Key Properties to Understand the Performance of Polycarbonate Reprocessed by Injection Molding

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ABSTRACT: The reprocessing of injection-molded polycarbonate was studied in an attempt to understand the physical background for the variation of its performance upon sequential molding cycles. The effect of reprocessing on different properties of the moldings and the regrind is presented and discussed. A quantitative analysis of the Fourier transform IR spectra indicates that phenol and carbon dioxide are released during the initial cycles, probably due to molecular scission near the chain ends. Most of the results obtained agree well with the findings reported elsewhere. Essentially, the molecular weight, the free volume, and the specific volume were found to be critical properties for understanding the global performance of the moldings. Both the free volume and the reciprocal of the molecular weight depend linearly on the number of reprocessing cycles. Based on these properties, it is possible to develop relatively simple relations to estimate the variation of the rheological, optical, and mechanical properties with the number of reprocessing operations. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1393–1400, 2000

Key words: polycarbonate; molecular weight; free volume; specific volume; mechanical properties; reprocessing

INTRODUCTION

Reclaiming postconsumer thermoplastic products and plant scraps has been a valuable approach for saving energy and raw materials, and for reducing costs. Some leading companies are currently marketing recycled engineering thermoplastics, such as polyethylene terephthalate (PET), acrylonitrile–butadiene–styrene (ABS), polypropylene (PP), and polycarbonate, for applications in the automotive, computer, and appliance industries.

These recyclates are reported to have high quality, comparable to that of virgin commercial grades.[1] Therefore, understanding the effect of repeated processing operations on the performance of parts made of, or containing, recycled polymers is of continuing practical importance. Bisphenol-A-polycarbonate (BAPC) can be considered as a good example, as it is a widely used engineering polymer that combines good properties (high stiffness and impact strength, transparency, thermal resistance, low creep, etc.) with a moderate price. However, some of these properties may be severely reduced by recycling.

Reprocessing of polycarbonate has been studied for more than 20 years[2] but still attracts attention nowadays. From the results reported in

the literature, it is evident that the effect of reprocessing on the properties of the recyclates depends mostly on the thermomechanical environment associated with the processing technique, which involves temperature, flow rate, and pressure profiles in the case of injection molding. The molecular weight of the polymer, the presence of moisture, and the nature of the additives are also important. La Mantia[3] claimed that the reduction in mechanical properties after several injection molding cycles is of small importance for dry Lexan polycarbonate. However, the presence of humidity leads to a significant decrease in mechanical performance upon reprocessing due to hydrolytic chain scissions. Similarly, Chrysostomou and Hashemi[4] reported that tensile, impact, and dynamic properties, as well as the glass transition temperature, varied negligibly with the number of the injection molding cycles. However, Abbas et al.[5,6] and Bernardo et al.[7,8] showed that molecular weight of dehumidified BAPC decreases with the number of recycling operations, greatly affecting some mechanical properties. In these studies, the presence of fiber reinforcement was shown to enhance the molecular degradation with reprocessing. The characteristics of the polycarbonate, as well as the nature of the additives, also had a dramatic impact on the rate of chain scission.[7,8] These apparently contradictory results may be explained by different polymer compositions or distinct thermal and mechanical loads associated with the machine setup and the molding geometries used in the studies.

Different thermal degradation mechanisms of polycarbonate have been identified based on distinct chemical structures and thermal treatments or using different pyrolysis techniques.[9−12] In the case of BAPC, the degradation routes proposed include the Davis–Golden mechanism (i.e., simultaneous occurrence of condensation and branching reactions), nonrandom chain scission, and homolysis. Furthermore, hydrolysis and oxidation may also occur when moisture and oxygen are present.

Subjecting a polymer to sequential injection molding operations can be considered equivalent to a pulsed thermal degradation, with a constant "pulse duration" equal to the residence time in each cycle. Based on Fourier transform IR (FTIR) data, which showed no structural differences between virgin and recycled polycarbonate samples, some investigators concluded that reprocessing can break down the chains but does not change the chemical structure significantly.[13,14] Conversely, other work, involving fluorescence measurements, revealed that the formation of insaturations, or the alteration of their original nature, occurred during recycling.[7] In any case, most reprocessing studies concur that chain scission is the prime mechanism determining the degradation of BAPC.

In the present work the effect of recycling on the physical properties (optical, rheological, and mechanical) of BAPC was studied. Its main purpose was to determine the key factors that control the variation of these properties, and to formulate some simple relations to predict the respective changes.

EXPERIMENTAL

A BAPC, Lexan 123R, supplied by GE Plastics, The Netherlands, was selected for this work. It was dried at 105°C for 4 h (on a dehumidified air drier) prior to molding. Injection molding was carried out on a Krauss Maffei KM60-210A machine. For all the moldings the melt and the mold temperatures were kept at 270 and 70°C, respectively. The melt temperature used is 20°C lower than that recommended by the raw-material manufacturer, to minimize the thermal degradation in the plasticating barrel. Fifteen tensile and 15 impact specimens were retained for testing in each cycle. The remaining ones were ground in a Colortronic M 200L granulator. A sample of the regrind (ca. 60 g) was also collected from the inlet of each cycle.

Infrared spectroscopy was performed with a Perkin Elmer 1600 FTIR spectrometer. A wave number resolution of 4 cm^{-1} and a number of scans of 21 were used throughout the analysis. The samples were molded from the regrind into 20 μm films in a Specac hot press equipped with a film-maker. Identical samples were prepared by casting extremely thin chloroform solutions of BAPC (concentration smaller than 0.01 g/mL) onto KBr crystals, and then drying with a hot blower.

The density of the moldings was assessed at ambient temperature (23°C) using a SCALTEC SBC 31 balance, equipped with a SDK 01 kit. In each measurement, five samples were tested. The specific volume is given by the reciprocal of the average of the five tests.

Molecular weight determinations were made with an Ubbelohde viscometer (Schott-Geräte, Typ.-Nr. 530 03 0c) at 25°C, using chloroform as
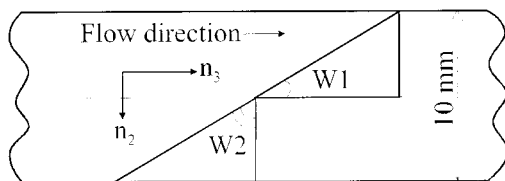
Figure 1 Schematic representation of the wedge cuttings of a tensile bar.

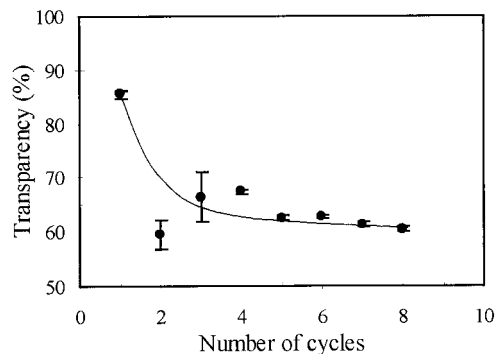**Figure 2** Effect of reprocessing on the transparency of the moldings.

solvent and performing the Hagenbach correction for flow times. The parameters K and α for BAPC in the Markin–Houwink–Sakurada equation were taken to be $K = 30.1 \cdot 10^{-3}$ mL/g and $\alpha = 0.74$.[15]

The molecular orientation in the tensile bars was assessed by means of the residual birefringence. The measurements were performed using an Olympus BH-2 transmitted light polarizing microscope with a green filter and other auxiliary equipment, according to the wedge method.[16] The wedges were cut from tensile moldings in such a way that the wedge tips, parallel or perpendicular to the flow direction, overlaid always the center of the rectangle bar (a schematic illustration is shown in Fig.1). The core birefringence ($n_3 - n_2$) was averaged through thickness (about 0.3 mm distance from the surfaces), in order to overcome the effect of localised birefringence inhomogeneity.

The transparency of the tensile specimens was measured using a HAZEGARD system XL-211, according to American Society for Testing and Materials (ASTM) D 1003-61.

The melt flow index (MFI) was measured with an extrusion plastometer Davenport model 3, according to ASTM D-1238 at 230°C, with a 2.16 kgf weight.

Tensile tests were carried out at 23°C and 50% relative humidity on an Instron 4505 testing machine, with a 50 kN load cell. The measurement procedure was in accordance with ASTM D-638M-87b. A cross head speed of 1 mm/min ($1.67 \cdot 10^{-5}$ m/s) was used until the strain reached 2%, which was determined using a 50 mm resistive extensometer. After removing the extensom-

eter, the testing velocity was changed to 50 mm/min ($8.3 \cdot 10^{-4}$ m/s) until breakage.

Charpy impact tests were done on a ROSAND IFW 5 instrumented impact machine at 3 m/s, according to International Standards Organization (ISO) R 527:1996. The crack propagation energy, divided by the effective cross section, was used for evaluating the impact strength of the specimens. The start and end points of the propagation were determined using a high-speed video system (up to 1000 frames per second). The specimens were notched with a radius of 1.75 mm.
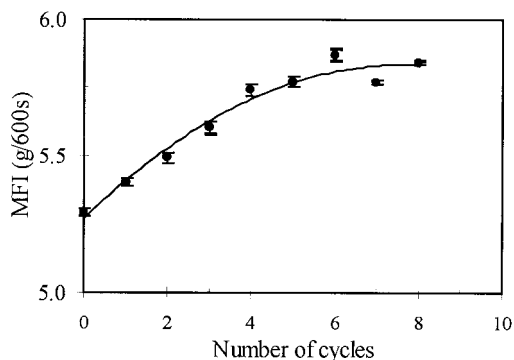
The main reference properties of the virgin polymer are presented in Table I. These properties were obtained either from the granules directly, or from test pieces collected from the first cycle of the molding sequence.

RESULTS AND DISCUSSION

Repeated processing leads to the discoloration of the moldings, quantified by the transparency loss shown in Figure 2. It can be observed that, after a sharp decrease in the second cycle, the transparency remains practically constant. On the other hand, as indicated in Figure 3, the MFI increases, slightly but continuously, through the first 4 cycles, stabilizing thereafter, following a pattern already reported for this property.[17]

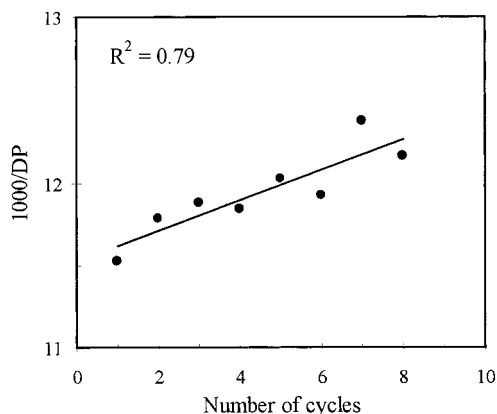**Table I   Main Reference Properties of Lexan 123R as Determined in the Present Work**

Property	M_w (g/mol)	MFI (g/600s)	Modulus (GPa)	Tensile Strength (MPa)	Impact Strength (kJ/m²)
Value	22030	5.4	2.35	60.4	47.2

Figure 3   Effect of reprocessing on the melt flow index.

Figure 5   Effect of reprocessing on the relative band intensities of the FTIR spectra (the figures in parentheses correspond to the characteristic wavenumbers).

It has been shown that the reciprocal of the degree of polymerization (DP) is a linear function of the heating time, irrespective of the dominant mechanism operative during thermal degradation.[18] As stated before, the thermal-oxidative processes to which the polymer is subjected during reprocessing can be considered equivalent to a pulsed thermal degradation. Therefore, a linear function should be obtained between the reciprocal of DP and the number of reprocessing cycles, which is proportional to the thermal exposure time. This is illustrated in Figure 4, for the 8 reprocessing cycles.

Similar to the findings reported above,[13,14] the modifications imposed by the reprocessing on the chemical structure of BAPC could not be detected by FTIR. However, a quantitative analysis of the relative intensity of the characteristic bands of the FTIR spectra does give some information about the operative degradation mechanisms, as shown in Figure 5. The bands used in the analysis
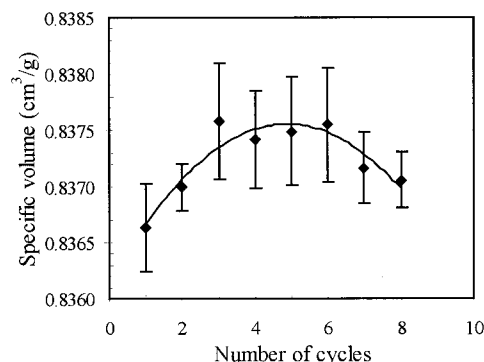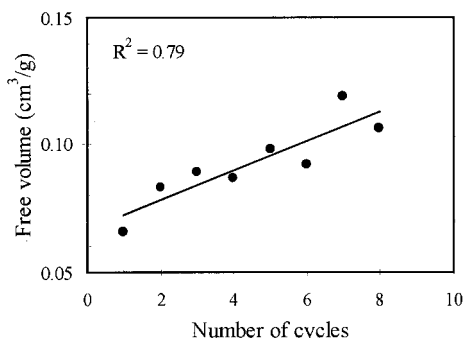
were as follows: 4073 cm^{-1}, attributed to stretching vibrations of —CH groups in the aromatic ring; 3673 cm^{-1}, assigned to vibrations of methyl groups; 3531 cm^{-1}, due to the stretching vibrations of hydroxyl groups; 1015 cm^{-1}, ascribed to internal planar bending vibrations of aromatic rings; and 1776 cm^{-1}, associated to stretching of the carbonyl groups. Significant increases can be observed in the $A(3673)/A(4073)$ and $A(1015)/A(1776)$ ratios in the first two cycles, suggesting the loss of both aromatic rings and carbonyl groups upon reprocessing. Moreover, the smaller variation of the $A(4073)/A(3531)$ ratio hints that the loss of aromatic rings is always accompanied by the release of hydroxyl groups in a near constant proportion. This may indicate that the initial controlling degradation mechanism is the release of phenol and CO_2, in agreement with the thermal degradation schemes proposed by Mc-

Figure 4   Plot of the reciprocal of the degree of polymerization vs the number of reprocessing cycles.

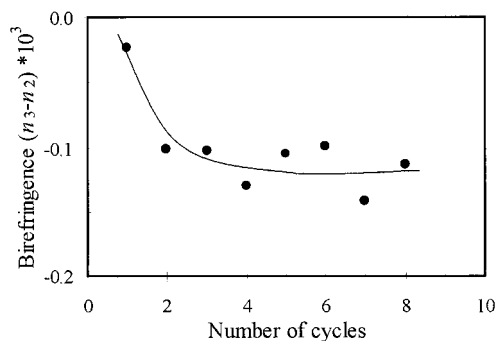**Figure 6**   Effect of reprocessing on the specific volume.

**Figure 7** Effect of reprocessing on the free volume.

Neill and Rincon.[11] According to these schemes, phenol is formed by chain scission at the bisphenol A residue nearest to the chain end (i.e., the phenolic end) and CO_2 is produced by scission at the carbonate group. The occurrence of scissions mostly near the chain ends explains why there is no great decrease in molecular weight upon reprocessing (Fig. 4). However, the relative intensities of the subsequent reprocessing cycles (that, for brevity, are not shown here) evidence an increased complexity of the degradation mechanisms. These mechanisms may involve chain scission, hydrogen abstraction, and competitive combinations of the great number of radicals produced by the scission reactions.

The specific volume v at ambient temperature (23°C) is plotted against the number of cycles in Figure 6. The data points, winged by error bars, can be trendlined by a parabolic fit with a maximum at around the fourth cycle. From the value of v, another important property, the free volume, v_f, can be obtained. Assuming that the occupation volume v^* varies linearly with the average molecular weight, v_f can be calculated by

$$v_f = v - v^* = v - K \cdot \bar{M} \qquad (1)$$

**Figure 8** Effect of reprocessing on the birefringence.
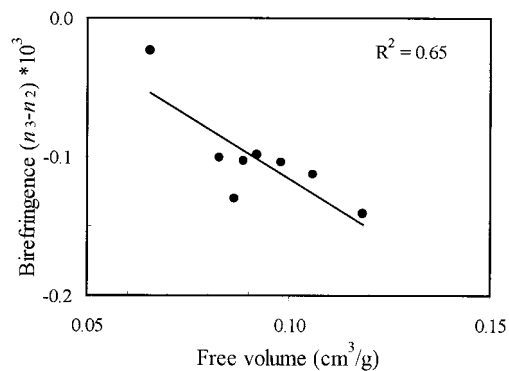
**Figure 9** Linear correlation between the birefringence and the free volume.

where $\bar{M}$ is the average molecular weight, and K is a coefficient equal to $3.50 \cdot 10^{-5}$ cm^3 mol/g^2.[19]

As observed in Figure 7, the free volume, derived from eq. (1), increases almost linearly with the number of cycles, suggesting that reprocessing promotes free space, enhancing the molecular motion. This is also reflected in the birefringence loss, which can be attributed to less oriented macromolecules (Fig. 8). Hence, a negative correlation should exist between the birefringence and the free volume, as observed in Figure 9. Conceivably, the transparency loss may also be associated to the increment of free volume, namely through the variation of the refractive index caused by inter- and intramolecular chain spacing changes (Fig. 10). Monitoring the way the free volume of BAPC varies with reprocessing is thus a good and simple way to predict the evolution of properties that depend on the degree of orientation.

Similar relations can be obtained for other properties. The apparent shear viscosity η of the polymer melt through a capillary can be expressed as
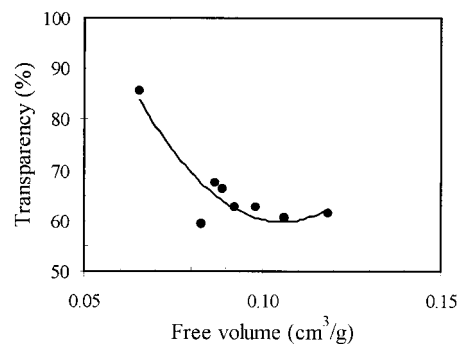
Figure 10 Relation between the transparency and the free volume.
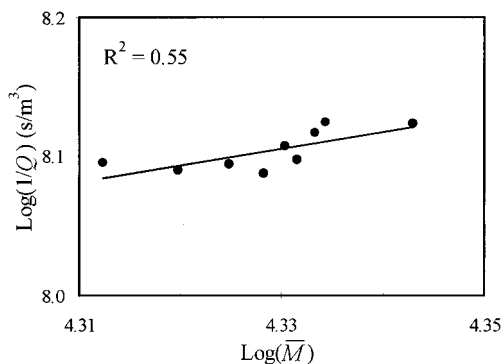
Figure 11 Logarithmic plot of the reciprocal of the volume output at constant shear stress vs the molecular weight.

$$\eta = \frac{\pi R^3 \cdot \Delta P}{8Q \cdot (L/R)} \qquad (2)$$

where ΔP is the pressure measured at the capillary entrance, L and R are the capillary length and radius, respectively, and Q is the melt volume output in cm³/s. Q can be obtained from the melt flow index, $Q = \text{MFI} \cdot v/600$, where MFI and v are expressed in g/10 min and cm³/g, respectively.

As $1/Q$ is directly related to the melt viscosity, it should be possible to equate it to the molecular weight, through a power law dependence similar to that of the viscosity:
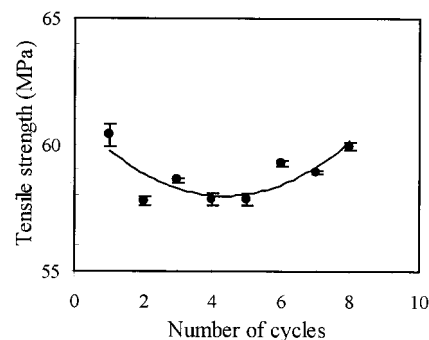
$$\eta = k \cdot \bar{M}^\alpha \qquad (3)$$

where k and α are constant characteristics of the material. Then, from eqs. (2) and (3), at constant shear stress,

$$\frac{1}{Q} = \frac{8k(L/R)}{\pi R^3 \cdot \Delta P} \cdot \bar{M}^\alpha \qquad (4)$$
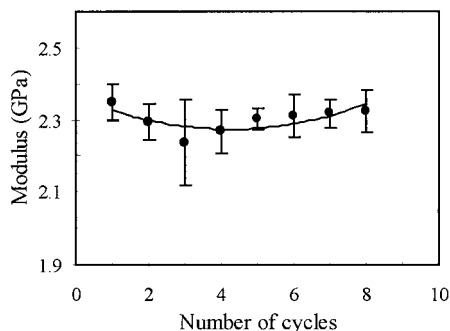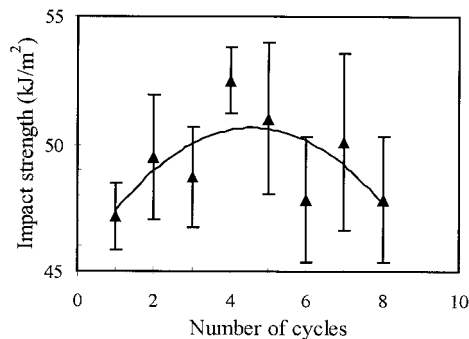

Figure 12 Effect of reprocessing on the modulus.

Figure 13 Effect of reprocessing on the tensile strength.

A logarithmic plot of $1/Q$ against the molecular weight of the polymer in each cycle is shown in Figure 11. A straight line can be well fitted to the data points, showing that the molecular weight can be used to derive the variation of the flowability with recycling.

Similar to the results of other work,[13,14] the variation of the tensile modulus is very small, being within the uncertainty of the experimental data (Fig. 12). Nevertheless, the trend is consistent with that shown by the tensile strength (Fig. 13). In both plots a property loss is noticeable in the first four cycles, followed by an increment in the subsequent ones. An opposite variation is exhibited by the impact strength (Fig. 14). In spite of the large scatter of the data, a maximum is clearly observed after four cycles. For a glassy, amorphous material like BAPC, the key parameters controlling the mechanical performance are expected to be the molecular weight, the free volume, as well as the chemical nature and the molecular orientation. In this context, the puzzling results presented in Figures 12–14 may be associated with complex degradation process, and the


Figure 14 Effect of reprocessing on the impact strength.

corresponding dominant mechanisms. One of these could be the enhanced mobility of the macromolecules due to the increment of the free volume. The other, most probably, is the increasing loss of capacity for energy absorption as the molecular scission progresses. When one of the mechanisms dominates, the property varies accordingly. This is clearly the case of the impact data, in which the former mechanism is dominant in the first four cycles, and the latter thereafter. The tensile strength and modulus variations are not so pronounced, and the minimum is not so clear. In any case, in the beginning of the recycling sequence the decrement of these properties could be due to the dominance of chain scissions. The situation is inverted after the fifth cycle, when some other effect becomes dominant. However, in all these situations, the free volume clearly plays a role in the variation of the properties. As v_f is related to the specific volume (and $\bar{M}$), it should be possible to correlate both the impact and tensile strengths and the modulus with v. These correlations are presented in Figures 15(a–c), evidencing that the properties depend quasi-linearly on the specific volume. Thus, using the corresponding intercepts and slopes it is possible to obtain any of them from the value of v in each cycle.

CONCLUSIONS

The reciprocal of the molecular weight and the free volume of bisphenol-A-polycarbonate were found to be linear functions of the number of reprocessing cycles. This indicates that more free space is generated for the motion of the polymer chains, leading to less oriented molecules and changing the optical properties. Accordingly, both the birefringence and the transparency can be correlated with v_f. Similarly, the melt volume output at constant shear stress can be correlated with $\bar{M}$. This shows that the molecular weight and the free volume are key parameters for assessing the variation of important optical and rheological properties with reprocessing.

The specific volume which is related to v_f and $\bar{M}$, is also of great importance, as it can be used to calculate the mechanical performance, namely the tensile and impact strengths and the modulus. Assuming a linear dependence of these properties on v, simple equations can be derived that allow their prediction from the value of v in each cycle.
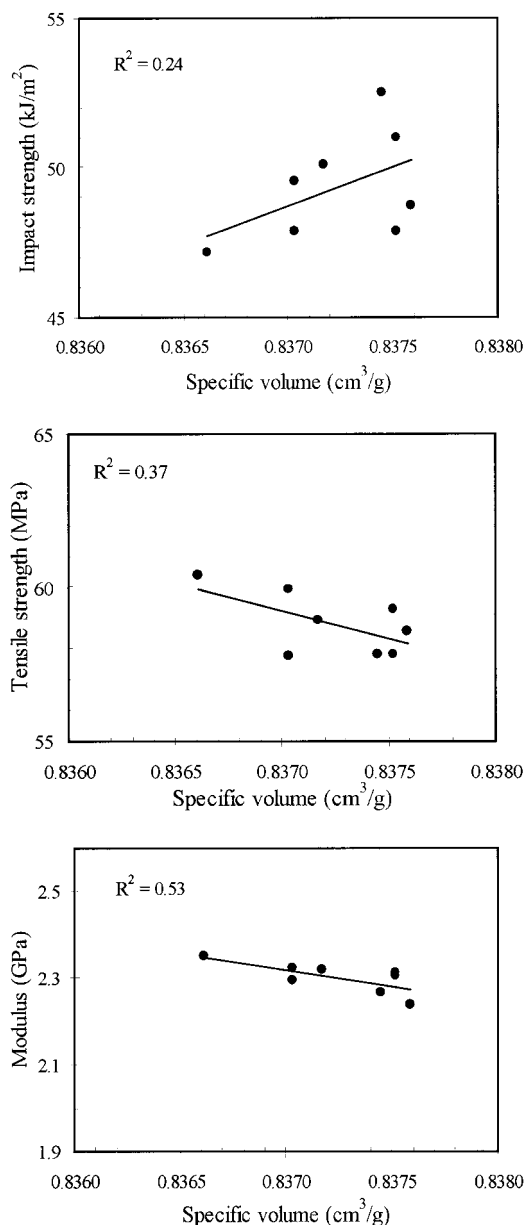
Figure 15 Linear correlation between the mechanical properties and the specific volume. (a) Impact strength, (b) tensile strength, and (c) modulus.

The properties of recycled polycarbonate determined in the present work—namely, the mechanical properties, are not very different from those of the original polymer. The recyclates can thus be easily incorporated in commercial parts, especially for applications in which optical or aesthetic considerations are not critical.

logical Co-operation, through the Scientific Co-operation Agreement between Portugal and the People's Republic of China, which allowed the completion of the present work (Proc. 423/China).

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