THE EFFECT OF RESIDUAL IMPURITIES ON THE RHEOLOGICAL AND MECHANICAL PROPERTIES OF ENGINEERING POLYMERS SEPARATED FROM MIXED PLASTICS

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Abstract

This paper reports the results of an investigation of the effects of purity level and nature of impurities on the properties of recycled polycarbonate and recycled acrylonitrile-butadiene-styrene polymers blended with the corresponding virgin resins. The relevant thermal, mechanical and flow properties were measured. It is concluded that properties of recycled polymers depend not only on the amount of impurity present but also on the kind of impurities and contaminants that are present. The latter factor even plays an important part in relation to compatibility of polymers. However, polymer melt rheology seems less sensitive to impurities than some mechanical properties such as impact strength. More than 99% purity is needed for recycling these polymers back into their original, high-value applications.

Introduction

Polycarbonate (PC) and Acrylonitrile-Butadiene-Styrene (ABS) are relatively expensive polymers that are widely used for the injection molding of computer and electronics housings. Recycling these polymers after the end of the first life cycle of the products is receiving more and more attention (1). In our previous paper, we had reported that for recycled polymers such as PC (having a high purity level), these could be re-used in their original applications by blending with chemically identical virgin resins; about 15% recycled polymer could be mixed with the virgin polymer without altering the rheological or mechanical properties of the virgin material (2).

Contaminants and high MW impurities are naturally present in polymers separated from commingled plastics. These have been cited as one of the barriers faced by the plastics recycling industry (3). Indeed, purity level and the kind of impurities present must be considered before making decisions concerning any applications of recycled polymers. Purity level means the amount of contaminants that are present in a certain amount of recycled polymer, and impurities means what they are. These factors not only relate to the end performance of the materials, but they also influence the cost of separation of the recycled polymers. In a particular separation operation line in a recycling plant, each separation step yields a certain purity level of the material, and different purity levels imply different separation costs. Different purity levels can give different properties, and this makes the separated material suitable for different applications. Since purity is a key parameter in the recycling of plastics, it will be helpful to have an understanding of how purity level and the chemical nature of impurities affect the properties of recycled materials. It appears to us that there are no publications that address this issue.

The present work is a continuation of our research on recycled PC and ABS recovered from electronics housings. Here recycled PC blended with virgin PC and recycled ABS blended with virgin ABS, each type at three different purity levels, were evaluated for their thermal, rheological and mechanical properties. In addition, samples were made with different amounts of known impurities added to virgin PC and virgin ABS. The intention was to come up with some general guidelines for applications of these recycled polymers.

Experimental

Materials

Granulated, recycled PC and recycled ABS were supplied by MBA Polymers of Richmond, CA. PC was recovered from monitor housings while ABS was recovered from printer housings. For each polymer, three samples each of a different purity level were used. The purity levels and contaminants included in these samples are listed in Table 1. Virgin PC used in the research was Lexan 101, a general purpose PC, manufactured by GE Plastics, and virgin ABS was Cycolac GPM 5500-1000, also manufactured by GE Plastics.

Blend Sample Preparation

All the samples were prepared using a Brabender twin screw mixer D6/2 by blending recycled polymer with virgin pellets. The sample preparation procedure was the same as described in our previous paper (2). The drying temperature was 120C for PC and 90C for ABS. The extrusion temperature settings from the feed inlet to the die were 220C, 265C, 315C, 300C for PC and 160C, 175C, 190C, 195C for ABS. The following compositions: 0, 5, 10, 15, 20, 50, and 100% by weight of recycled polymer were selected for the highest purity PC or ABS; 0% 15% 100% were used for other purity samples.

Molding of Test Specimens

Pre-dried samples of the blends (at 120C for PC; 90C for ABS) were pressed into sheets using a hydraulic press with electrically heated platens and self-made molds. The sheets were prepared using 30g polymer per mold at a temperature of 200C for PC and 180C for ABS with a pressure of about 5.1MPa applied for 5 min. Then the molds holding a sheet were taken out of the press and cooled in air. The molded sheets, with a thickness of 1 mm, were used for rheological and thermal testing. The compression molding cycle was run in a way that prevented the formation of bubbles inside the sheets.

The specimens for tension and Izod impact tests were also made by compression molding using the lab-manufactured molds in terms of ASTM standard specimen dimensions at a temperature of 250C for PC and 200C for ABS, with a pressure of about 5.1MPa for 5 min. The molded tension specimens had a thickness of 3.15mm, a dog-bone shape with an end width of 25mm, and a test width of 6.5mm. The total sample length was 110mm with an effective length of 35.56mm. The molded impact test coupons had a length of 63.5mm, a width of 4.8mm, and a thickness of 12.7mm. The sample was notched at one side center in the direction of width with a residual thickness 10.1mm at the notch. The specimens for tension testing were also used for Shore's hardness tests.

Thermal Characterization

A TA Instruments DSC 910 differential scanning calorimeter was used to measure glass transition temperatures of the blends in order to identify possible effects of contamination and aging on the properties of recycled polymers as described in (2). Measurement was started at an equilibrium temperature of 50.0C, and then the temperature was ramped to 250.0C at a rate of 10.0C per minute. All test samples were weighed and were approximately 10.5mg.

Rheological Characterization

Rheological measurements were carried out on a Rheometrics Mechanical Spectrometer RMS800. Data were obtained using parallel plate fixtures of diameter 25mm with a gap of 1mm. The testing temperature was 250C for PC and 200C for ABS. When loading samples, the pre-pressed sheet was cut into a 25mm diameter disk to fit into the fixture. Dynamic strain sweep was run at a frequency of 1rad/s while dynamic frequency sweep was at a strain of 10%. More details are available in (2).

Mechanical Characterization

Tensile tests were conducted on an Instron Testing Machine Model 1011 at room temperature. The specimen was gripped and stretched at a speed of 2 in/min for PC blends and 0.2 in/min for ABS. No slip was noted between specimen and grip. Izod impact tests were conducted on an Instron/Satec BLI Impact Testing Machine. An 8 ft.-lb pendulum was used for PC blends while a two ft.-lb pendulum was used for ABS blends. Impact strength was determined after making suitable corrections for friction and windage losses. Shore's hardness was measured using an Instron/ Wilson/Shore DuroTronic Model 2000 Durometer in combination with a lever loader which enhances the reproducibility and repeatability of the readings. It is designed to meet ASTM D2240. The reading was taken after loading the weight for 15 seconds. All test specimens were stored at a room temperature of about 25C for at least two days before testing and tests were done at room temperature.

Results

Glass Transition Behavior

High purity recycled PC (R-PC) has the same glass transition temperature of 143C as that of virgin PC. But the other two recycled PCs (R-528PC and R-630PC) show a Tg of 135C. A lower Tg implies a lower molecular weight, and this should give rise to a lower melt viscosity. The result on recycled ABS polymers at different purity levels shows a significant difference in glass transition behavior. V-ABS and R-594ABS have a Tg of about 103C, but R-ABS and R-612ABS have a Tg of about 90C. The transition temperature range for R-ABS and R-612ABS is also wider than that of V-ABS and R-594ABS. These results indicate that Tg does not relate to the purity level of the material because R-ABS has a very high purity level but has a lower Tg. As explained below, this is not unexpected.

It should be noted that ABS resins typically consist of a rubber phase (BS, BA, PB) as the dispersed phase and a glassy phase (SAN and PS) as the continuous phase. Since rubber phases have a low Tg about ~ -25C, current DSC measurements only detect glass transition behavior from the plastics phases. The softening temperature range for PS is from 70 to 98C, and for SAN it is from 82 to 105C. Therefore, glass transition temperature and its range as determined from DSC thermal characterization reveals information on structural composition of the material.

Rheological Behavior

Material purity and composition variations can have a large influence on the observed rheology. A typical pattern is shown in Figure 1 where complex viscosity is plotted vs. frequency for three recycled PC and three recycled ABS materials with different purity levels. Viscosity data of virgin PC and ABS are also plotted for reference. Figure 1 typically reflects batch-to-batch variations of recycled polymers. As expected from Tg data, R-528PC and R-630PC have lower complex viscosity than R-PC and V-PC. R-ABS and R-612ABS have lower complex viscosity than R-594ABS and V-ABS. A word of caution here is that the recycled polymers come from unknown sources and are not expected to be identical to the virgin polymers. But Figure 1 does show the difference in flow property between PC and ABS, that is, ABS is more shear-thinning than PC. More about the rheological properties of these recycled polymer melts can be found in the paper (4).

Complex viscosity vs. frequency data are shown in Figure 2 for three 15% recycled PC blends, and these are compared with data on virgin PC. Two of them, that is, blends of R-PC and R-528PC, give complex viscosity of the same value as that of the virgin PC. However, the 15% R-630PC blend exhibits a complex viscosity of much smaller magnitude. Complex viscosity vs. frequency data for three 15% recycled ABS blends are compared with virgin ABS in Figure 3. All three blends have a complex viscosity of the same value as that of the virgin resin. The result demonstrates that for these recycled ABS polymers, the batch-to-batch variations can be masked by blending with 85% virgin resin. The data as represented in Figure 2 and 3 on recycled PC and ABS of different purity levels further verify the '15% blending rule' except for R-630PC. This fact is of great significance to any strategy that may be employed for reusing these polymers.

Tensile Behavior

It is found that the purity level of recycled polymers has a more significant effect on elongation-at-break than on tensile yield strength. Figure 4 shows the effect of recycled PC purity on yield strength as a function of recycled PC content; the yield strength is only slightly reduced in the presence of the impurities. A relatively obvious decrease in yield strength is observed for 15% R-630PC. Figure 5 shows the effect of recycled PC content and impurities on tensile elongation-at-break. Remarkable reductions in elongation-at-break are observed for the three recycled polymers in comparison with virgin PC and for 15% recycled R-528PC and R-630PC blends, with R-630PC being the most brittle.

The effect of recycled ABS content and purity on yield strength is shown in Figure 6. R-612ABS has similar yield strength to that of R-ABS. R-594ABS has the lowest yield strength though a higher purity level than R-612ABS. But three 15% recycled ABS blends do show the same yield strength as in the case of shear viscosity. ABS materials exhibit small elongation-at-break of about 6%. It is observed that R-612ABS has relatively larger elongation-at-break, followed by R-ABS and then R-594ABS.

Impact Strength

R-528PC has similar impact strength to that of R-PC, but R-630PC presents very poor impact strength, as seen in Figure 7. This is consistent with the known purity levels. Among recycled ABS polymers as shown in Figure 8, R-ABS has the strongest impact strength. However, R-612ABS has much higher impact strength than R-594ABS that has a much higher purity level than R-612ABS. In particular, three 15% recycled ABS blends also show remarkable differences in impact strength in the same order, that is, 15% R-ABS > 15% R-612ABS > 15%R-594ABS, although these blends have similar rheological properties (see Figure 3). This experimental observation indicates that the '15% blending rule' is not valid for impact strength properties of R-594ABS and R-612ABS materials.

Shore’s Hardness

For recycled R-PC blends with virgin PC, Shore’s hardness hardly changes with the contents of recycled PC. But there are some differences in Shore’s hardness among three recycled polymers at different purity levels, as typically seen from Figure 9 for recycled PC polymers.

Discussion and Conclusions

Examining the thermal, rheological and mechanical characterization results with the composition information of these materials as shown in Table 1 reveals that some properties, such as elongation-at-break and impact strength, are more sensitive to material purity level than others such as rheology, tensile yield strength, and Shore’s hardness. The presence of slightly higher amount of incompatible polymers (e.g. HIPS, POM, in the case of R-630PC vs. R-528PC) may obviously deteriorate the mechanical properties of the material. R-612ABS has a lower purity level (88%) than R-594ABS (96%), but R-612ABS has much better mechanical properties. This is because most of the impurities present in R-612ABS (ABS-FR, PC/ABS) have a better compatibility with the main component (ABS) of the material, but R-594ABS consists of incompatible high melting-point impurities (PPO + Nylon) and slightly higher amount of incompatible HIPS. Therefore, information on both the purity level and the nature of impurities is needed, and the compatibility of polymeric systems should be taken into account, in order to understand the effect of residual impurities on the properties of the recycled materials. These results will be discussed together with those obtained from the blends prepared by adding known contaminants into virgin resin at different controlled amounts.

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References

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Table 1. Characteristics of Recycled Polymers Tested

Designation	Purity Level	Contaminants
Recycled PC I R-PC	>99%	No appreciable Contamination
Recycled PC II R-528PC	99%	HIPS 0.016% PC/ABS 0.03% PMMA 0.05% PE 0.07%
Recycled PC III R-630PC	98%	HIPS 0.29% PC/ABS 0.11% PMMA 0.25% PE 0.07% ABS 0.6% POM 0.16%
Recycled ABS I R-ABS	99.9%	No appreciable Contamination
Recycled ABS II R-594ABS	96%	HIPS 2.4% PPO + Nylon 1.3%
Recycled ABS III R-612ABS	88%	ABS-FR 9.8% HIPS 1.4% PC/ABS 0.2%

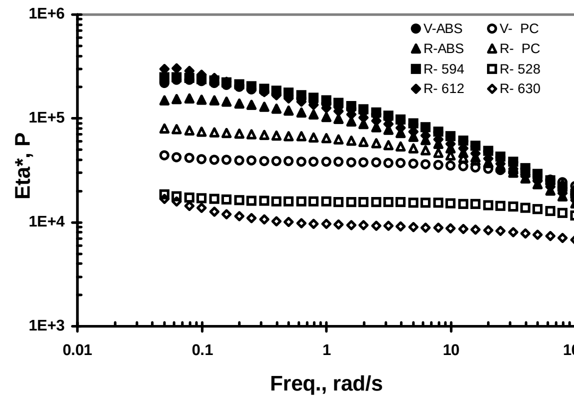

Figure 1. Complex viscosity vs. frequency for recycled PC melts (open symbols, bottom four curves) and recycled ABS melts (solid symbols) with different purity levels.

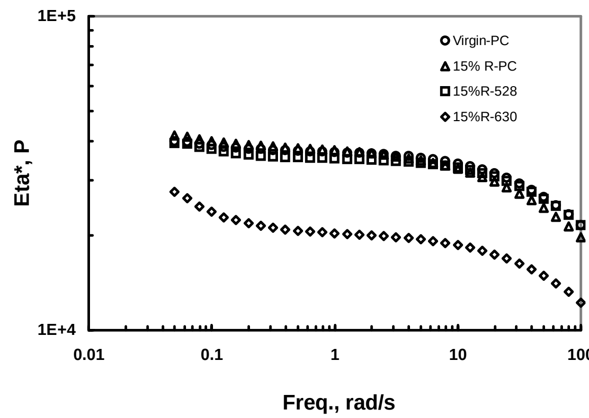

Figure 2. Complex viscosity vs. frequency for 15% recycled PC blends in comparison with virgin PC (250C, strain 10%).

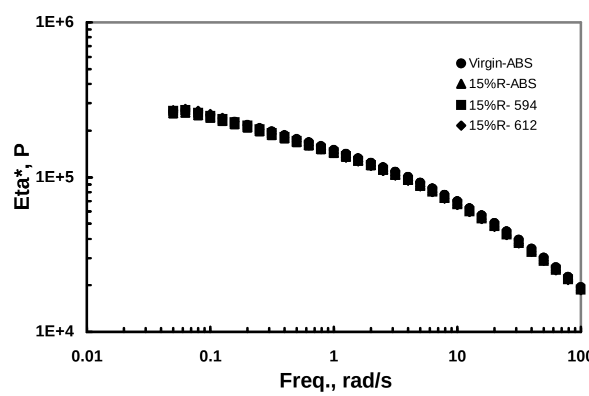

Figure 3. Complex viscosity vs. frequency for 15% recycled ABS blends in comparison with virgin ABS (200C, strain 10%).

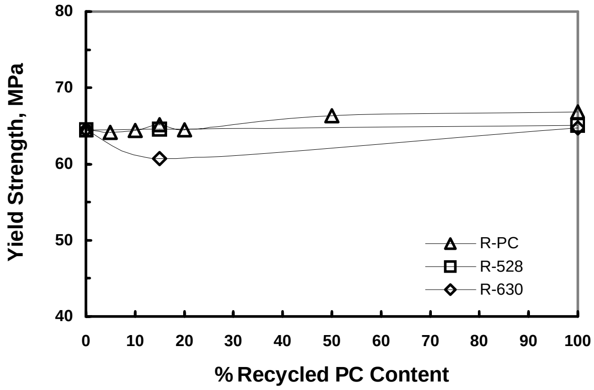

Figure 4. Effect of recycled PC content and residual impurities on tensile yield strength.

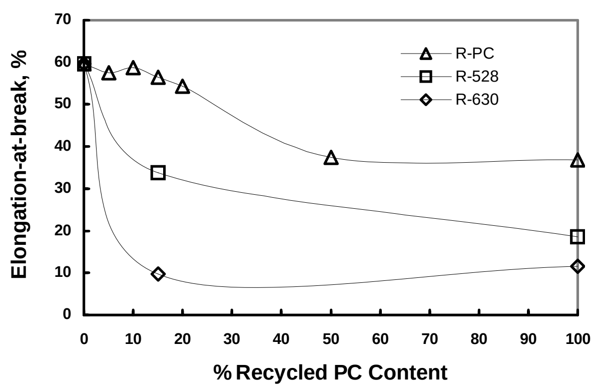

Figure 5. Effect of recycled PC content and residual impurities on tensile elongation-at-break.

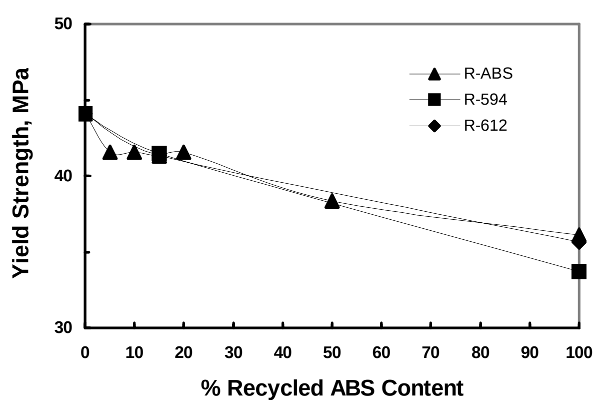

Figure 6. Effect of recycled ABS content and residual impurities on tensile yield strength.

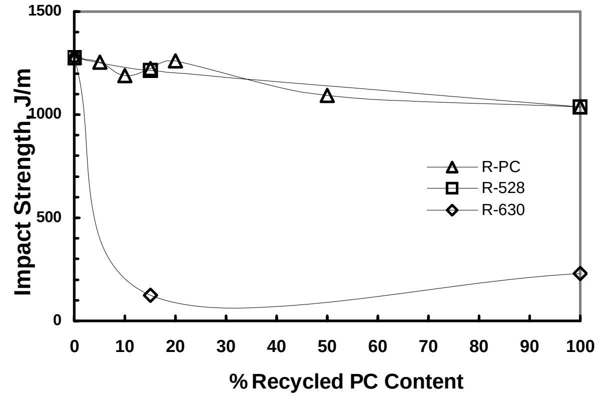

Figure 7. Effect of recycled PC content and residual impurities on Izod impact strength.

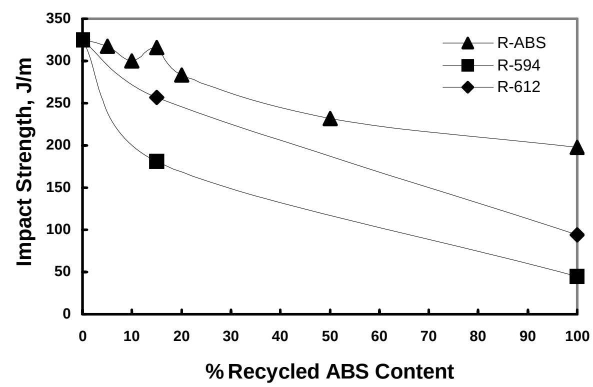

Figure 8. Effect of recycled ABS content and residual impurities on Izod impact strength.

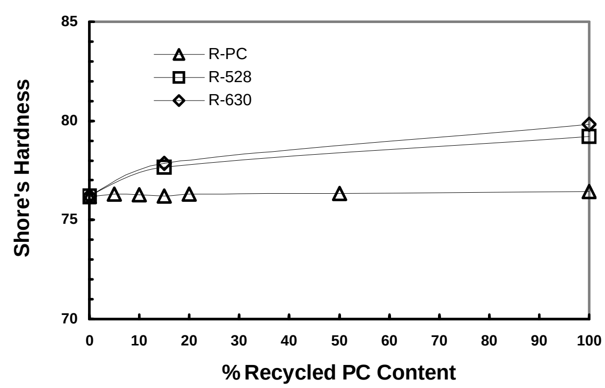

Figure 9. Effect of recycled PC content and residual impurities on Shore's hardness.

Keywords: Residual impurities, mechanical properties, recycled polycarbonate, recycled acrylonitrile-butadiene-styrene