Recycling of ABS and ABS/PC Blends

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ABSTRACT: The aim of this work within the framework of mechanical recycling of polymers is upgrading recycled engineering plastics by means of a blending technique. Four different plastics from dismantled Volvo cars have been investigated. They are poly(acrylonitrile-butadiene-styrene) (ABS) and ABS-polycarbonate (ABS/PC) as major components and poly(methyl methacrylate) (PMMA) and polyamide (PA) as minor components. Blending recycled ABS and PC/ABS (70/30) with a small amount of methyl methacrylate-butadiene-styrene core-shell impact modifiers gives the mixture better impact properties than any of its individual components. Some 10% of PMMA from tail light housings can follow the PC/ABS blends made. The property profile will rather be improved. However, PA is an incompatible component that should be sorted out from the mixture. Antioxidants and metal deactivators do not help the recyclates show better mechanical properties. Two toughness measurements, Charpy impact strength and J-integral method, show complimentary results for such blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 510–515, 1999

Key words: engineering plastics; mechanical recycling; blending; impact strength; J-integral method, compatibilizer

INTRODUCTION

In the last decades a great deal of attention has been focused on recycling of plastics, both post-consumer commodity products and engineering plastics. In this project we are concentrated on the upgrading of engineering plastics.

The global figure of dismantled cars was around 24 million in 1995, generating 2.2 million tons of plastics scrap.[1] The engineering plastics from dismantled cars contain poly(acrylonitrile-butadiene-styrene) (ABS), polycarbonate (PC), and other engineering plastics like poly(buthylene terephthalate) (PBT), poly(ethylene terephthalate) (PET), polyamide (PA), poly(methyl methacrylate) (PMMA), and so on. Among these plastics, ABS is among the cheapest but has the largest amount. The main problem for recycling ABS is the oxidative degradation of the butadiene rubber phase during service time. Due to this, ABS loses the impact strength that is its most important property.

In a car dismantling plant, the plastic scraps are sorted manually by material type. The workers want to decrease the number of containers for different plastics. It is of interest to find possibilities for mixing different plastics without losing mechanical properties, for example, a mixture of ABS and ABS/PC blends. It is also important to find possibilities to upgrade the average properties of the mixture, especially toughness, by adding minimum amounts of compatibilizer or impact modifier.

Previous work[2] showed that the impact strength of artificially or naturally aged ABS could be improved by mixing with 20% of neat PC and 5 to 10

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Table I Identification of Plastic Scraps B in the First Batch

Sample	Solubility	DSC Results
1	Soluble	Blunt transition around 105°C
2	Not Soluble	Sharp transition around 135°C, a small transition around 105°C
3	Not Soluble	Sharp transition around 134°C, a small transition around 107°C
4	Soluble	Blunt transition around 103°C

phr methyl methacrylate-butadiene-styrene (MBS) core-shell modifier. The Charpy impact strength of this system was 20 to 60% higher than those without core-shell modifier. Since the core-shell modifier will improve the interfacial adhesion between ABS and PC, and retard the coalescence of dispersed phase, it acted also as a compatibilizer.

In current work two kinds of plastics from dismantled cars, which are initially considered as ABS and ABS/PC blend respectively, and the effects of MBS core-shell impact modifiers are studied. The influence of small amount of other engineering plastics like PMMA and PA are also investigated. A relatively new method for characterizing the toughness, the J-integral method, has been carried out, as well as the "classic" Charpy impact strength test. These two methods are complimentary for these material systems.

Materials

The recycled materials are all from dismantled Volvo 700 series cars. They are ABS (coded A), PC/ABS blend (coded B), PMMA, and PA, shredded in a knife mill into pellets about 5 mm in size.

Different analytical measurements were used to identify the composition of recycled material. The solubility and differential scanning calorimetry (DSC) results in Table I indicate that the first batch of "Bayblend"-type plastic scraps from Volvo were actually a mixture of ABS and PC/ABS blend. Four kinds of parts have been studied. According to the results in Table I, samples 1and 4 were ABS, and samples 2 and 3 were "Bayblend"-type ABS/PC blends.

Electron spectroscopy for chemical analysis (ESCA) and energy dispersive spectrometry (EDS) study did not detect halogen or metal elements in the recycled materials. DSC measurements showed that the recycled PA has two melting peaks around 220 and 260°C, corresponding to PA6 and PA66. Scanning electron microscope (SEM) observation showed that the recycled PA was glass fiber reinforced.

Size exclusion chromatography (SEC) and infrared spectroscopy (IR) techniques were also employed to detect possible degradation products of PC. There was not very pronounced evidence showing existing of degradation products.

The pristine ABS Terluran 967 K from BASF (Ludvigshafen, Germany), and PC Makrolon 2800 and Bayblend T45 from Bayer (Leverkusen, Germany) are used as references in this study. The impact modifier used is Paraloid EXL 3647 from Rohm & Haas (Philadelphia, USA). It is a highly stabilized MBS core-shell impact modifier and has the particle diameter 0.1 to 0.2 μm. The glass transition temperature (T_g) of the rubber phase is -70°C. The random copolymer styrene-maleic anhydride (SMA) with 8% of maleic anhydride by weight, Dylark 232 from Arco (PA, USA), is used as compatibilizer for nylon-containing blends. Stabilizers from Ciba (Basel, Switzerland), like phenolic antioxidant Irganox 1076 and metal deactivator Irganox MD1204, are also tried.

EXPERIMENTAL

Compounding and Forming

All the materials were dried in a hot air-circulated oven at 105°C for 6 h before compounding. Blends were prepared in a corotating twin-screw extruder, Werner&Pfleiderer ZSK 30 M 9/2. The screws have the configuration for best mixing efficiency. The processing was carried out at temperature 240°C and screw speed 200 rpm. The extrudates were pelletized with a granulator.

Test specimens were injection molded with an ENGEL 330/80 machine at melt temperature 240°C and mold temperature 50°C.

Mechanical Property Characterization

Tensile properties were measured with Zwick UTM 1455. The yield strength, E modulus, and elongation at break were characterized at a cross-

Table II Results from Pristine Materials

Composition	E, GPa	Yield Strength, MPa	Elongation at Break, %	Notched Charpy, kJ/m^2	J_C, kJ/m^2
ABS	2.3	37.8	17	11.3	9.1
ABS/PC 80/20	2.1	41.8	14	6.42	8.2
ABS/PC 80/20 + 5 phr MBS	1.9	38.7	19	11.6	11.8
ABS/Bayblend 50/50 + 5 phr MBS	2.1	42.7	21	17.5	9.3

head speed of 5 mm/min. The Charpy impact strength was determined by Zwick Pendulum impact tester 5110, according to ISO 179 specimen type 2, at temperature 21°C.

The J-integral measurement has been described in more details elsewhere.[3] The J_C values in this work represent the energy required for a crack to start to propagate.

SEM

The fracture surface of the specimen was observed in a SEM Zeiss DSM 940A. The specimen surfaces were coated with a thin layer of gold, about 50 Å thick.

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties of pristine materials and their blends are shown in Table II. A mix of 20% PC with ABS will depress the mechanical properties, especially Charpy impact strength and J_C value. This result is in agreement with Paul and colleagues,[4] who showed that ABS/PC blends with ABS as a majority component has lower impact strength than neat ABS. The toughness and processibility reach an optimum only when the PC content is around 70%. Only 5 phr MBS can improve the toughness of neat ABS/PC (80/20) blend and change the figure proposed in ref. 4. E modulus decreases only slightly. More improvement of toughness shows in ABS/Bayblend 50/50+5phr MBS blend.

Two batches of recycled ABS and ABS/PC plastics from dismantled Volvo cars have been tested. For the first batch as shown in Table III, the ABS (A) or ABS/PC (B) itself does not have very good toughness. However, mixing A and B with 5phr of MBS impact modifier can improve Charpy impact strength, as well as J_C value, by 20%. If we assume the composition of B is ABS/PC 30/70, in the range of most commercial ABS/PC blends, then the composition of A/B 50/50 will be ABS/PC 65/35. Furthermore, if MBS is added to B only, that is, ABS/PC around 30/70, a dramatic increase in toughness, as reflected by Charpy impact test, is seen.

It has been shown[2,5,6] that MBS particles would be trapped at the interface of PC/styrene-acrylonitrile (SAN) by surface tension. Such particles can initiate and extend the local shear yielding of PC phase, as well as retard the coalescence of the dispersed phase during processing. Therefore, they are in a certain sense acting as compatibilizer for ABS/PC blends. Paul and colleagues[6] showed that if the PC/SAN was mixed before the adding of the MBS, 90% of MBS will locate at interface. When mixing the three com-

Table III Mechanical Properties of First Batch of Recycled Plastics

Composition	E, GPa	Yield Strength, MPa	Elongation at Break, %	Notched Charpy, kJ/m^2	J_C, kJ/m^2
A	2.4	39.2	12	7.4	5.1
A/B 50/50 + 5 phr MBS	2.3	40.9	14	9.8	5.7
B	2.4	46.1	12	6.5	5.5
B + 5 phr MBS	2.3	43.2	20	12.4	7.4

Table IV Mechanical Properties of 2nd Batch of Recycled Plastics

Composition	E, GPa	Yield Strength, MPa	Elongation at Break, %	Notched Charpy, kJ/m^2	J_C, kJ/m^2
A/B 50/50 + 5 phr MBS	2.1	43.6	15	10.0	6.0
A/B 50/50 + 5 phr MBS + stabilizers	2.2	43.5	10	7.2	4.6
B + 5 phr MBS	2.0	42.9	39	28.3	10.6
A/B/PMMA 45/45/10 + 5 phr MBS	2.3	45.8	26	9.7	7.8
A/B/PMMA/PA 40/40/10/10 + 2 phr SMA + 5 phr MBS	2.7	49.3	10	6.6	6.8
A/B/PMMA/PA 40/40/10/10 + 2 phr SMA + 5 phr MBS + stabilizers	2.7	48.8	10	6.5	8.1

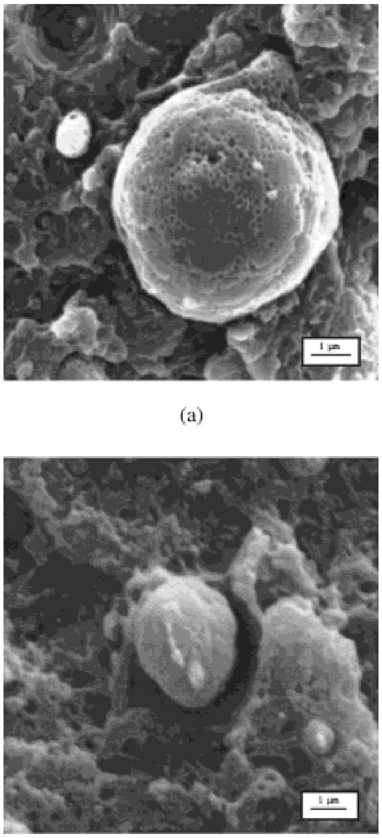
ponents simultaneously, the MBS particles would primarily stay at the interface, less in PC phase, but very few in the SAN phase. Thus the situation of mixing A and B with MBS simultaneously will be the case in between.

In the second batch as shown in Table IV, the blend of A/B/MBS 50/50/5 shows properties similar to that from the first batch. The blend of B + 5phr MBS shows even better toughness with respect of Charpy impact strength, J-integral value, and elongation at break. The reason is that this "Bayblend" type of plastic has been carefully sorted, in comparison to the first batch. The "B" plastic in first batch was actually a mixture of ABS and "Bayblend" type of ABS/PC blend.

It has been suspected if there was oxidative degradation of A during the reprocessing, or degradation of B due to the possible existence of metal ions from A.[7] So 0.5 phr of antioxidant Irganox 1076 and 0.5 phr of metal deactivator MD1204 were added to the system. The metal deactivator can react with metal ions and form complex, shielding the harmful metal ions that cause degradation of PC during processing. However, there is no improvement of mechanical properties by adding these stabilizers, but rather a depression in toughness. Such a result indicates that the degradation during reprocessing is not a severe problem in this case. The influence of phenolic and phosphite antioxidants on the mechanical and processing properties of ABS/PC 30/70 blends has been studied by Yan and colleagues.[8] For such blends with antioxidants, decrease of the Izod impact strength and tensile modulus were reported. However, the melt flow index (MFI) increased dramatically. Elongation at break also increased if the amount of antioxidant was less than 0.7%. The authors concluded that as little as 0.1 to 0.4% of such an antioxidant would change the blend morphology from dual continuous to ABS as a dispersed phase. The ABS phase became more scattered and greater with increasing the phosphite antioxidant content. Since the antioxidants do not have good miscibility with polymer matrices, they will stay at the PC/ABS interface and increase the interfacial tension. Thus, even very small amounts of antioxidants will change the morphology. Such a morphology change was the reason for property changes.

The addition of 10% of PMMA to the A/B/MBS blend does not depress the mechanical properties due to the fact that PMMA is mutually miscible with SAN, depending on the AN level, and compatible with PC. The elongation at break and the J_C increase to some extent, so there might be a certain enhancement of interfacial adhesion between ABS and PC by adding PMMA.

The addition of PMMA and PA to the A/B system is a complicated situation because PA is miscible to none of other three components. Styrene maleic anhydride with 8% maleic anhydride (SMA8) is introduced to the system as a compatibilizer. SMA8 reacts with PA at processing temperature and has some interaction with the other three components. It is expected that the interfacial tension of PA towards the other three will be decreased. In fact, rubber-modified SMA such as SMA/ABS blend, which has similar mechanical properties as ABS, has been used recently for producing the plastic parts in the car. It can work at temperature between 120 and 135°C.[9] Thus SMA can be one component of recycled automotive plastics in the future. Due to the presence of glass fiber reinforced PA, the modulus and yield strength increase; so does the J_C. However, the notched Charpy impact strength decreases. The presence of 0.5 phr of antioxidant Irganox 1076 and 0.5 phr of metal deactivator MD1204 in such



(a)

(b)

Figure 1 SEM fractography of impact fracture surface of (a) A/B/MBS 50/50/5 and (b) A/B/PMMA/MBS 45/45/10/5.

a four-component blend does not lead to any improvement on Charpy impact strength but some enhancement on J_C value.

Morphology

In Figure 1(a), an impact fracture surface of an A/B/MBS 50/50/5 blend is shown. The craters of the MBS compatibilizer (0.1 to 0.2 μm) can be found on the surface of the bigger particles of diameter up to 3μm, which are believed to be polycarbonate. However, the presence of 10% PMMA in the A/B/PMMA/MBS blend changes the morphology at PC/ABS interface [see Fig. 1(b)]. It is important to note that the mechanical properties are improved by the introduction of the 10% of PMMA. Fewer particles were found on PC surface; instead there is another phase attached on the PC phase, probably the PMMA. The MBS particles have a PMMA shell, and thus a redistribution of them is expected. An encapsulation of them is probable. Paul and colleagues reported that in a PC/PMMA/MBS 60/30/10 blend, the MBS particles would reside in PMMA phase. The interfacial tension between PMMA and PC is 0.17 $\times 10^{-3}$Nm^{-1} at 270°C, 0.48 $\times 10^{-3}$Nm^{-1} between SAN25 and PC, and 0 Nm^{-1} between SAN25 and PMMA since they are fully miscible.[6] It is therefore logic to presume that there is a PMMA-rich interphase between PC and SAN in the A/B/PMMA/MBS 45/45/10/5 blend and that the MBS particles reside in the interphase.

If 10% of PA also is added to the ABS/PC/PMMA blend, the property profile becomes deteriorated. The PA added here from the car dismantling are glass fiber reinforced grades of both PA6 and PA66. SMA8 is also added to provide some compatibilization between PA and SAN. When looking on the fracture surface of the blend, a large number of channel-like holes in the material become visible. In most of the holes a glass fiber is found. From Figure 2 we can see the glass fiber originally from PA in a channel-like hole of about 20 to 30 μm diameter. The unbounded fiber has a typical diameter of 10 μm. Therefore the glass fibers act as flaws or voids. This is at least partially responsible for the low impact strength of A/B/PMMA/PA/MBS/SMA8 40/40/10/10/5/2 blends. The fiber/matrix debonding was seen in a PC/ABS 80/20 blend with 10%wt. glass fiber content,[10] which indicates a weak fiber/matrix interface. The PA can not be seen on the glass fiber surface; this is probably due to the fact that PA6 has lower viscosity at processing temperature, thus being wiped from the glass fiber surface.

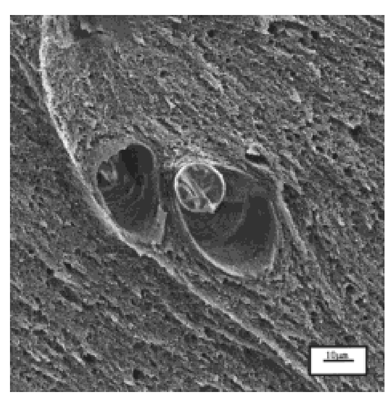


Figure 2 SEM fractography of impact fracture surface of A/B/PMMA/PA/SMA8/MBS 40/40/10/10/2/5 shows unbonded glass fibers in channel-like holes.

CONCLUSIONS

Toughness is one of the main concerns of recycled engineering plastics. Four different plastics from dismantled Volvo cars have been investigated. They are ABS and ABS/PC as major components and PMMA and PA as minor components. Blending recycled ABS and PC/ABS (70/30) with small amount of MBS core-shell impact modifiers gives the mixture better impact properties than any of their individual components. Some 10% of PMMA from tail light housings can follow the PC/ABS blends made. The property profile will rather be improved. However, PA is an incompatible component that should be sorted out from the mixture. Compatibilization effects with SMA8 did not result in satisfying properties. Antioxidants and metal deactivators do not help the recyclates show better mechanical properties. Two toughness measurements, Charpy impact strength and J-integral method, show complimentary results for such blends.

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