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Original Paper

Investigation of wear properties of elastomer modified wollastonite and hazelnut shell flour reinforced polypropylene composites

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ABSTRACT

In this study, hybrid composites were produced by using polypropylene (PP) polymer as matrix material, and hazelnut shell (HS) and wollastonite (W) as reinforcement in different ratios. Hazelnut shell flour (HSF) and wollastonite reinforced polypropylene mixtures were modified with poly(styrene-*b*-ethylene-co-butylene-*b*-styrene) (SEBS) triblock copolymer and maleic anhydride grafted SEBS (SEBS-*g*-MA). Wear properties of the hybrid composites were investigated as a function of elastomeric component. First, the reference hybrid composites were prepared from PP and W + HSF mixtures in the ratio of 80/10+10 by weight through extrusion method. SEBS and SEBS-*g*-MA modified hybrid composites (%, by weight ratios - 3, 6, 9) were then prepared by using these reference mixtures. The goal of this study is to investigate the effect of elastomeric modifications on the wear properties of the hybrid composites. Wear test samples prepared out of those mixtures by injection molding. In order to avoid any degradation due to the temperature sensitivity of the hazelnut shell, temperatures were kept close to lower limits during extrusion processing. Wear features of the samples were investigated by using an abrasion tester. Scanning electron microscopy was used for analyzing morphological features of the worn surfaces. It was found that SEBS and SEBS-*g*-MA modifications resulted in the reduction of the weight loss.

I. INTRODUCTION

Composite materials are produced with approximately 90% by polymer based matrices. Advanced plastic-polymer group matrix materials are composite materials in this group that are reinforced materials mostly in fiber form. However, fibers with superior physical, chemical and mechanical properties are used in the advanced composites group. These materials have high strength (tensile and compressive strength), high elastic modulus and high toughness. Because of these advantages, polymer composites are widely used in important areas such as aircraft and space industry [1-3]. The use of organic and inorganic fillers in polymer-based composites is common, recently organic and inorganic fillers are used together in polymer-based composite materials. The use of two different filler materials in polymer based composite materials gives different properties to the composite material that cannot be achieved with a single type filler. These properties are briefly considered as cost, ease of processing, low density, aesthetic, strength and abrasion resistance [4-12].

Polypropylene (PP) is a widely used polymer with various applications in the market. However, its relatively poor impact resistance, especially at low temperatures limits its application as an engineering thermoplastic. Plastic deformation ability of the matrix can be increased to increase the toughness. Addition of elastomers in order to improve the fracture toughness of PP is a common approach, but the strength and stiffness of PP are also

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simultaneously reduced. On the other hand, although using inorganic fillers generally improves strength, stiffness, hardness, and abrasion resistance of PP, it usually reduces the fracture strength of PP [13-20].

Hard fillers such as silica and alumina increase the wear resistance by providing high hardness and strength to the composite material. Hard fillings minimize surface wear and deformations in composite materials, which extends the life of the material. However, the high hardness of hard fillings can lead to brittleness under certain conditions (for example, under high impact), which can cause the surface to crack quickly and wear faster.

Hazelnut shells are used as fillers in composites because they are biodegradable, renewable and environmentally friendly. Natural fillers such as hazelnut shells add lightness to composite materials while also contributing to the improvement of certain mechanical properties. Especially when used in polymer matrix composites, hazelnut shell fillers can increase the wear resistance of the composite and provide cost-effectiveness. However, organic fillers such as hazelnut shells do not provide as high abrasion resistance as hard inorganic fillers; however, they improve impact resistance by increasing flexibility. The use of hazelnut shell fillers in composites is an important step in sustainable material development and an ideal approach to reduce environmental impacts [20]. In such systems, both properties can be improved by the simultaneous utilization of rigid fillers such as wollastonite and elastomeric phase such as SEBS. This approach has been successful in providing rigidity-toughness balance [21-26]. In multi-phase materials, it is suggested that the fillers in the matrix change crack propagation direction and increase the fracture surface area thereby increasing the toughness. Another way to increase the toughness is to encapsulate the fillers by using a low modulus component which is an elastomeric phase. Elastomeric components absorb some of the impact energy in multi-phase polymer composites [20, 27-28].

Moreover, the mechanical and other properties of multi-phase polymer composite systems are improved by creating interfacial interactions between the phases. For this purpose, functional groups are grafted to polymers in neutral state, usually by reactive extrusion, and these polymers are used to bring about interfacial interactions with other phases. SEBS elastomer grafted with maleic anhydride interacts with active groups such as hydroxyl (-OH) through carboxyl groups present in maleic anhydride resulting in an esterification reaction [13, 28].

In this study, it is aimed to investigate wear properties of polypropylene having the additions of both rigid fillers and soft elastomeric phases. The world's center of hazelnut production is Turkey, with an annual hazelnut harvest of over 700,000 tons. Considering that half of the hazelnut weight is shell, a very large amount of hazelnut shell is obtained as waste. The aim of this study is to evaluate waste hazelnut shell, which is mostly consumed as fuel, in composites to improve wear properties and thus to have high added value. In this respect, the study differs from the literature.

II. MATERIALS AND METHOD

2.1 Materials

In this study, homopolymer polypropylene (PP MH418; polymer known as Petkim's Petoplen) was used as matrix material. Poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) block copolymers (SEBS; KratonTM G-1652) and the corresponding maleated SEBS block copolymer grafted with 1.7 wt% of maleic anhydride (SEBS-*g*-MA;

KratonTM FG-1901) were supplied by Kraton (Kraton Polymers LLC) and were used as thermoplastic elastomers. SEBS and SEBS-*g*-MA are linear triblock copolymers with ~30 wt% of styrene and have number average molecular weights (Mn) of 65.900 and 47.300 g mol^{-1}, respectively. Structural views of SEBS and SEBS-*g*-MA elastomers were given in Figures 1a and 1b. Two types of fillers, which are hazelnut shell flour (HSF) and wollastonite, were used to get a hybrid composite structure. Hazelnut shell flour was ground in a mill. It can be clearly seen that the shell consists of two main layers when viewed as a macro on the hazelnut shell. The outer layer is of a hard structure, which is surrounded by a soft, loose layer. Therefore, the crushed hazelnut shell contains these two parts.

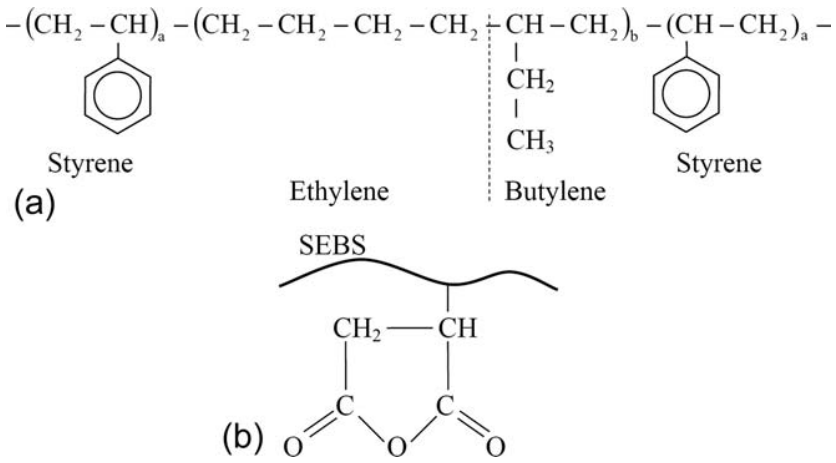

Figure 1. Structural Views of SEBS (a) and SEBS-*g*-MA (b).

In this study, the powder obtained from the hard part of the shell was separated from the soft part and used. Hazelnut shell is basically a wood-like cellulosic structure, so it is a very sensitive material against water. This sensitivity increases as the surface becomes bigger through the formation of smaller dust. For this reason, the hazelnut shell powder was dried before processing in the extruder. In the study, HSF with dimensions in the range of 200-250 microns was used. A macrophotograph of a lump of HSF was presented in Figure 2.

Figure 2. An Optical Image of Hazelnut Shell Flour

Wollastonite (W;Nyglos1 8) with an aspect ratio of nearly 19/1 (~150 µm/8 µm), a specific gravity of 2,9 g cm^{-3} and a specific surface area of 1,2 m^2 g^{-1} was supplied by Nyco Minerals Ltd. and was used as received with its original surface treatment. Polyethylene wax OX.PE WAX LE 262 produced by Innospec Leuna was supplied by ERAL Turkey to facilitate processing as a lubricant. The IRGANOX 1010 antioxidant (supplied by the Ciba Geigy Turkey) was used to minimize any possible oxidation during the mixing in the extruder and during the injection molding.

2.2 Preparation of Test Specimens

An extruder (screw diameter: 30 mm, L/D ratio: 25) at a speed of 120 rpm was used for compounding of PP with the elastomers and the fillers. The barrel temperature profile was set at 160, 170, 180, and 185 °C for zones from feed to die.

The strands obtained from the extruder were cooled immediately in water and then granulated. The granules were dried in an oven at 100 °C for 4 hours before injection molding. Test specimens were molded in accordance with ISO 527 using a Supermaster SM-60HC injection molding machine. The cylinder temperature profile of the injection molding equipment was set at 200 °C, and the mold temperature was set at 40 °C.

HSF was dried at 100 °C for 2 hours just before mixing with PP and, wollastonite, SEBS, SEBS-*g*-MA were weighed with respect to the specified weight ratios. In order to avoid degradation due to the sensitivity of the HSF to heat, temperatures during extrusion process were kept close to the lower limits. In addition, slip agent and antioxidant were added to all mixtures to minimize degradation.

First, binary hybrid composites were prepared from polypropylene + wollastonite (PP/W) and polypropylene + HSF PP/HSF in certain ratios (%, by weight ratios - 80/20), ternary PP/W/HSF composites (%, by weight ratios - 80/15/5, 80/10/10, 80/5/15), quaternary PP/W/HSF/SEBS and PP/W/HSF/SEBS-*g*-MA composites (%, by weight ratios - (80/10/10)/3, (80/10/10)/6, (80/10/10)/9) were prepared. 10% W + 10% HSF filled polypropylene composite from these hybrid group composites was considered as the reference group. Toughness was increased by adding SEBS or SEBS-*g*-MA elastomers while rigidity increased by incorporating wollastonite and hazelnut shell flour into polypropylene. This reference group was modified by adding SEBS and SEBS-*g*-MA at 3-6 and 9% by weight of the hybrid composite.

2.3 Characterization

2.3.1 Wear tests

A standard single pin-on-disc machine at dry conditions was used for performing abrasive wear tests. All specimens were tested at a constant load of 30 N and a sliding speed of 8,75 m/s at room temperature. Each test was performed at least in triple to ensure the reliability and the average of these results was reported. Five different sliding distances (100, 200, 300, 400, 500 m) were adopted for the wear tests. After completing each sliding distance, the test was interrupted and the weight was measured after carefully cleaning the samples.

2.3.2 Morphology investigations

Worn surfaces were investigated by using a JEOL JSM-5910 LV scanning electron microscope.

III. RESULTS AND DISCUSSIONS

The combined use of organic and inorganic fillers enables high-performance properties to be achieved in composite materials. This hybrid structure combines the hardness, strength and thermal resistance provided by inorganic fillers with the flexibility, lightness and environmental sustainability properties of organic fillers. As a result, composite materials are optimized in terms of both mechanical strength and workability, while at the same time being environmentally friendly and economically advantageous. This combination enables the production of versatile materials, offering innovative solutions for a wide range of applications.

As can be understood from Figure 3 the highest wear loss occurred in the pure PP sample. The lowest mass loss was observed in 20% W filled composite. As expected, the wear loss increased as the organic filler added to the mixture increased. Wear properties of organic fillers are weaker than inorganic fillers. PP-10% HSF-10% W sample was selected as a reference sample from these composite groups.

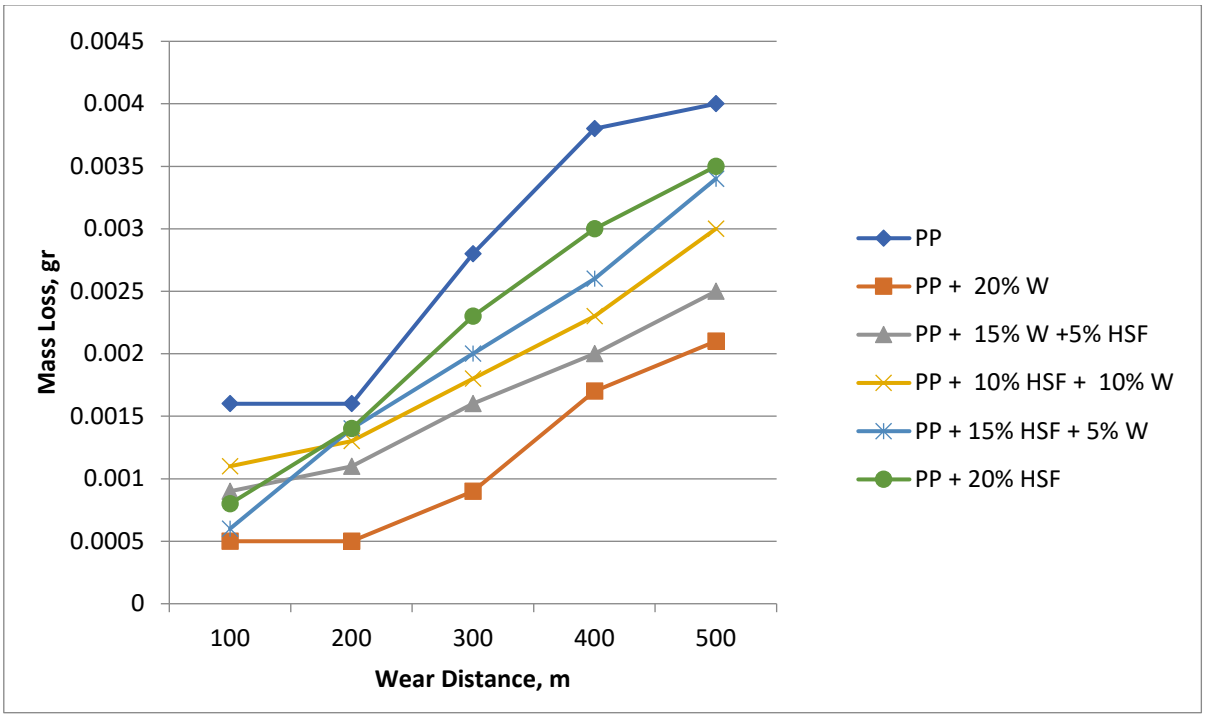

Figure 3. Mass Loss vs. Wear Distance for Hybrid Composites

The mass loss of the reference sample PP-HSF-W composite can be significantly reduced by the addition of SEBS as seen in Figure 4. This improvement can be attributed to the wear behavior of elastomeric materials.

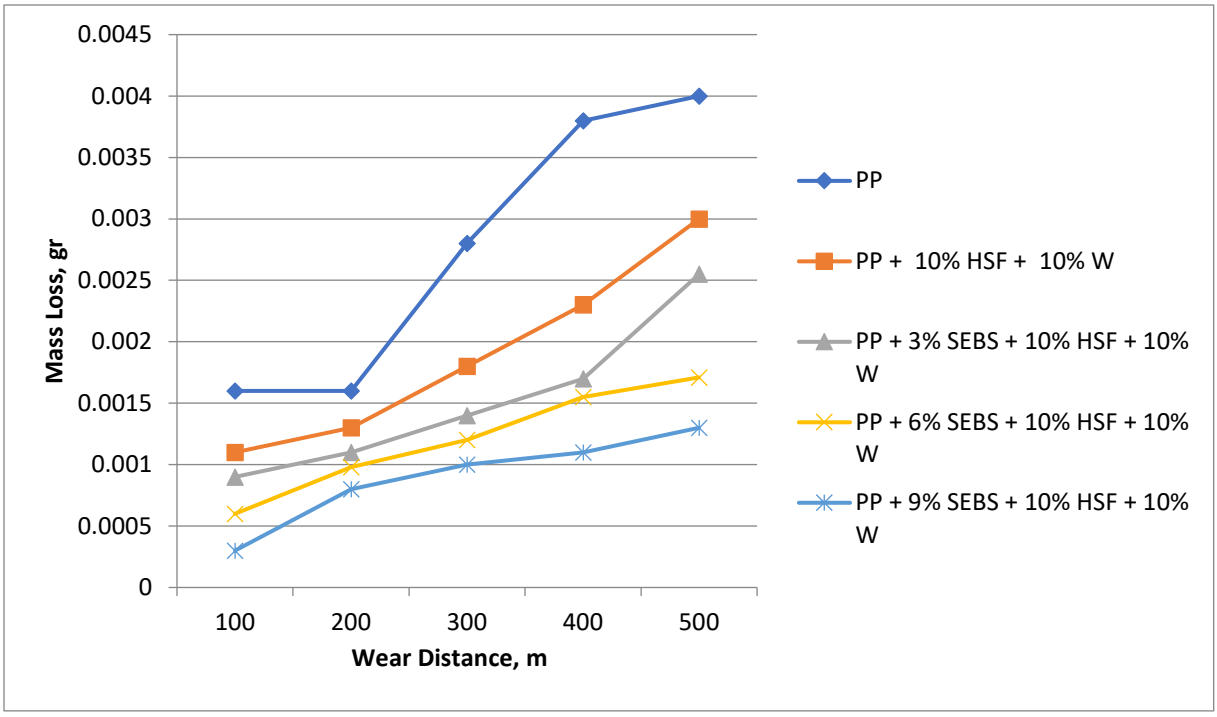

Figure 4. Mass Loss vs. Wear Distance for SEBS Modified Composites

Again, as seen in Figure 5 the mass loss of PP-HSF-W composite can be significantly reduced by the addition of SEBS-*g*-MA. This improvement can also be stemmed from the wear behavior of elastomeric materials.

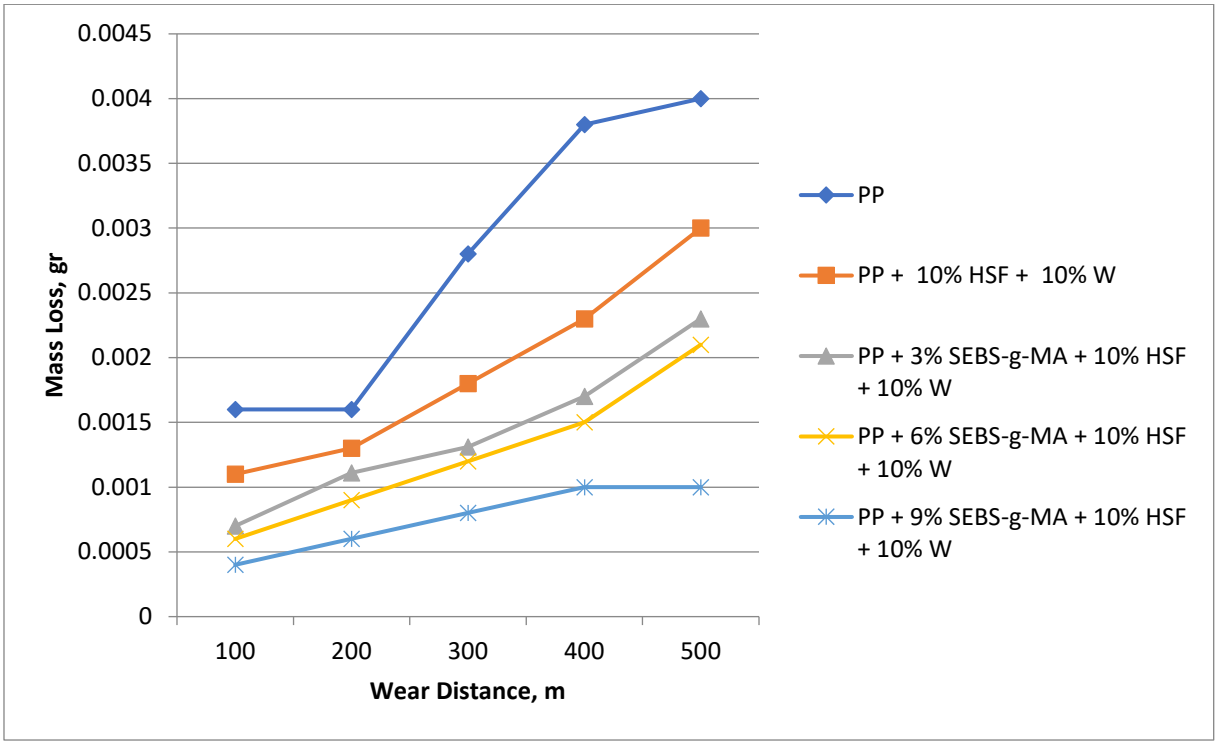

Figure 5. Mass Loss vs. Wear Distance for SEBS-g-MA Modified Composites

From Figure 6 it is clearly seen that the mass loss of SEBS-*g*-MA modified composites is lower than the SEBS modified composites. This difference is related to the differences in the adhesion behavior of these elastomers. Between the phases of hybrid composites, SEBS-*g*-MA exhibits stronger bonds than the SEBS modified ones.

Worn surfaces of 10% W + 10% HSF filled polypropylene hybrid composites, PP/W/HSF/SEBS hybrid composites, and PP/W/HSF/SEBS-*g*-MA hybrid composites were presented in Figures 7a, 7b, and 7c respectively. As clearly shown in Figure 7, the additions of the SEBS and SEBS-*g*-MA as elastomeric phases affected considerably the wear behavior of hybrid composites. The number of scratches and the scratch intensity reduced with the elastomeric additions.

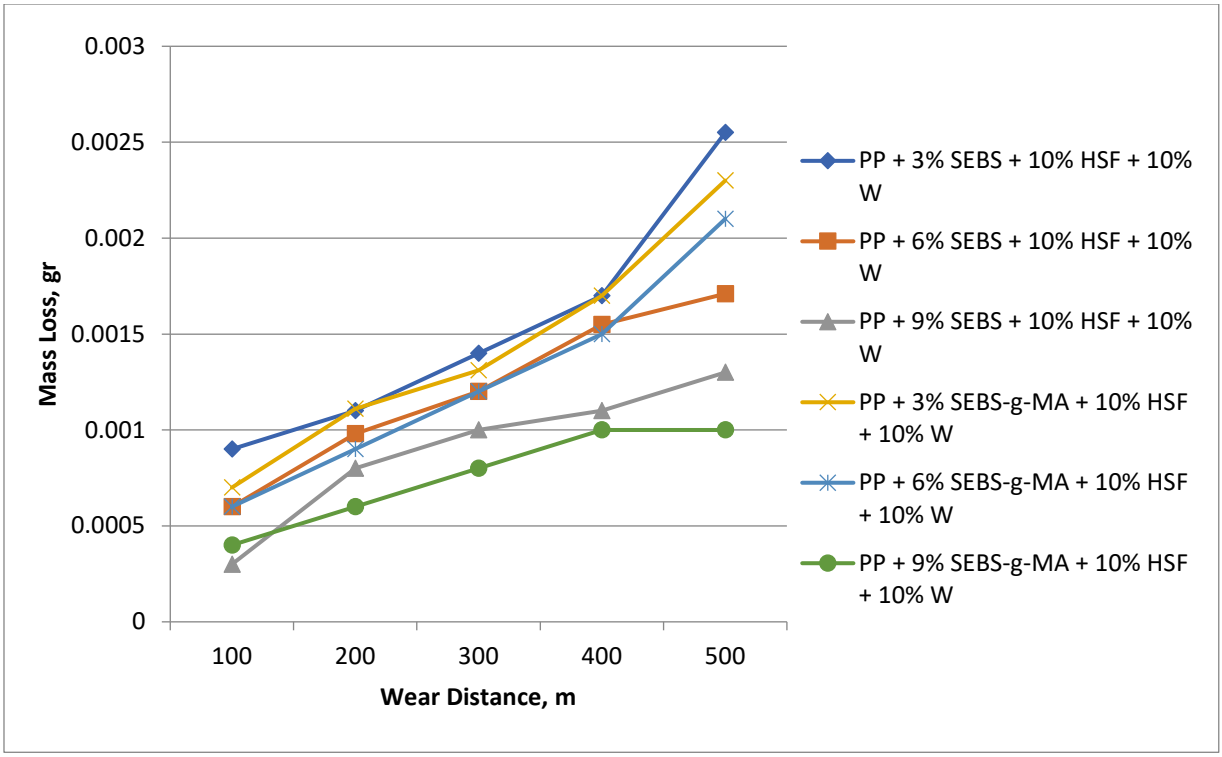

Figure 6. Mass Loss vs. Wear Distance for SEBS and SEBS-*g*-MA Modified Composites

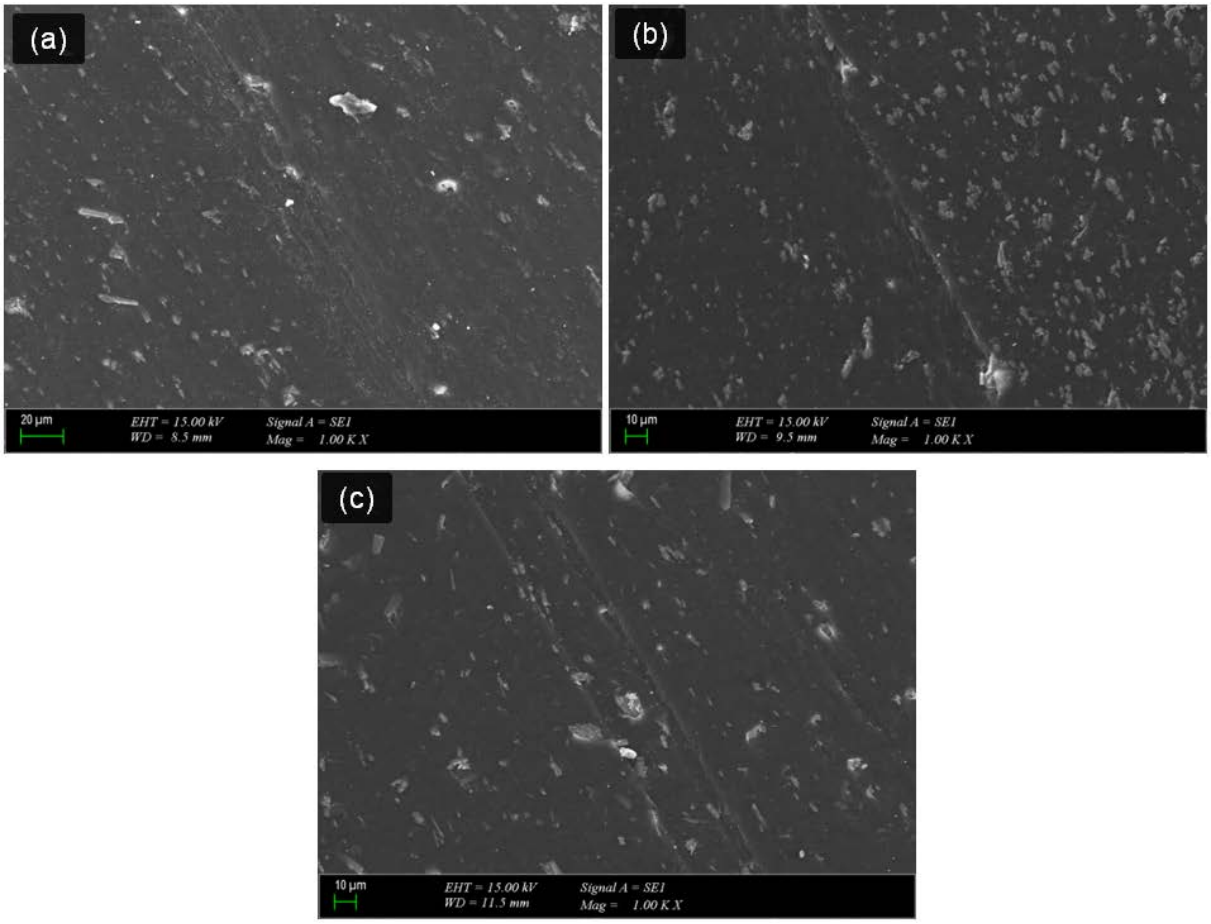

Figure 7. SEM Images of the Worn Surfaces of Hybrid Composites

IV. CONCLUSIONS

In this study, the effect of hazelnut shell, which is produced intensively in Turkey, on wear properties was investigated by using it together with inorganic filler in thermoplastic based composites. Hazelnut shell was used as an organic filler and wollastonite was used as an inorganic filler. From the above-mentioned data, the following conclusions can be drawn:

1. Pure PP has the lowest abrasion resistance
2. Only inorganic filled composite exhibited higher abrasion resistance than only organic filled composites
3. Elastomeric additions improved the abrasion resistance of hybrid composites
4. SEBS-g-MA modified composites exhibited lower mass loss than the SEBS modified composites due to the increases in bond strength of the constituent phases.

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Declaration of conflicting interests

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