod impact resistance, hardness, and melt flow index with and without an annealing UV treatment, and the thermal properties, such as the Vicat softening point, heat deflection temperature and melt-flow index, of the composites were investigated.

Keywords: high-density polyethylene, red mud, UV annealing

INTRODUCTION

Nowadays there is a significant interest for the development of environmentally friendly polymers and polymer composites based on renewable resources due to the increasing environmental concerns and the decreasing fossil resources (Kalia *et al.*, 2011). Utilization of waste materials has become more pressing than ever. Red mud is accumulating at a rate of 30 million ton annually throughout the world. Under normal conditions when 1 ton of alumina is produced from bauxite, an equal amount of red mud is generated as a waste. Disposal of red mud is a severe problem as it is highly alkaline and produced in huge quantities (Bhat *et al.*, 2011; Milacic *et al.*, 2012).

The higher cost of composites is the only factor hampering its use in majority of industrial application in spite of possessing customized properties specific to given application. Some researchers have found that adding low cost and readily available filler is the easiest way to bring down the cost of composites. However, mechanical properties of the composites should not be affected adversely in the attempt of reducing the cost. Therefore, fillers are added firstly to improve the mechanical and tribological properties and secondly to reduce the cost of the components (Rothon, 1997). Red mud has been suggested as filler for polymer reinforcement or as a cheap adsorbent for removal of toxic metals or an acid by several researchers. Chand and Hashmi (1999) tried to improve the mechanical properties and abrasive wear properties of polymer blend filled with red mud. Pradhan *et al.* (1999) had reported that activated red mud as a good adsorbent was used for adsorption of phosphate or chromium. In addition, the mechanical and thermal properties of polymers are generally improved by the addition of inorganic fillers. The challenges in this area of high-performance organic–inorganic hybrid materials are to obtain significant improvements in the interfacial adhesion between the polymer matrix and the reinforcing material since the organic matrix is relatively incompatible with the inorganic phase.

Thermoplastics have a big potential for applications in the industry as well as in construction, electrical applications and food packaging. One of the few disadvantages associated with the use of nano fillers, is their high cost. The present research work has been undertaken with an objective to explore the use of red mud as a reinforcing material as a low cost option. This is due to the fact that red mud alone contains all these reinforcement elements and is plentifully available (Bhat *et al.*, 2011).

EXPERIMENTAL PROCEDURES

Six different polymer composites were prepared. Compositions of HDPE/RM polymer composites that were formed are given in Table 1.

Table 1. Composition of the HDPE/RM polymer composites formulations

Groups	HDPE Content (wt %)	RM Content (wt %)
1	100	-
2	90	10
3	80	20
4	70	30
5	60	40
6	50	50

High-density polyethylene (HDPE) (I 668 UV) was supplied by Petkim (Izmir-Turkey). Specific gravity is 0,970 g/cm^3. Melt flow rate is 5.2 g/10 min (190°C–2.16 kg). Yield strength is 28,0 MPa and notched Izod impact (23°C) is 12 kJ/m^2. Red Mud was supplied Güray Seramik Company (Avanos-Turkey).

Sample Preparation

Red mud was first heat treated at 150°C for decomposition of hydrates combined with red mud and then dry grinded with Siemens simatic C7-621 control system device to obtain unsegregated powders. The size of red mud particles varied between 10–80 µm and the mean particle size was 35 µm. HDPE and Red mud were dried overnight at 105°C in a vacuum oven prior to melt blending. Mechanical premixing of solid compositions was done using a LB-5601 liquid-solids blender (The Patterson-Kelley Co., Inc. east Stroudsburg, PA - USA) brand batch blender for 15 min. Samples with various proportions of HDPE/RM polymer composites were produced between 190-220°C at 12 bar pressure, and a rotation rate of 20-25 rpm, with a Microsan extruder (Microsan Instrument Inc. Kocaeli - Turkey). Polymer composites were also dried in vacuum oven at 105°C for 24 hours after extrusion. Subsequently, test samples were manufactured by injection molding. Injection temperature was 190-220°C, pressure was 100-120 bar and screw speed was 23-25 rpm.

Mechanical Characterization

The tensile modulus, tensile strength and strain at tensile strength of the compressed plates were measured by using a tensile testing machine (Zwick Z010, Germany) according to ASTM D638 at room temperature and crosshead speed of 50 mm/min. For every composition, six samples were tested, and the averages of the six measurements were reported. The hardness test was done according to the ASTM D2240 method with Zwick hardness tester. To investigate fracture behavior, Izod impact test (notched) was done at room temperature according to the ASTM D256 method with Zwick B5113 impact tester (Zwick, Germany). Flow behavior testing of all the mixtures was done according to ISO 1133 standard with Zwick 4100 MFI equipment. Heat deflection temperature (HDT) and Vicat softening point tests were done according to ISO 75 and ISO 307 standard with determined by CEAST 6521 (Ceast SpA, Italy) HDT-Vicat test equipment.

UV Annealing

The UV annealing test was done according to the ASTM D 5208 method with Devotrans pre-heated UV oven treatment device. UV holding time is 100, 200 and 300 hours and UV holding temperature is 100°C. The distance of the light is 50 mm and Osram 300 W ultra-vıtalux type lamp was used.

Microscopy

The fractured surfaces of the HDPE/RM polymer composites were coated to thickness of 20 Å of a gold (Au) to prevent electrical charging by Polaron SC7640 (high resolution sputter coater) (United Kingdom). The surfaces of the prepared samples were observed by the FEI Sirion XL30 FEG (Nederland) scanning electron microscopy (SEM) at an acceleration voltage of 15 kV.

RESULTS AND DISCUSSION

Elasticity modulus of HDPE/Red Mud specimens measured in tensile test. Figure 1/A shows the variation of the elasticity modulus as a function of the red mud content of the composites. Since red mud has much higher stiffness values than the HDPE matrix, the elasticity modulus of the HDPE/RM polymer composites increased as the red mud concentration increases from 0 to 50 wt %. On the other hand, the elasticity modulus of the HDPE/RM polymer composites increased as the UV holding time increases from 100 hours to 300 hours. The maximum elasticity modulus is observed at Group 6 (100°C-UV 300h). In comparison with the elasticity modulus of virgin HDPE, the elasticity modulus increased by 241% for the composites with a 50 wt % red mud concentration. This was probably due to the improved dispersion quality of red mud particles in the HDPE matrix. The results showed that the elasticity modulus of composites improved with increasing red mud concentration. The tensile strength of the HDPE/RM polymer composites is shown in the Figure 1/B. With the addition of red mud in HDPE has been a change in tensile strength values. A systematic decrease in tensile strength was observed as red mud contents increase. At high weight fractions of red mud, tensile strength decreases due to the filler high volume incorporated into the HDPE matrix For example, the tensile strength of virgin HDPE and HDPE/RM (50/50) polymer composites (without UV) were 33.2 MPa and 25,6 MPa respectively. In comparison with the tensile strength of virgin HDPE, the tensile strength decreased by 23% for the composites with a 50 wt % red mud concentration.

Similar situation was seen in tensile strength values (with UV). For example, the tensile strength of virgin HDPE and HDPE/RM (50/50) polymer composites (with UV, holding time: 100 hours) were 30,3 MPa and 3,1 MPa respectively. On the other hand, the tensile strength of virgin HDPE and HDPE/RM (50/50) polymer composites (with UV, holding time: 300 hours) were 25,3 MPa and 1,5 MPa respectively. The agglomeration and the poor dispersion of the red mud into the HDPE matrix had a significant impact on the mechanical properties of the composite in comparison to the neat matrix strength. This behavior might be attributed to the grinding method applied which affects the red mud granule size as well as their physical and morphological characteristics.

The elongation at break of red mud filled composites was measured, as shown in Figure 1/C. The minimum elongation at break is observed at the 50 wt % red mud powder concentration for HDPE. In comparison with the elongation at break of virgin HDPE, the elongation at break decreased by approximately 98 % for the composites with a 50 wt % red mud concentration. A decrease in elongation at break as the red mud content increases is observed indicating the presence of a poor interfacial adhesion between the red mud and the HDPE which does not allow efficient stress transfer between the two phases of the composite. For red mud, agglomerates induce a decrease in strength. On the other hand, the elongation at break of the HDPE/RM polymer composites did not significant change as the UV holding time increases from 100 hours to 300 hours.

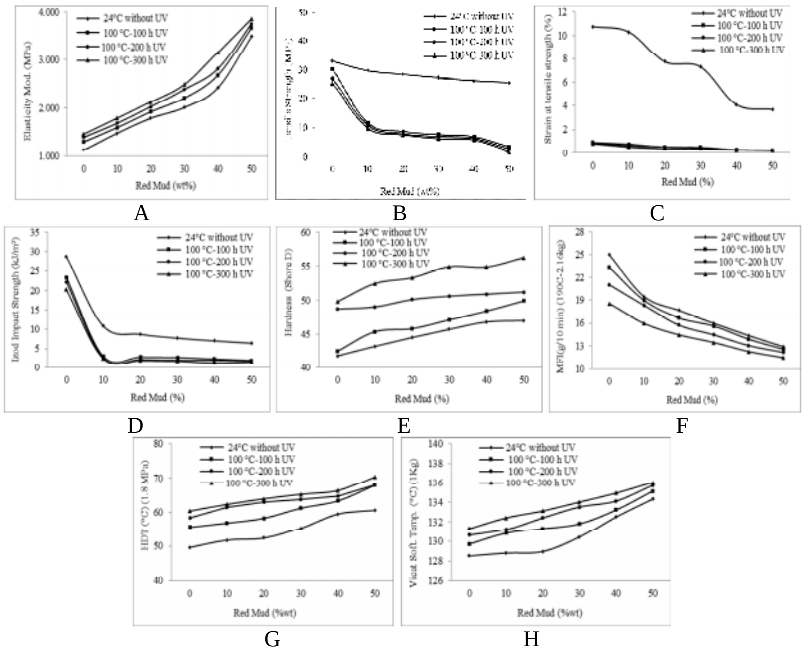

Figure 1. Mechanical properties of HDPE/RM polymer composites

The measured values of the Izod impact strengths are presented in Figure 1/D. The impact strength decreased as the red mud concentration increased from 0 to 50 wt %. This means that the energy not absorbed by the specimen decreases and with it its toughness also decreases. For example, the Izod impact strength of virgin HDPE and HDPE/RM (50/50) polymer composites (without UV) were 28,7 kJ/m^2 and 6,4 kJ/m^2 respectively. Similar situation was seen in Izod impact strength values with UV. For example, the Izod impact strength of virgin HDPE and HDPE/RM (50/50) polymer composites (with UV aging 100 hours) were 23,4 kJ/m^2 and 1,9 kJ/m^2 respectively. On the other hand, the Izod impact strength of virgin HDPE and HDPE/RM (50/50) polymer composites (with UV, holding time: 300 hours) were 20,2 kJ/m^2 and 1,5kJ/m^2 respectively. The minimum Izod impact strength is observed at the 50 wt % red mud (UV 300 h) concentration. In comparison with the Izod impact strength of virgin HDPE, the Izod impact strength decreased by approximately 94% for the composites with a 50 wt % red mud (UV 300 h) concentration. The impact strength is the ability of a material to withstand fracture or the amount of energy required to propagate a crack. It depends on certain factors such as fiber and matrix strength, load transfer efficiency, resistance to crack propagation, bonding strength, volume fraction, fiber distribution, and geometry (Bax and Mussig, 2008). The relationship between the red mud content and the hardness of the polymer composites is shown in Figure 1/E. The hardness of the composites increased (from 0 to 50wt %) linearly with an increase weight percentage of filler. The Hardness of the HDPE/RM polymer composites increased as the UV aging time increases from 100 hours to 300 hours as well. The maximum and minimum Hardness are observed at Group 6 (100°C- UV 300h) and Group 1 (24°C- UV 0h) respectively. The relationship between the red mud content and the MFI of the polymer composites is shown in Figure 1/F. The MFI of the composites decreased (from 0 to 50wt %) linearly with an increase weight percentage of red mud. For example, the MFI of virgin HDPE and HDPE/RM (50/50) polymer composites (without UV) were 24,9 g/10 min and 12,8 g/10 min respectively. Similar situation was seen in MFI values (with UV). For example, the MFI of virgin HDPE and HDPE/RM (50/50) polymer composites (with UV aging 100 hours) were 23,3 g/10 and 12,5 g/10 respectively. On the other hand, the MFI of virgin HDPE and HDPE/RM (50/50) polymer composites (with UV holding time: 300 hours) were 18,5g/10 and 11,4 g/10 respectively. The relationship between the red mud content and the HDT of the polymer composites is shown in Figure 1/G. The HDT experiment was started at room temperature with a heating rate of l20°C/h and under a load of 1.8 MPa. The HDT of the composites increased (from 0 to 50wt %) linearly with an increase weight percentage of red mud. For example, the HDT of virgin HDPE and HDPE/RM (50/50) polymer composites (without UV) were 49,6°C and 60,5°C respectively. Similar situation was seen in HDT values (with UV aging). For example, the HDT of virgin HDPE and HDPE/RM (50/50) polymer composites (with UV, holding time: 100 hours) were 55,6°C and 67,7°C respectively. On the other hand, the HDT of virgin HDPE and HDPE/RM (50/50) polymer composites (with UV aging 300 hours) were 60,3°C and 70,3°C respectively. The maximum HDT is observed at the 50 wt % red mud concentration (UV holding time: 300 h) for HDPE. In comparison with the HDT of virgin HDPE, the HDT increased by 41% for the composites at a 50 wt % red mud (UV holding time: 300 h) concentration. The relationship between the red mud content and the Vicat softening temperature of the polymer composites is shown in Figure 1/H. The Vicat softening temperature experiment was started at room temperature with a heating rate of 120°C/h and under a load of 1 Kg. The Vicat softening temperature of the composites increased (from 0 to 50wt %) linearly with an increase weight percentage of red mud. For example, the Vicat softening temperature of virgin HDPE and HDPE/RM (50/50) polymer composites (without UV) were 128,5°C and 134,3°C respectively. Similar situation was seen in Vicat softening temperature values (with UV aging). For example, the Vicat softening temperature of virgin HDPE and HDPE/RM (50/50) polymer composites (with UV, holding time: 100 hours) were 129,7°C and 135,1°C respectively. On the other hand, the Vicat softening temperature of virgin HDPE and HDPE/RM (50/50) polymer composites (with UV aging 300 hours) were 131,3°C and 136°C respectively. The maximum Vicat softening temperature is observed at the 50 wt % red mud concentration (UV holding time: 300 h) for HDPE.

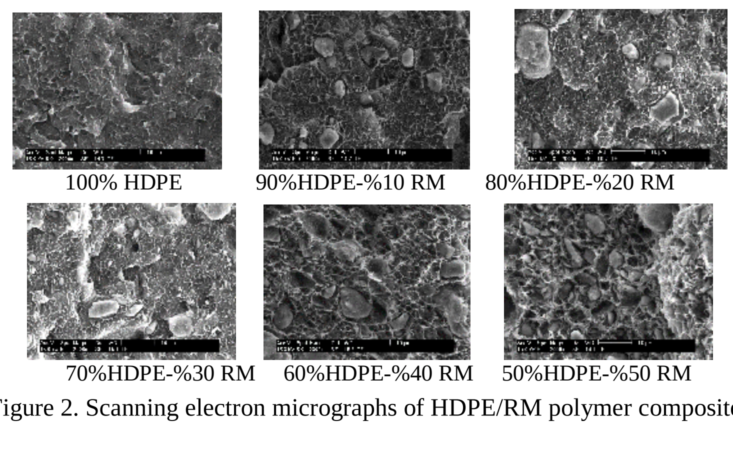

Figure 2. Scanning electron micrographs of HDPE/RM polymer composites

The fractured surfaces of polymer composites were examined with SEM are presented in Figure 2. Interfacial tension between polymer and filler is very important for phase morphology. It is clear that the filler at low loading level (10%) morphology slightly differs from that of pure HDPE polymer. Low level pullout was observed which reflects a relative good tensile stress performance of the polymer composite compared to that of pure HDPE. At high red mud loading, (%50) as shown in Figure 2, more filler pullout and deponding were observed. This was probably due to poor adhesion between red mud and HDPE polymer matrix.

CONCLUSIONS

In the present work a novel composite material containing red mud dispersed in HDPE matrix was manufactured and studied. The aim of this study was to investigate the effect of red mud at different weight fractions without coupling agent on mechanical, morphological, and thermal properties of HDPE matrix composite. The results indicate the variation of the composite properties with varying the filler content. Substantial improvements in the mechanical properties were obtained by the addition of red mud in the HDPE polymer matrix. The results showed that the elasticity modulus, hardness, Vicat softening temperature, and HDT of composites improved with increasing powder content. The annealing UV treatment increased the elastic modulus, hardness, Vicat softening temperature and HDT values, and different holding times showed similar effects on the increased elastic modulus values as well. In contrast, the tensile stress reduction at high red mud loading may be due to the poor interfacial bonding between red mud powder and HDPE. The annealing UV treatment decreased the tensile strength and strain at tensile, different holding times showed similar effects on the decreased these values. MFI decreased as the red mud content and UV holding times increased. At high red mud loading (%50), more filler pullout and deponding were observed. This was probably due to poor adhesion between red mud and HDPE polymer matrix.

Acknowledgement

This work was supported by Scientific Research Project Program of Marmara University (FEN-C-YLP-250416-0188).

REFERENCES

Bax, B. and Mussig, J. (2008), “Impact and tensile properties of PLA/cordenka and PLA/flax Composites”, *Composites Science and Technology*, 68, 1601–1607.

Bhat, A.H., Abdul Khalil, H.P.S. and Banthia, A.K. (2011), “Thermoplastic polymer based modified red mud composites materials”, in Attaf, B. (ed.), *Advances in composites materials - Ecodesign and analysis*, 3, 55-86.

Chand, N. and Hashmi, S.A.R. (1999), “Effect of red mud addition on abrasive wear rate of isotactic polypropylene/low density polyethylene blend under low stress conditions”, *Journal of Scientific and Industrial Research*, 58, 795.

Kalia, S., Kaith, B.S. and Kaur, I. (eds.) (2011), *Cellulose Fibers: Bio- and Nano-Polymer Composites*, Green Chemistry and Technology, Springer.

Milacic, R., Zuliani, T. and Scancar, J. (2012), “Environmental impact of toxic elements in red mud studied by fractionation and speciation procedures”, *Science of the Total Environment*, 426, 359–365.

Pradhan, J., Das, S.N. and Thakur, R.S. (1999), “Adsorption of hexavalent chromium from aqueous solution by usin activated red mud”, *Journal of Colloid and Interface Science*, 217, 137.

Rothon, R.N. (1997), “Mineral fillers in thermoplastics”, *The Journal of Adhesion*, 64, 87–109.