

## IMPROVING THE INTERFACIAL PROPERTIES OF GLASS FIBRE REINFORCED AND UNREINFORCED WASTE SOURCED LOW DENSITY POLYETHYLENE/ACRYLONITRILE BUTADIENE STYRENE/POLYSTYRENE COMPOSITES

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This work is focused on compatibilization of immiscible waste sourced low density polyethylene (LDPE), acrylonitrile butadiene styrene (ABS), and polystyrene (PS) blends by different surface modifying routes. To reach better mechanical properties of the given reused waste blends 20% glass fibre was used. The ratio of waste LDPE/ABS/PS was 3.6/2.0/1.0 both in the presence and absence of glass fibre, while the applied concentration of the surface modifying routes was 1% in each case. Blends of raw materials had been manufactured by two roll mill, and specimens were obtained by the press moulded plates. The properties of samples were studied by mechanical testing. Results show that blending of the three kinds of waste polymers without compatibilizers resulted immiscible blends with poor mechanical properties. This could be significantly improved by the application of the commercial and synthetic surface treatment additives. Generally, favourable properties were found in the presence of 20% glass fibre. Especially AD-1 and AD-2 experimental and commercial  $\gamma$ -aminopropylsilane additives showed the best results.

**Keywords:** immiscible, compatibilizer, waste mechanical recycling, tensile strength

### Introduction

Owing to the increasing application of polymers, the utilization of wastes plastics causes serious challenges. According to reports the energetic utilization of polymer wastes were mainly investigated, such as incineration, chemical recycling, and/or mechanical recycling [1–7]. It is also well known that the industrially used plastics are not exchangeable with other constructional materials (glass, metals, etc.). Excess energy use and/or more greenhouse gas emissions would be incurred upon replacement of plastics with other materials. Therefore most of the key industrial segments, such as transportation, aviation, packaging, civil engineering, cannot function without polymers. From the 50s' the plastic industry went through a significant development, which is a reason for their wide-spread and diverse applications often for highly specific purposes. In the case of plastic composites, they provide alternative solutions to problems of increasing strength, maintaining compatibility and malleability [2, 4, 6–14].

The mechanical recycling of polymers is a reshaping process using waste polymeric materials or even the mixtures of unused and waste polymers. Basically the

waste polymer can be originated from two sources. In “closed-loop” recycling, the same product is manufactured from the same recycled components. For instance, the material of bottles (in some cases) can be recycled. In contrast, there is a recycling route, when the repeated remanufactured products are becoming less valuable [10–12, 15, 16]. A major challenge in mechanical recycling of polymers is immiscibility that leads to phase separation causing significant reductions in mechanical properties of the polymer mixtures. There are specific kinds of polymers that are immiscible with each other, such as polyolefin-PA, polyolefin-ABS, polyolefin-PET. Therefore, polymer blends may contain two phases, such as disperse and continuous.

Generally, the difference in chemical and physical properties of phases are the source of the above mentioned immiscibility problem. Therefore, coupling agents with special chemical structure can be used to create adequate chemical/physical interaction between the constituents of polymer mixtures. For this purpose grafted-MA or silane based compounds are widely used. These compatibilizers are able to increase the interfacial tension in boundary layer of polymer blends, which results in better chemical/physical interactions [17, 18].

Table 1: The main properties of waste polymers

	LDPE	ABS	PS
tensile strength, MPa	15.8±1.4	34.4±2.5	25.6±1.9
tensile modulus, MPa	420±33	1750±88	1720±95
elongation, %	351.5±35.5	4.7±0.3	189.6±10.2
flexural strength, MPa	-	29.0±2.2	21.0±1.7
flexural modulus, MPa	-	1820±79	1140±73
CHARPY strength, kJ mm <sup>-2</sup>	3.8±0.4	10.5±1.1	5.9±0.4

Table 3: Sample compositions without glass fibre in weight %

Sample No.	1	2	3	4	5	6	7	8
LDPE	55	54	54	54	54	54	54	54
ABS	30	30	30	30	30	30	30	30
PS	15	15	15	15	15	15	15	15
C-1	-	1	-	-	-	-	-	-
C-2	-	-	1	-	-	-	-	-
AD-1	-	-	-	1	-	-	-	-
AD-2	-	-	-	-	1	-	-	-
AD-3	-	-	-	-	-	1	-	-
AD-4	-	-	-	-	-	-	1	-
Peroxide	-	-	-	-	-	-	-	1

In this work, the feasibility of mechanical recycling of automotive industry waste mixtures of low-density polyethylene (LDPE), acrylonitrile butadiene styrene (ABS), and polystyrene (PS) were studied. The effects of various compatibilization techniques on mechanical properties of the prepared ternary ABS/LSPE/PS systems were studied.

## Materials and Methods

### Raw Materials

Waste polymers used as raw materials in our experimental work were selectively collected directly from automotive industry. The main properties of the plastic wastes are summarized in Table 1. The LDPE has the lowest tensile strength (15.8 MPa), which is followed by the polystyrene (25.6 MPa), and the ABS (34.4 MPa). Tensile modulus showed similar order as well. Due to the chemical structure of plastics, the LDPE had the highest elongation (351.5%), while ABS the lowest (4.7%). The average particle size for each tested plastic wastes were in the range of 4–5 mm, with moisture content of 0.7–0.8 %. Moreover, significant differences were noticed in the CHARPY impact strength of samples; because the maximum value was measured in the case of ABS (10.5 kJ mm<sup>-2</sup>), while the smallest regarding LDPE (3.8 kJ mm<sup>-2</sup>).

Table 2: The main of experimental coupling agents

	AD-1	AD-2	AD-3	AD-4
appearance	solid	dense liquid	solid	solid
side chain	C <sub>16</sub> -C <sub>18</sub>	polyisobutylene	styrene	C <sub>20</sub> -C <sub>22</sub>

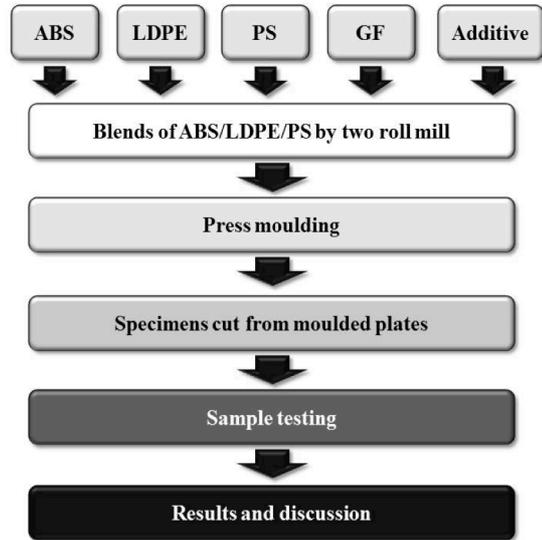


Figure 1: Sample preparation and testing

As known, blends of ABS and LDPE are immiscible phases in the most cases. Therefore, the mechanical properties of ABS and LDPE blend are significantly worse than that of the constituents, either ABS or LDPE. In order to enhance their properties, the interfacial forces must be improved between the constituents. In our work, different commercial and synthetic compatibilizers were used for improving the interfacial properties and decrease the interfacial tension of composites. Two commercially available compounds of  $\gamma$ -aminopropyl silane (C-1) (Aldrich Chemistry), and polyethylene grafted with maleic anhydride (C-2) (Viba Spa) were used as compatibilizer agents. The synthetic agents were maleic anhydride intermediates made from different olefins at the Department of MOL Hydrocarbon and Coal Processing, University of Pannonia with significantly different physical and chemical properties. The main properties of the four additives are summarized in Table 2.

### Sample Preparation

Blends of waste LDPE/ABS/PS were prepared by two roll mill. Then sample plates were manufactured by press moulding. Fig.1 demonstrates the flow of the experimental work.

For composite manufacturing a Labtech two roll mill (Labtech Ltd, Thailand) was used. The temperatures of the rolls were 170 °C and 190 °C with friction ratio of 0.5. The compositions of samples are summarized in Tables 3 and 4.

In selected cases E-type unsized glass fibre with 4–5 cm average length was also added to the composites in its 20%. The E-type GF was produced by Ovens

Table 4: Sample compositions with glass fibre in weight %

Sample No.	10	11	12	13	14	15	16
LDPE	43	43	43	43	43	43	43
ABS	24	24	24	24	24	24	24
PS	12	12	12	12	12	12	12
GF	20	20	20	20	20	20	20
C-1	1	-	-	-	-	-	-
C-2	-	1	-	-	-	-	-
AD-1	-	-	1	-	-	-	-
AD-2	-	-	-	1	-	-	-
AD-3	-	-	-	-	1	-	-
AD-4	-	-	-	-	-	1	-
Peroxide	-	-	-	-	-	-	1

Corning and it contained mainly SiO<sub>2</sub>, CaO and Al<sub>2</sub>O<sub>3</sub>. The ratio of waste LDPE/ABS/PS was 3.6/2/1 both in the presence and absence of glass fibre, while the applied concentration of the additives was 1% in each case. The additives were directly added to the molten polymer during the sample sheet manufacturing. In two cases organic peroxide (di-*tercier*-butyl-peroxide) was used to modify the interfacial surface of composites.

The sample blending composites were press moulded at 180 °C using 6.8 ton loading and then specimens with dimension of 1 mm x 10 mm x 100 mm were cut from the composite plates.

#### Determination of Tensile Strength

The tensile properties of the composites were determined by Instron 3345 universal tensile machine using 90 mm/min crosshead displacement rate. During the tests, the ambient temperature was 23 °C, and the relative humidity was 35 % in all cases. Preloading was not applied.

#### Determination of Flexural Strength

The three point flexural tests were performed by also the before mentioned Instron 3345 universal tensile tester. The crosshead displacement rate was 20 mm min<sup>-1</sup> in all cases.

#### Determination of Charpy Impact Properties

A CEAST Resil IMPACTOR was used for determination of Charpy impact strength. The machine was equipped with a 4J hammer, while the specimens were cut.

## Results and discussion

### Tensile properties

Fig.2 compares the tensile strength of samples. It can be seen that the tensile strength has changed in the range of

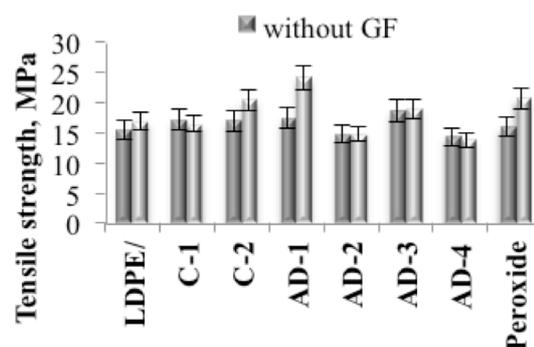


Figure 2: Tensile strength of samples 13.8 and 24.1 MPa. However, the reinforced composites

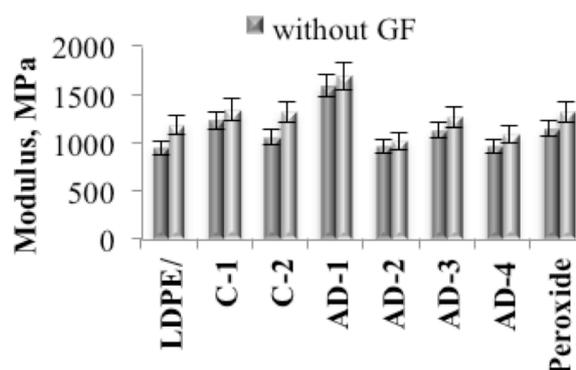


Figure 3: Tensile modulus of LDPE/ABS/PS samples

have significantly better resistance against constant tensile loading (13.8–24.1 MPa), than that of unreinforced (14.2–18.5 MPa). According to data the highest values were obtained in the case sample containing A-1 surface modifier agent in the presence of GF (24.1 MPa), while that was the highest in using AD-3 additive without GF (18.5 MPa).

From Table 1, the raw materials had 34.4 MPa (ABS), 25.6 MPa (PS) and 15.8 MPa (LDPE) tensile strength. On the contrary, the untreated LDPE/ABS/PS composites have tensile strength of 15.3 MPa without fibres, and 16.8 MPa in the presence of 20% glass fibre. It means that presumably owing to the immiscible phases the LDPE/ABS/PS composites without surface modifying additive has lower strength than its constituents. In three samples (C-1, AD-2, and AD-4) the tensile strength of glass fibre free, but treated composites was lower than that of untreated. This is probably due to the reason of the additive has been disadvantageously altered in surface characteristics of the plastic mixture. The largest increase in the tensile strength occurred for AD-1 (+12%) and AD-3 (+21%) additives without GF, while the peroxide (+23%), and AD-1 (43%) samples have resulted the best properties using 20% glass fibre, as well.

The Young's modulus, as the measure of the elastic property of sample, changed in the range between 1015 and 1685 MPa in the presence of glass fibre, while the values were between 937 and 1579 MPa without GF reinforcing (Fig.3). The maximum value of tensile modulus was found by the using AD-1 surface treating agent both presence and absence of GF (1579 MPa and

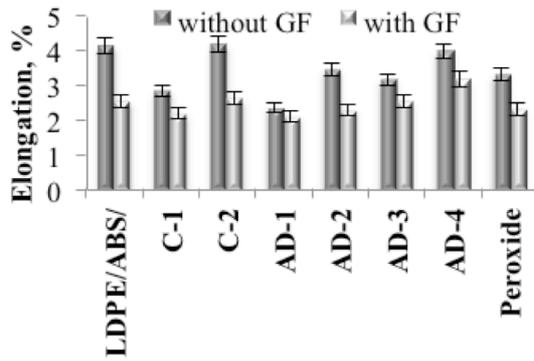


Figure 4: Elongation of samples measured at tensile test

1685 MPa). On the basis of data in Table 1, the tensile modulus of LDPE, ABS and PS raw materials were 420, 1750 and 1720 MPa, respectively. The untreated LDPE/ABS/PS samples had significantly lower tensile moduli with 937 MPa and 1173 MPa in the presence and absence of GF, respectively. Presumably it was the consequence of the phase separation occurring the immiscible polymers. The compatibility of immiscible polymer blends could be significantly improved by the above mentioned additives, because not only the tensile strength, but also the tensile modulus was significantly increased e.g. by the application of AD-1 additive (+44% with GF and +69% without GF). In general, the tensile modulus was higher in the presence of glass fibre than without that.

The relative elongation refers to the change in sample length during the tensile tests. Rigid materials (polyamide, ABS, etc.) have low value of elongation, while that of significantly higher in case of soft or rubber like elastic polymers (polyethylene, PP, PS, rubber, etc.).

The relative elongation (Fig.4) follows the opposite trends than tensile strength or modulus. It is changed in the range of 2.33 and 4.29% without GF, or 2.09 and 3.16% with GF. It means that the glass fibre presence resulted lower values of relative elongation. The surface treating agents have only slight effect to the elongation apart from AD-1 sample, because the difference between the treated and untreated samples was 63% in case of AD-1. In any other cases this value was less than 20%.

#### Flexural Properties

Results from flexural tests are summarized in Figs.5 and 6. The flexural strength was in the range of 17.3 and 22.6 MPa in case of GF reinforced LDPE/ABS/PS composites and between 13.7 and 19.9 MPa in case of unreinforced specimens. The best result was found when the interfacial surface of LDPE/ABS/PS composite and/or the glass fibre surface were modified by AD-3 additive (22.6 MPa). In the presence of AD-3 additive the unreinforced LDPE/ABS/PS blend had 19.9 MPa flexural strength value. Generally, the tensile properties were favourable in case of reinforced, than that of unreinforced samples. According to Table 1, the waste ABS and PS raw materials had flexural strength

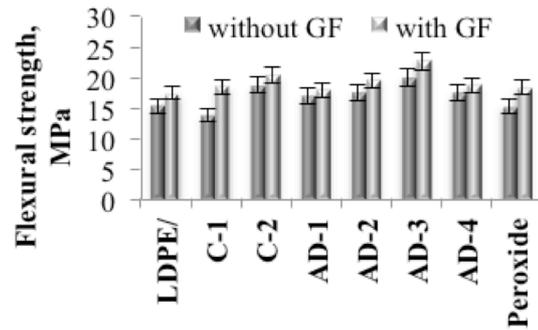


Figure 5: Flexural strength of LDPE/ABS/PS samples

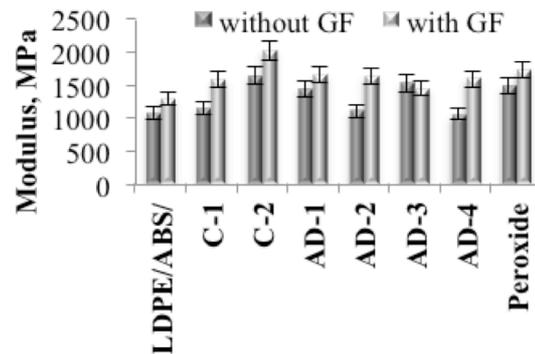


Figure 6: Flexural modulus of ABS/LDPE/PS samples

of 29.0 MPa and 21.0 MPa, respectively. On the other hand, the flexural strength of unreinforced LDPE/ABS/PS was 15.3 MPa, which can be increased to 17.3 MPa in the presence of GF. It means that the flexural strength was below the lowest value of constituent (PS, 21.0 MPa) even in the presence of GF. Comparing tensile and flexural strength, it can be concluded that the effect of the surface modifying agents were more significant to the tensile than to the flexural properties. The negative effect of surface modifying agents was observed in some cases. For instance, flexural strength was reduced in case of C-1 and peroxide additives. Regarding the flexural strength the largest increase occurred in the presence of AD-3 (+30%) and C-2 (+22%) additives without glass fibre reinforcements. The increasing in flexural strength was 30% (without GF) and 31% (with GF) in case of AD-3 additive, while that of was 22% (without GF) and 17% (with GF).

Regarding flexural modulus, similar results were obtained as discussed above. ABS and PS raw materials have 1820 and 1140 MPa flexural modulus, respectively. According to Fig.6, the flexural modulus was 1080 MPa and 1285 MPa in case of unreinforced and reinforced LDPE/ABS/PS composite without surface treating agents. The flexural modulus indicates the rigidity. Higher modulus means greater rigidity. Results demonstrate that the flexural modulus changes in the range 1285 and 2015 MPa in the presence of GF, whereas values were between 1040 and 1637 MPa in case of the non-reinforced composites. The maximum value of flexural modulus was given specimens

containing C-2 surface treating additives both with and without glass fibres.

### CHARPY Impact Strength

The CHARPY impact test determines the amount of energy absorbed by a material during fracture. Fig.7 summarizes the CHARPY impact strength of samples as a function of surface treatment additives. The impact strength of the samples ranged from 4.7 to 9.1 kJ mm<sup>-2</sup>, in which reinforced composite materials was between the higher range of 5.9 and 9.1 kJ mm<sup>-2</sup>. The highest value was in a sample including AD-1 surface modification agent, and glass fibre (9.1 kJ mm<sup>-2</sup>). In case of the same additive without reinforced fibre the impact strength was 7.1 kJ mm<sup>-2</sup>.

Results show that the impact strength could be increased in each case due to surface treatment. The impact strength of LDPE/ABS/PS composite was 4.7 kJ mm<sup>-2</sup> without reinforced and 6.8 kJ mm<sup>-2</sup> in reinforced by glass fibres. The largest growth was observed in the case of the sample containing C-2 (+53%) and AD-1 (+51%) additives for samples without glass fibres. Contrary, the least growth was observed in the case of the sample containing AD-2 (+4%) additives. Regarding the GF reinforced samples, the largest growth was observed when the AD-1 (+34%) and C-2 (+29%) additive were used. Only the AD-2 additive resulted in lower impact strength, than ABS/LDPE/PS excluding any additive (-13%).

### Conclusion

In this paper the efficiency of different compatibilizers in waste sourced LDPE/ABS/PS composite were investigated both in absence and presence of 20% E-type glass fibre. It was found that both the tensile and flexural properties of samples could be significantly improved by both synthetic and commercial coupling agent. The tensile strength and elastic modulus were the best when AD-1, a C<sub>16</sub>-C<sub>18</sub> olefin containing polyakanyl polymaleic anhydride compatibilizers and 20% GF were applied. Thus, compared to the LDPE/ABS/PS composite without glass fibre and surface modifying additives, the tensile strength showed 58 %, and the elastic modulus showed an 80 % increase. Regarding flexural properties similar result were observed, but not with AD-1, rather than AD-3, a polyakanyl polymaleic anhydride additive that resulted in the best properties, such as increase of 22.6 MPa in flexural strength. CHARPY impact strength increase was the largest (9.1 kJ mm<sup>-2</sup>) in a sample containing AD-1 agent in the presence of glass fibres, which converts to about 90% increase relative the LDPE/ABS/PS blend without GF and compatibilizing additives. Synergistic effect of glass fibres and some of the compatibilizers can lead to increase of CHARPY impact strength by 94% in comparison to unmodified LDPE/ABS/PS sample.

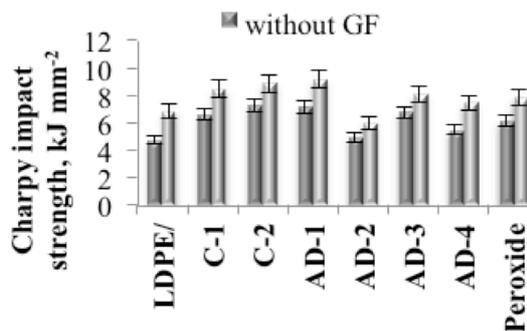


Figure 7: Charpy impact strength of LDPE/ABS/PS samples

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