Quality Assurance of Recycled Engineering Plastics Using Blend Technology

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Abstract: The automotive, electrical and electronic sectors account for over 12 % of all plastics consumed. A large fraction of these polymers are engineering plastics representing a value considerably higher than that of commodity thermoplastics; hence, mechanical recycling including upgrading efforts appears economically attractive. This paper shows some methods of upgrading the property profile of ABS from dismantled automobiles using polymer blend technology. The results for blends of ABS with PC or PA are reported. The aim of blending of the waste materials is twofold: to reduce the number of plastic materials to be recycled in car dismantling plants, and to improve properties of the ABS scrap, which is the main engineering plastic in the waste stream from automobiles.

INTRODUCTION

An 8 % growth in plastics use has been revealed in a study on plastics consumption and recovery launched by APME (Association of Plastics Manufacturers in Europe). The figures relating to 1994 show plastics consumption at 26.26 million tonnes compared with 24.36 million tonnes in 1993, confirming that plastics are increasingly the material of choice.

Households remain the greatest end users of plastics, followed by the building and construction sector. The automotive, electrical and electronic sectors account for over 12 % of all plastics consumed. The following table shows the total plastics consumption by the end-use sector (Western Europe, 1994):

Households	45.3 %
Distribution	12.0 %
Automotive	7.1 %
Electrical and electronic	5.2 %
Large industry	4.8 %
Agriculture	3.7 %

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The APME study shows the use of *different recovery routes for plastics waste*, as illustrated in Figure 1, and confirms that an integrated waste management policy remains a priority in order to increase total recovery. The total plastics waste is approximately 14 million tonnes, and less than 20 % of the plastics waste is recycled today. *Energy from waste* is the most used method of recovery, treating 13.4 % of the total waste, and should be used for mixed plastics waste containing dirt. *Mechanical recycling* of plastics waste increased by more than 22 % to 1.1 million tonnes in 1994, representing 8 % of the total plastics waste. Plastics waste disposal figures for the automotive industry show that only 5 % of the plastics waste is treated by mechanical recycling, 2 % is recovered as energy and 93 % is used as landfill. Therefore, the automotive industry is promoted to find routes alternative to landfill for recycling of plastics waste. *Feedstock recycling* is treating 0.3 % of the plastics waste, but is gaining a foothold and increased to 50 000 tonnes in Germany by 1994; its potential is still to be recognized.

Plastics Recovery

Materials Recycling
Reprocessing plastics waste for use in its original form or for other purposes

Energy Recovery
Generating energy from plastics waste combusted with or without other waste, by recovering the heat

Mechanical Recycling
Physical reprocessing of plastics waste into new plastics products

Feedstock Recycling
Chemical reprocessing of waste into basic chemicals, monomers or hydrocarbon feedstock

Figure 1. Options available for plastics recovery

Of the three methods of recycling, mechanical recycling is a straightforward and easy method of recycling as long as the plastics waste is clean and well defined. Another advantage of mechanical recycling is that it conserves natural resources and reduces the amount of waste disposal in landfill. There are, however, several problems associated with mechanical recycling to be solved in order to ensure the broad use of recycled plastics. Therefore, there is a need for intensified research on mechanical recycling. We have studied two specific problems in connection with mechanical recycling:

- loss of properties during the use of plastic products and in connection with reprocessing of the plastics waste, and
- quality assessment of plastics waste

The objective of our Swedish research project, funded since 1992 by a governmental institution, the Swedish Waste Council, is to reduce or bypass these two problems. The study involves joint research between Chalmers University of Technology (Gothenburg) and two institutes, the Swedish National Testing and Research Institute (SP, Bor•s) and the Swedish Institute for Fibre and Polymer Research (IFP, Mölndal). The work programme consists of the following four important topics:

- possible use of blending technologies in order to improve properties of recycled engineering plastics;
- systematic investigation of the mechanisms involved in degradation processes, both during the use of plastic products and at the reprocessing stage;
- development of methods for measuring the antioxidant content in polymers, and
- quality assessment of polymer recyclates.

Parts of this ongoing project have been published (Refs. 1-4).

Recycling of engineering polymers

Several processes have been developed to recycle commodity plastics into cheap products (Refs 5-8), but only few papers deal with recycling of the more valuable engineering polymers. An excellent study of mechanical recycling of glass-fibre-reinforced polyamide 66 has been presented by Eriksson (Ref. 9), and various methods of polymer modification and compatibilization have been summarized by Bisio and Xanthos (Ref. 5). Adding fillers and cellulose or glass fibres is a method of improving mechanical properties of PP scrap (Refs. 8, 10, 11). Impact modification of ABS scrap by compatibilization with PPE/PS (Noryl®) has been studied by Scobbo (Ref. 12). The effects of repeated reprocessing on properties of ABS, PC and PC/ABS blends have been investigated earlier (Ref. 13). The impact strength of both ABS and PC/ABS blends decreases on reprocessing. PC and ABS are not miscible but compatible and are frequently used in commercial blends with composition around PC/ABS 70/30, which gives the highest impact strength. On the other hand, the impact strength of PC/ABS blends shows a minimum at about 30 % PC. Unfortunately, this is exactly the composition of the waste stream in car-dismantling plants. In this case, PC occurs in the form of PC/ABS blends containing around 70 % of PC. Thus, it is a challenge to find methods of improving the impact properties of blends made from ABS waste and PC/ABS waste emerging from car-dismantling plants.

This paper aims at describing the upgrading of ABS by adding PC or PA6 and impact modifiers. The dominant type of aging in ABS is thermo-oxidative degradation of the rubber phase, which degrades the impact strength of the material. The morphology of the rubber phase created during polymerization offers an optimum balance between impact strength, tensile strength and stiffness. It is, therefore, very difficult to improve the impact strength of recycled ABS just by adding an impact modifier, unless it is added in very large amounts. Also, larger amounts of the impact modifier reduce the stiffness and increase the price.

EXPERIMENTAL

The following materials have been used:

- virgin ABS (Terluran 967 K, BASF)
- virgin PC (Makrolon 2800, Bayer)
- waste ABS from dismantled Volvo 240 cars and from office appliances
- waste PA6 from dismantled cars

The modifiers used for the ABS/PC blends were core/shell modifiers from Rohm and Haas with PMMA in the shell: Paraloid EXL 3847, an MBS (methyl methacrylate-butadiene-styrene) type with poly(butadiene-*co*-styrene) rubber in the core, and Paraloid EXL 3300, an all-acrylic modifier with butyl acrylate rubber in the core.

The additives for the ABS/PA6 blends were SMA (poly(styrene-maleic anhydride)) as a reactive compatibilizer and core/shell MBS particles and poly(SEBS-*graft*-MA) (maleic anhydride-functionalized SEBS) as an impact modifier (SEBS = polystyrene-*block*-poly(ethene-*co*-butene)-*block*-polystyrene).

The waste plastics were granulated in a knife mill. Upgrading and blending were performed in a twin-screw extruder (Werner & Pfleiderer ZSK 30). Finally, test specimens were injection-moulded. The experiments are described in detail in Refs. 1 and 4.

RESULTS AND DISCUSSION

Upgrading of ABS/PC blends

A mixture of 30 % ABS from the office appliances waste and 70 % ABS from dismantled cars was selected for upgrading tests with PC and MBS impact modifiers added. The effects of the MBS modifier alone on the mechanical properties are shown in Table 1. Surprisingly, there was no improvement at all in impact strength upon addition of the MBS modifier, rather a slight decrease accompanied by the expected slight decrease in stiffness and strength. A still higher amount of added MBS might improve the impact behaviour, but at the cost of inadequate stiffness and questionable economy.

Table 1. Mechanical properties of recycled ABS/PC blends

Composition phr			Notched impact strength kJ/m^2	Young modulus GPa	Yield strength MPa	Yield strain %
ABS	MBS	PC				
100	0	0	7.1	2.2	41	2.3
100	5	0	6.1	2.2	41	2.5
100	10	0	6.3	2.0	39	2.5
80	0	20	6.0	2.4	43	2.6
80	10	20	9.7	2.1	38	2.7
100[a]	0	0	5.0	-	-	-
100[a]	10	0	4.1	-	-	-
90[a]	10	10	1.8	-	-	-

[a] ABS with flame retardant

According to Table 1, the blend of waste ABS with 20 % PC gives a stiffer and stronger material, but the notched impact strength is reduced from 7.1 to 6.0 kJ/m^2. However, only 5 phr of the MBS modifier added to the ABS/PC blend changes the picture; with 10 phr MBS, an acceptable balance between the impact strength, stiffness and yield strength is achieved.

The interpretation of the enhanced impact strength derived from the MBS particles in the ABS/PC blend, but not in ABS is that the rubber particles at the surface of the PC particles convert stress concentrations to a plain state of stress, which facilitates yielding and impact energy uptake by PC. An improved interfacial strength imparted by the particles is more likely to act in the opposite direction. In other studies performed by us, where the ABS/PC interface has been strengthened by the addition of small amounts of PCL (polycaprolactone), improvements in strength and stiffness were noticed but the impact strength decreased.

Often, ABS contains a flame retardant. In this case, it is very difficult to upgrade the properties of ABS by adding PC and MBS because the flame retardant may degrade the PC phase. Thus, the impact strength shows a very low value with recycled ABS containing flame retardant on addition of PC and MBS (Table 1).

Upgrading of ABS/PA6 blends

In this part of the project, blends of waste ABS and PA6 from dismantled cars were studied. ABS and PA6 are not miscible and reactive SMA has been used as a compatibilizer. MBS and SEBS particles were used as impact modifiers. ABS and PA6 were blended in the proportions 80:20, and 2.5 or 5 phr of an impact modifier was added. Mechanical properties of the blends are shown in Table 2.

Table 2. Mechanical properties of recycled ABS/PA6 blends

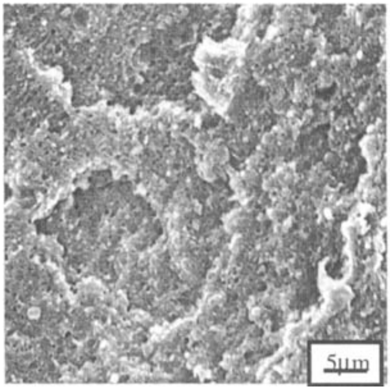
Composition phr				J-integral kJ/m^2	Notched impact strength kJ/m^2	Young modulus GPa	Yield strength MPa	Yield strain %
ABS	PA6	MBS	SMA					
100	0	0	0	5.1	7.1	2.2	41	12
80	20	5	5	7.5	2.5	3.5	53	3
80[a]	20	5	5	5.0	1.7	2.3	39	10

[a] ABS with flame retardant

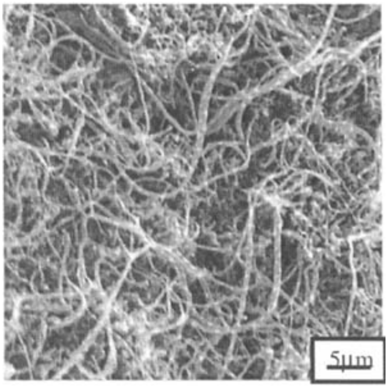
However, during this study it was observed that the usual Charpy impact test may give wrong information about the inherent impact properties of polymer blends. Therefore, both the Charpy test and another type of impact test, the J-integral method, were used to characterize the impact behaviour of the blends. The J-integral values and the Charpy values in Table 2 are conflicting.

It should be mentioned that the impact strength according to the J-integral method is improved for the recycled ABS when blended with PA6, compatibilized with SMA and impact-modified with MBS particles. For the ABS/PC blends, however, the same upgrading method does not seem efficient in ABS containing flame retardants.

In order to understand the differences between the Charpy and J-integral results for the ABS/PA6 blends, the morphologies of the fractured surfaces were studied using SEM. The Charpy and J-integral impact methods represent two different fracture conditions, fast fracture and slow fracture, respectively. In some cases, the energy absorption (toughness) of these two kinds of fractures shows the same trend resulting in that either of the two methods can be used to characterize the toughness of the materials. Other materials may show different fracture mechanisms in fast and slow tests. As a result, Charpy and other types of rapid loading tend to cause brittle failure, whereas the J-integral shows the ductile type of failure.



(a)



(b)

Fig. 2 SEM micrograph of (a) Charpy impact fracture surface and (b) slow (2 mm/min) three-point-bending fracture surface of ABS/PA6 sample containing SEBS-MA and SMA additives

In ABS/PA6 blends, the two polymers form co-continuous structures. Thus, PA is a continuous phase, although PA is the minority component (20 %). Figure 2 shows SEM micrographs of a Charpy impact surface and a slow three-point bending fracture surface of the ABS/PA6 blend containing both SEBS-MA and SMA additives. The strain rate of the J-integral test is low as for the three-point bending test. From Fig. 2, it is evident that the PA phase is pulled out, and such a process will consume extra energy; therefore, the J value increases. Such process also indicates that the ABS/PA interfacial adhesion is weak.

This part of our study is in progress and the results reported are preliminary; further experiments are necessary.

Quality assessment of recycled ABS blends

One of the problems to be solved before recycling of plastics may increase to the desired extent is development of an understanding of the evolution of properties during subsequent recycling in order to predict the performance of products made of recycled materials. A new method of combined repeated processing and thermo-oxidative aging has been presented by

Boldizar et al. for LDPE (Ref. 3). Their results strongly support the assumption that neither repeated processing nor aging alone can be used to predict the quality of a recycled LDPE. Instead, the results show that combined extrusion and ageing should be used. The ABS blends are tested by this method. However, the measurements are in progress and no results are available for this report.

CONCLUSION

This study has shown that there is no simple method of upgrading waste ABS and other engineering polymers. Engineering plastics are of a higher value than commodity plastics and there is no economic interest in producing recycled engineering plastics with a bad profile of mechanical performance. Commodity plastics may be used for simple products, but engineering polymers must retain at least some of its original performance upon recycling.

It has been demonstrated that it is possible to upgrade mechanical properties of waste ABS by using concepts of blend technology. For example, PC and PA6 may be blended into ABS together with suitable impact modifiers and compatibilizers. It is important, however, to assure that the waste ABS fraction is free from flame retardants.

The impact behaviour should be tested with more than one test method. Moreover, the morphology of the blends has to be studied carefully in order to understand the effect of various polymeric additives.

Finally, long-term properties and quality assessment of the recycled blends should be tested by the repeated processing and thermo-oxidative aging method.

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REFERENCES

(1) H. Larsson, H Bertilsson, Polym. Recycl., **1**, 243 (1995)

(2) P.-A. Löfgren, H. Bertilsson, Polym. Recycl., **1**, 217 (1995)

(3) A. Boldizar, T. Gevert, M. Markinger, Polym. Recycl., **1**, 249 (1995)

(4) H. Larsson, H. Bertilsson, Polym. Networks Blends, **6**, 99 (1996)

(5) A. L. Bisio, M. Xanthos, *How to Manage Plastics Waste*, Hanser, New York 1995

(6) R. Iijima, Makromol. Chem., Macromol. Symp. **57**, 33 (1992)

(7) J. Brandrup, Polym. Recycl., **2,** 95 (1996)

(8) C. Klason, J. Kubát, H.R. Skov, "Recycling of Commingled Plastics Waste Containing Paper and Board", in: Proceedings ReC'93, International Recycling Congress at the Re'93 Trade Fair, Vol. 1, Eds.: M.E. Henstock, H.R. Skov, Hexagon Ltd, Copenhagen 1993, p. 345

(9) P.-E. Eriksson, *"Mechanical Recycling of Glass Fibre Reinforced Polyamide 66"*, Ph.D. Thesis, Royal Inst. Technol., Stockholm, Sweden, 1997

(10) S.F. Bush, F. Yilmaz, P.F. Zhang, Plast. Rubber Compos. Process. Appl., **24**, 139 (1995)

(11) P. Hedenberg, P. Gatenholm, J. Appl. Polym. Sci., **56**, 641 (1995).

(12) J.J. Scooby, Makromol. Chem., Macromol. Symp., **57**, 331 (1992).

(13) J.I. Eguizabal, J. Nazabal, Polym. Eng. Sci., **30**, 527 (1990)