STUDIUL PROPRIETĂȚILOR COMPOZITELOR PE BAZĂ DE POLIETILENĂ DE JOASĂ DENSITATE ARMATE CU PULBERE DIN COCHILIILE MOLUŞTELOR MARINE

STUDIES ON THE PROPERTIES OF LOW DENSITY POLYETHYLENE COMPOSITES FILLED SEAFOOD WASTE SHELL POWDER

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In this study low density Polyethylene (LDPE)-based composites are prepared using mussel-oyster shell powder as natural filler. Filler contents in the LDPE were 5, 10 and 15 wt%. The mechanical properties of the polymer composites were investigated. Some mechanical properties of low density polyethylene bio composites have effected much by the addition of mussel-oyster shell powder. For example, the results showed that the elasticity modulus, Izod impact strength, hardness and density of composites improved with increasing the mussel and oyster contents. The addition of fillers to the LDPE changed the wear rate of the composites. LDPE filled with a high level content of mussel and oyster showed higher wear rate than pure LDPE under dry sliding. The structure and properties of the composites are characterized using a scanning electron microscopy (SEM). This study has shown that the composites treated with mussel-oyster shell powder as natural additive and as an inorganic particle-filled polymer will be attractive due to their improved mechanical properties of LDPE.

Keywords: *low density polyethylene, mussel, oyster, mechanical properties, wear*

1. Introduction

Fillers, in the form of particulates and fibers, are often added to polymeric materials to improve their stiffness and strength. Polymers and their composites are being increasingly employed in view of their good strengths and low densities. Besides, a wider choice of materials and ease of manufacturing make them ideal for engineering applications [1]. Enormous amount of waste mussel and oyster shells were dumped into public waters and landfills, which cause a bad smell as a consequence of the decomposition of organics attached to the shells. Also, marine pollution by waste mussel and oyster shells has become one of the serious problems in mariculture industry [2]. The mussel and oyster shells are discarded into the environment. The improper disposal of solid waste from shellfish cultivation decreases water oxygen and microalgae that are responsible for the nutrition of mussels and oysters, thus hindering the growth of these shellfish [3,4]. Low density polyethylene is an important commercial polymer which is widely used for different applications in modern technology. In order to reduce cost or enhance physical and mechanical properties of LDPE, some additives can be added to it.

Fillers and reinforcement used including talc, calcium carbonate, mica, wollastonite, glass fibre, glass bead, jute, etc. [5,6]. According to Passipoularidis et al [7], high performance synthetic fiber reinforced polymer composites have been used in such diverse applications such as composite armouring designed to resist explosive impacts, fuel cylinders for natural gas vehicles, windmill blades, industrial driver shafts, and paper making rollers. However, the widespread use of synthetic fiber reinforced polymer composites has a tendency to decline because of their high initial costs and more importantly, their adverse environmental impact [7,8]. Today, the growing environmental awareness throughout the world has triggered a paradigm shift from synthetic fibers and their composites towards composites made from natural reinforcing constituents (natural fibers and natural particulate fillers) which are more environmentally friendly [9]. In the light of this, researchers have focused their attention on composites composed of natural or synthetic resins, reinforced with mineral particulate fillers or natural fibers and manufacturing of high-performance engineering materials from these renewable resources has also been pursued by researchers since renewable raw materials are environmentally sound and do not cause health problems [10,11]. During the last decade, eco-friendly, biodegradable bio-flours and fibers have been used as reinforcing fillers in the commercial plastic industry to produce composite materials [12,13]. These bio-fillers exhibit a number of

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attractive advantages, including low cost, low density, low processing requirements, less abrasion during processing, renewability, eco-friendliness and bio degradability. It therefore shows promise as a bio-filler in composites to replace various materials such as construction materials, furniture and many plastic products in a variety of future industrial applications [12]. Oyster shells are one of the renewable natural products found in a large amount in different area near to the water environmental areas but it have limited use in industrial applications especially in polymer fields. Oyster shell is a biomaterial containing 95% by weight of compound in the form of calcium carbonate ($CaCO_3$) and 4% by weight of organic materials such as SiO_2, MgO, Al_2O_3, SrO, P_2O_5, Na_2O, SO_3. It is clear that the oyster shell powder can change the properties of LDPE matrix because of its nature, size, shape and distribution. In the scientific literature, different materials (sisal, calcite, talc, and copper ex.) have been used to fill low density polyethylene. The use of mussel and oyster shell powder in filling low density polyethylene has not been good enough reported in the scientific literature [14]. M.H. Chong and his co-workers [15] used this material as fire-retardant for polyethylene and the results of his study show that the Oyster shell decomposed to calcium oxide and carbon dioxide at temperature higher than 800°C, thus preventing fire from access of oxygen by the produced carbon dioxide. This fire-retardation mechanism is environmental-friendly. Funabashi et al.[16] evaluated method of biomass carbon ration of polymer filled with calcium carbonate using poly(butylene succinate) (PBS) with oyster shell powder and poly (lactic acid) (PLA) with no biobased inorganic calcium carbonate. They observed that the estimation method is effective for polymer composites with $CaCO_3$.

In the present study, we attempt to use powder of mussel-oyster as natural filler and reinforce material in LDPE to produce composite structure and then evaluate its mechanical properties to study the effect of mussel and oyster filler on mechanical properties of LDPE.

2. Experimental

2.1. Compositions and Materials

Seven different polymer composites were prepared. Compositions of LDPE/Mussel and Oyster powder polymer composites that were formed are given in Table 1.

Table 1

Composition of the different polymer composites formulations

Groups	LDPE (wt %)	Mussel (wt %)	Oyster (wt %)
1	100	-	-
2	95	5	-
3	90	10	-
4	85	15	-
5	95	-	5
6	90	-	10
7	85	-	15

Low-density polyethylene (density 0,920 g/cm^3, melt flow rate 0,23-0,37 g/10 min at 190^{o}C–2.16 kg, hardness 47 shore D from Petkim-Turkey) was mixed with fine powder of mussel and oyster (obtained from the beach of Marmara Sea) after (washed, dried, grinded then sieved to the size less than 50 μm.)

2.2. Sample preparation and mechanical characterization

Mechanical premixing of solid compositions was done using a LB-5601 liquid-solids blender (The Patterson-Kelley Co., USA) brand batch blender for 15 min. Samples with various proportions of LDPE polymer composites were produced between 130-190 ^{o}C at 20-30 bar pressure, and a rotation rate of 25 rpm, with a Mikrosan extruder (Mikrosan Instrument Inc. Turkey). L/D ratio is 30, Ǿ:25 mm, Polymer composites were also dried in vacuum oven at 80 ^{o}C for 24 hours after extrusion. Subsequently, test samples were molded in injection molding machine. For every composition, five samples were tested, and the averages of the five measurements were reported.

Tensile tests were prepared according to the ASTM D638 standards by using a Zwick Z010 (Ulm-Germany) testing machine with a load cell capacity of 10 kN at a cross-head speed of 50 mm/min. The hardness test was done according to the ASTM D2240 method with Zwick hardness measurement equipment. To investigate fracture behavior, Izod impact test (notched) was done at room temperature according to the ASTM D256 method with Zwick B5113 impact test device (Zwick, Ulm-Germany). 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 Pianezza, Italy) HDT-Vicat test equipment.

The wear tests were done according to the DIN 53 516 method with Devotrans DA5 (Devotrans quality control test equipment, Turkey) abrasion test equipment (sand paper #60 and 0,32 m/s abrasion speed). The thickness of the test specimens was 7.0 mm and diameter was 15.5 mm. Cylinder rotational speed was selected as 40 rpm and normal load (F_N) of 10N was used. Total sliding distance (L) was 40 m. The mass loss of the samples (Δm) was measured after the wear process, and the specific wear rates (Ws) were calculated using the following equation:

$$Ws=(\Delta m)/\rho.F_N.L \ (cm^3/Nm) \quad (1)$$

Where Δm is the specimen's mass loss, ρ is the density of specimen, F_N is the normal load applied, and L is the total sliding distance. The friction coefficients and wear rates reported in the present study were the averages of three separate tests.

The fractured surfaces of the LDPE polymer composites were coated to thickness of 10-12 nm of a gold (Au) (80%)/palladium (Pd) (20%) alloys to prevent electrical charging by Polaron SC 7620 (Gala Instrumente GmbH, Germany). The surfaces of the prepared samples were observed by the JEOL-JSM 5910 LV (JEOL Ltd., Japan) scanning electron microscopy (SEM) at an acceleration voltage of 20kV.

3. Result and discussion

The relationship between the elasticity modulus and the percentage of the filler of LDPE composites is shown in the Figure 1-A. The elasticity modulus of LDPE/oyster composites increases as the oyster concentration increases from 0 to 15 wt %. The maximum elasticity modulus is observed at the 15 wt % oyster concentration for LDPE. In comparison with the elasticity modulus of virgin LDPE, the elasticity modulus increased by 69% for the composites with a 15 wt % oyster concentration. This observation is a clear indication that the addition of powdered filler into low density polyethylene matrix improves the stiffness of the polymer composite. On the other hand, the elasticity modulus of LDPE/mussel composites shows an increment as the filler concentration increases from 0 to 15 wt %. The maximum elasticity modulus is observed at the 15 wt % mussel concentration. However, the mussel composite show a lower elasticity modulus than the oyster composites. At a larger mussel concentration, the value of the elasticity modulus was not much changed. The elongation at break of mussel and oyster filled LDPE composites was measured, as shown in Figure 1-B. With increased loading, the elongation at break of composites filled with mussel and oyster is decreased for all. The minimum elongation at break is observed at the 15 wt % oyster concentration for LDPE. In comparison with the elongation at break of virgin LDPE, the elongation at break decreased by 68 % for the composites with a 15 wt % oyster concentration. The increase of the mussel or oyster content in the LDPE matrix resulted in the stiffening and hardening of the composite which reduced its ductility, and led to lower elongation property. The reduction of the elongation at break with the increasing filler content indicates the incapability of the filler to support the stress transfer from filler to polymer matrix [14]. The relationship between the ratio percentage of the filler and ultimate tensile strength of LDPE composites is shown in the Figure 1-C. Ultimate tensile strength of composites shows an decrement as the filler concentration increases from 0 to 15 wt %. Above 5 wt %, the value of the ultimate tensile strength was not much changed. The maximum ultimate tensile strength is observed at the pure LDPE. Figure 1-D illustrates the effect of mussel and oyster on the Izod impact strength (notched) of LDPE composites. The impact strength increased as the mussel and oyster particle concentration increased from 0 to 15 wt %. The maximum Izod impact strength is observed at the 15 wt % oyster concentration for LDPE. In comparison with the Izod impact strength of virgin LDPE, the Izod impact strength increased by 10 % for the composites with a 15 wt % oyster concentration.

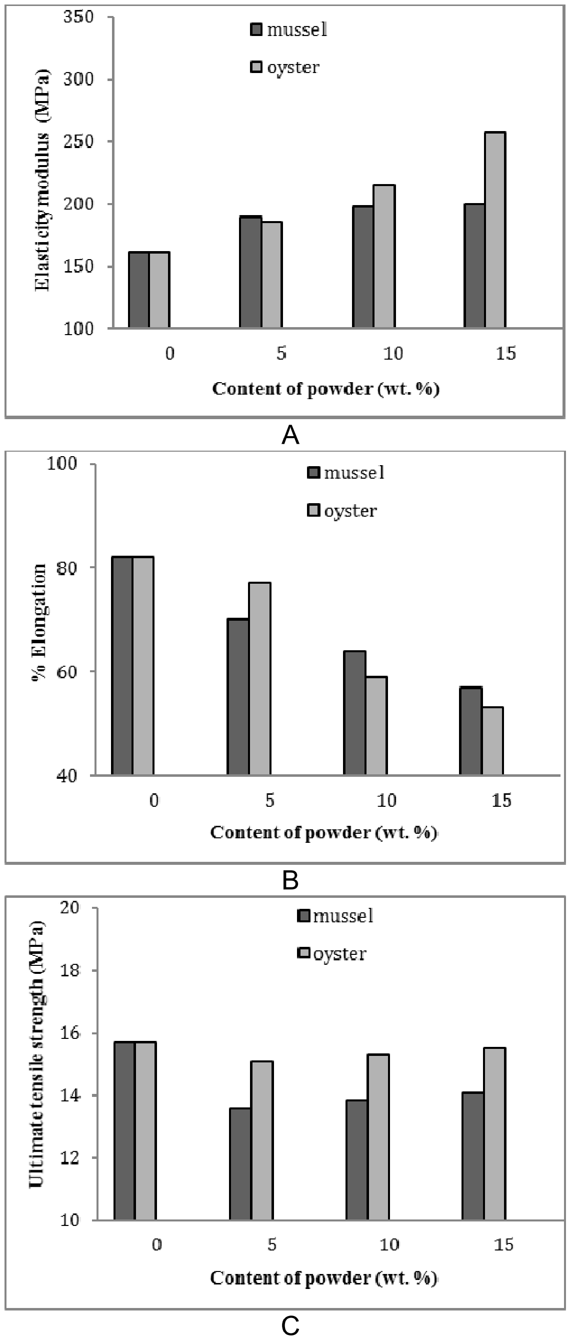
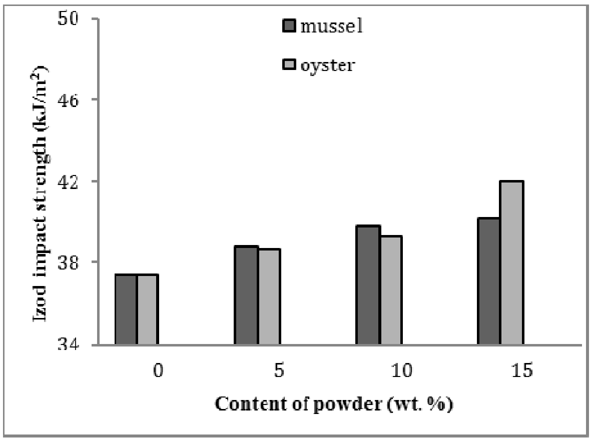


Fig. 1 - Mechanical properties of the LDPE/mussel-oyster polymer composites

Fig. 1 continues on next page



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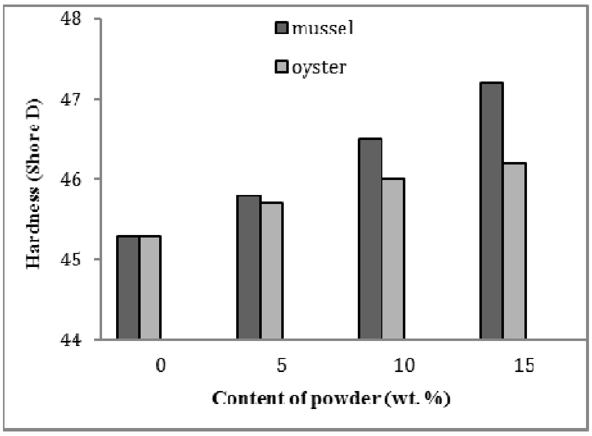

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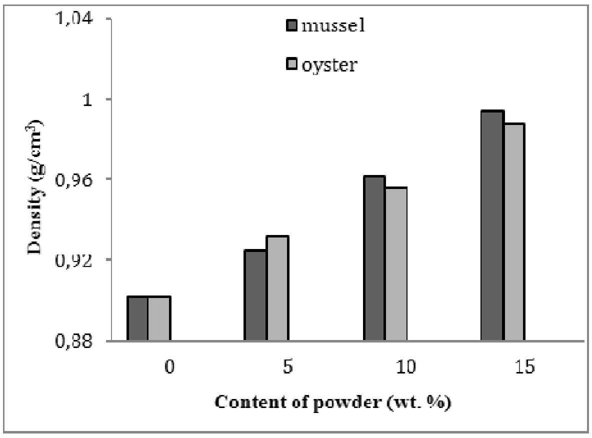

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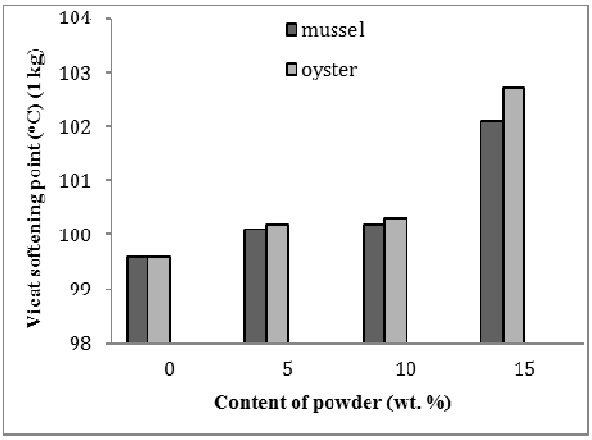

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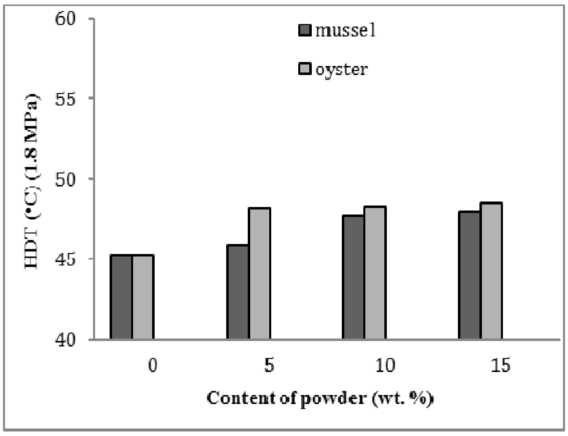

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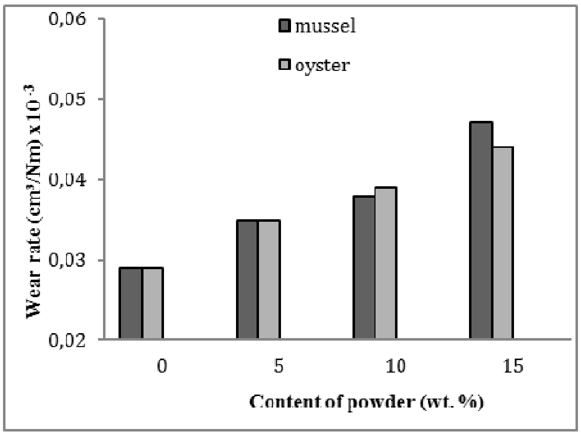

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The relationship between the filler content and the hardness of the polymer composites is shown in Figure 1-E. The hardness of the composites increased (from 0 to 15wt %) linearly with an increase weight percentage of mussel and oyster. The maximum hardness is observed at the 15 wt % mussel concentration for LDPE. The results showed that the hardness of composites improved with increasing filler content. This is attributed to the fact that hardness is generally considered to be a surface effect or property, therefore the addition of the mussel or oyster shell powder leads to a decrease in the elasticity and increase in the matrix surface resistance to indentation. The specific gravity or density of polymer composites is a very important property that determines specific load application of the composite. This is because specific gravity or density has a direct relationship with the load bearing capacity of the composite as well as the cost [13]. The relationship between the filler content and the density of the polymer composites is shown in Figure 1-F. The density of the composites increased (from 0 to 15wt %) linearly with an increase weight percentage of mussel and oyster. The maximum density is observed at the 15 wt % mussel concentration for LDPE. The relationship between the Vicat softening

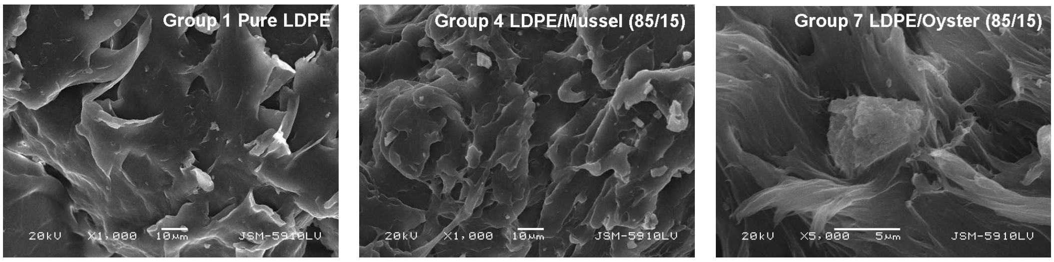

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Fig. 2 - SEM micrographs of impact test of LDPE with a) pure LDPE; b) mussel shells; and c) oyster shells.

temperature and the percentage of the filler of LDPE composites is shown in the Figure 1-G. The Vicat softening temperature of LDPE/mussel and oyster composites increases as the mussel and oyster concentration increases from 0 to 15 wt %. The maximum Vicat softening temperature is observed at the 15 wt % oyster concentration for LDPE. On the other hand, HDT of LDPE/mussel and oyster composites shows an increment as the filler concentration increases from 0 to 15 wt % (figure 1-H). The maximum HDT is observed at the 15 wt % oyster concentration. The mussel composite show a lower Vicat softening temperature and HDT than the oyster composites. At a larger mussel or oyster concentration, the value of the HDT was not much changed. The values of powder content and wear rate relationship were obtained and are shown in Figure 1-I . By comparing with the LDPE without filler, it can be observed that the addition of mussel and oyster increased the wear rate of the composites. Based on these results, it could be postulated that the level of the filler can affect the matrix hardness and bonding strength between the filler and polymer matrix. The weak bond led to the filler particles detaching from the matrix and the matrix pulling out more easily, which could increase the wear rate of the composite. So, a high level of the filler led to the high wear rate of the composite.

The SEM study was carried out to study the dispersion of fillers in the LDPE matrix. The boundaries and the contrast can be obviously seen between the mussel-oyster and LDPE matrix on the fractured surfaces of polymer matrix. Figure 2 indicate that the all particulates are homogeneously dispersed on the fractured surfaces of LDPE matrix. No adhesion between the domains in the matrix can be observed, probably due to the weak interfacial bonding in all composites.

4. Conclusions

Mussel and oyster shell powder have been utilized efficiently in preparing low density polyethylene composites. The increase of the mussel or oyster content in the LDPE matrix resulted in the stiffening and hardening of the composite which reduced its ductility, and led to lower elongation property. So, the elasticity modulus, Izod impact strength, hardness and density of the linear low density polyethylene composites were found to increase with increase in mussel and oyster contents. Generally these properties investigated were greatly enhanced and the trend of property improvement observed in the prepared composites is outstanding evidence that mussel and oyster shell powders can play significant role in the plastic industry. On the other hand, the elongation at break of the prepared composites decreased with increase in mussel and oyster contents. The reduction of the elongation at break with the increasing filler content indicates the incapability of the filler to support the stress transfer from filler to polymer matrix.

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