Investigation of the Polycarbonate/Crushed-Rubber-Particle Interphase by Nanoindentation

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ABSTRACT: Nanoindentation tests were carried out to determine the nanomechanical characteristics of recycled polycarbonate (PC)/crushed-rubber blends. Both the modulus and hardness of the matrix, particles, and PC/rubber interphase were obtained. Different blends with untreated, flamed, and washed rubber particles were characterized. The results proved the good recyclability of PC. Indentations performed in the PC matrix showed that the rubber acted as a plasticizer for the PC matrix, probably because of a diffusion of free rubber chains. This plasticizing effect was accentuated by flamed rubber particles in the blends. The results showed that flame and methanol treatments modified the morphology of the rubber particles. These treatments induced a significant increase in the nanomechanical properties of the rubber particles. In the interface region between the PC matrix and rubber particles, a gradual change in the mechanical properties was confirmed. Profiles of the interface modulus and hardness helped to determine the interface width according to the particle treatment. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2687–2694, 2007

Key words: hardness; indentation; modulus; polycarbonates; rubber

INTRODUCTION

Waste management will be one of the major challenges of industrial countries in forthcoming years and has been the subject of different governmental directives concerning sorting and recycling. Therefore, the recycling of polymers is an interesting solution for solving part of the environmental problem by saving energy and raw materials. However, thermomechanical reprocessing generally alters the properties of polymers, and unfortunately, the compatibility between polymers is generally very poor. Nevertheless, several studies have shown that it is possible to achieve good-performance recycled polymers and blends by precise control of the physicochemistry, interfaces, and processing conditions of the regenerated systems.

The mechanical properties of recycled polycarbonate (PC) are not very different from those of the virgin polymer.[1,2] This recycled polymer can be easily incorporated into commercial parts even though a decrease in the PC molecular weight occurs during recycling.[1] Therefore, the brittle character of PC, which may arise from recycling, can be balanced out by the incorporation of rubber particles.

Several authors have investigated the mechanical properties of rubber-toughened PC. Cho et al.[3] reported that it was possible to enhance the notch sensitivity of PC by the incorporation of rubber particles. Another study has shown that the best rubber particle size and rubber content in PC/rubber blends for optimizing the blend impact strength are 0.25 μm and 4 wt %, respectively.[4]

A number of researchers[5–7] have investigated the mechanical properties of recycled rubber. For example, Kumnuantip and Sombatsompop[5] investigated the dynamic mechanical properties of tire-tread reclaimed rubber/natural rubber blends after vulcanization. Fukumori et al.[6] studied the tensile properties of devulcanized rubber stemming from recycled tires. They found that the tensile strength and breaking elongation were satisfactory in a new tire with up to 10% recycled rubber,. Sombatsompop and Kumnuantip[7] investigated the rheological, physical, and mechanical properties and cure characteristics of blends of tire-tread reclaimed rubber and natural rubber.

Many authors have studied nanoindentation in various polymers. For example, Cross et al.[8] carried out indentations in polystyrene films after nanoimprinting. Different regions of the polymer were tested. The mechanical properties of polystyrene films were similar in the different areas. Shen et al.[9] investigated nylon 66/organoclay nanocomposites by nanoindentation.

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They used different strain rates to explore the strain-rate effect on the mechanical properties of the composites. Park et al.[10] worked on crosslinked, ultra-high-molecular-weight polyethylene. They used nanoindentation to investigate the polymer stiffness according to the different methods used to crosslink the ultra-high-molecular-weight polyethylene. The recent development of nanoindentation has enabled the characterization of mechanical properties on micrometer scales for heterogeneous polymer blends. Zhu et al.[11] studied the modulus and hardness of poly (vinyl chloride) (PVC)/rubber blends with nanoindentation. They showed an interface region characterized by an abrupt change in the modulus and hardness. Mina et al.[12] used microindentation to study the microhardness of poly(methyl methacrylate) (PMMA)/natural-rubber blends. They also investigated the micromechanical properties of the PMMA/rubber-particle interphase.

Several authors have studied PC by nanoindentation.[13–16] Fang and Chang[13] performed nanoindentation on PC polymer films. They showed the importance of the loading rate, strain rate, applied load, and hold time on the elastic modulus and hardness. In another work, Fang et al.[14] studied the effects of the speed, surface depth, roughness, and applied load on the modulus and hardness. Charitidis et al.[15] investigated the effect of an antiscratch coating on the nanomechanical properties of PC lenses. Hochstetter et al.[16] attempted to figure out the macroscopic tensile-test-equivalent stress–strain curves for some amorphous polymers (and particularly PC) with different tip shapes.

In this work, a nanoindentation technique was used to study the mechanical properties of the bulk and interfaces of a rubber-toughened PC developed with recycled materials. The aim of this study was to assess the width of the interphase between PC and rubber particles according to their treatment.

EXPERIMENTAL

Materials

Two main materials were used:

1. PC scraps were obtained from Self-Signal Co. (Rennes, France). The original material was taken from Palsun sheets elaborated by Polyglass. PC sheets were cut and transformed into pellets by mechanical grinding.
2. Tire-tread reclaimed rubber (based on natural rubber) was supplied by Delta-Gom Co. (Noyon, France). The rubber waste was roughly crushed into small pieces less than 5 mm in size for recycling. Those particles were frozen with liquid nitrogen and mechanically ground. Particles less than 100 μm in size were selected through sieving. The crushed-rubber-particle size is a very important parameter for rubber/epoxy blends; several researchers[17,18] have indicated that the use of fine rubber particles may lead to slightly improved mechanical performances of blends.

Two surface treatments were carried out. A flame treatment was carried out to activate the surface of crushed rubber and achieve a satisfactory level of adhesion with PC. This treatment was performed with a propane blowtorch. The flame temperature was about 2500°C, and the particles were flamed for 0.5 s from a distance of 20 cm. The second treatment was a solvent wash with methanol.

Particles of rubber free chains were extracted by immersion in chloroform. This extraction was performed on untreated, flamed, and washed particles. The particles were dipped in chloroform for 48 h, dried, and weighed. For each sample, the free-chain concentration was 10 wt %, whatever the aforementioned treatment was.

Processing

All the materials were dried in a hot-air-circulating oven at 90°C for 12 h before compounding. Crushed rubber particles were blended with PC pellets in a Brabender (Friedrichshafen, Germany) internal mixer for 12 min. Processing was carried out at 260°C at a rotation speed of 40 rpm. The rubber-particle concentration in the blends was 20 wt %.

Four different samples were studied (all concentrations are weight percentages):

1. 100% PC.
2. 80% PC/20% untreated crushed rubber.
3. 80% PC/20% flame-treated crushed rubber.
4. 80% PC/20% solvent-treated crushed rubber.

After the compounding, the blends were compression-molded into 2-mm-thick plates. The specimens were then cut into small pieces suitable for nanoindentation tests.

All indentation surfaces were polished up to a 3-μm particle size with a solution finish. With the nanoindentation method, the sample preparation is very important because accurate results are obtained only if the indentations are significantly deeper than the surface topography of the specimen. Meticulous polishing can significantly reduce the uncertainty in determining the surface properties when nanoindentation experiments are performed.[19]

The average surface roughness was measured with a profilometer at 0.4 μm.

The polished samples were mounted on aluminum cylinders with superglue for subsequent indentation tests.

Nanoindentation measurements

Nanoindentation tests involve the contact of an indenter on a material surface and its penetration to a specified load or depth. The load is measured as a function of the penetration depth. Figure 1[20] shows a typical load–penetration curve [Fig. 1(a)] and an illustration of the unloading process showing the parameters characterizing the contact geometry [Fig. 1(b)]. In this case, the penetration depth is the displacement into the sample starting from its surface. Calculation methods used to determine the modulus and hardness are based on the work of Oliver and Pharr.[21]

For a perfectly sharp Berkovitch indenter, the projected contact area (A) can be calculated as follows:

$$A = 24.56h_c^2 \tag{1}$$

where h_c is the contact depth ($h_c = h_{\max} - h_s$, where $h_{\max}$ is the maximum depth and h_s is the surface depth; see Fig. 1). The hardness (H) is defined as the indentation load divided by A:

$$H = P_{\max}/A \tag{2}$$

where $P_{\max}$ is the maximum load. We can obtain the elastic unload stiffness (S) as follows:

$$h_c = h_{\max} - \varepsilon\frac{P_{\max}}{S} \tag{3}$$

where ε is a constant that depends on the geometry of the indenter (0.72 for a Berkovich indenter).

The effective elastic modulus (E_r) can be calculated as follows:

$$S = 2aE_r = \frac{2\beta}{\sqrt{\pi}}E_r\sqrt{A} \tag{4}$$

where, a is the contact radius, A is the projected contact area between the indenter and the sample surface at $P_{\max}$, S is the contact stiffness of the material, and β is a constant depending on the geometry of the indenter (1.034 for a Berkovitch tip).

E_r, which accounts for the deformation of both the indenter and the sample, is given by

$$\frac{1}{E_r} = \frac{(1-v^2)}{E} + \frac{(1-v_i^2)}{E_i} \tag{5}$$

where E_i (1140 GPa) and ν_i (0.07) are the elastic modulus and Poisson's ratio of the diamond indenter, respectively, and E and ν are the elastic modulus and Poisson's ratio of the sample, respectively.

Indentation tests were performed with a commercial nanoindentation system (Nanoindenter XP, MTS Nano Instruments, Oakridge, TN) at room temperature (23 ± 1°C) with a continuous-stiffness-measurement technique. In this technique, an oscillating force at a controlled frequency and amplitude is superimposed onto a nominal applied force. The material, which is in contact with the oscillating force, responds with a displacement phase and amplitude.

A three-side, pyramidal (Berkovitch) diamond indenter was employed for the indentation tests. The area function, used to calculate the contact area from h_c, was carefully calibrated with a standard sample before the experiments.

The strain rate during loading was maintained at 0.05 s^{-1} for all the samples. We used a 3-nm-amplitude, 70-Hz oscillation under identical load-rate conditions. The nanoindenter tests were carried out in the following sequence: first, after the indenter touched the surface, it was driven into the material at a constant strain rate of 0.05 s^{-1} to a depth of 1500 nm (700 nm for indentations at PC/rubber interfaces); second, the

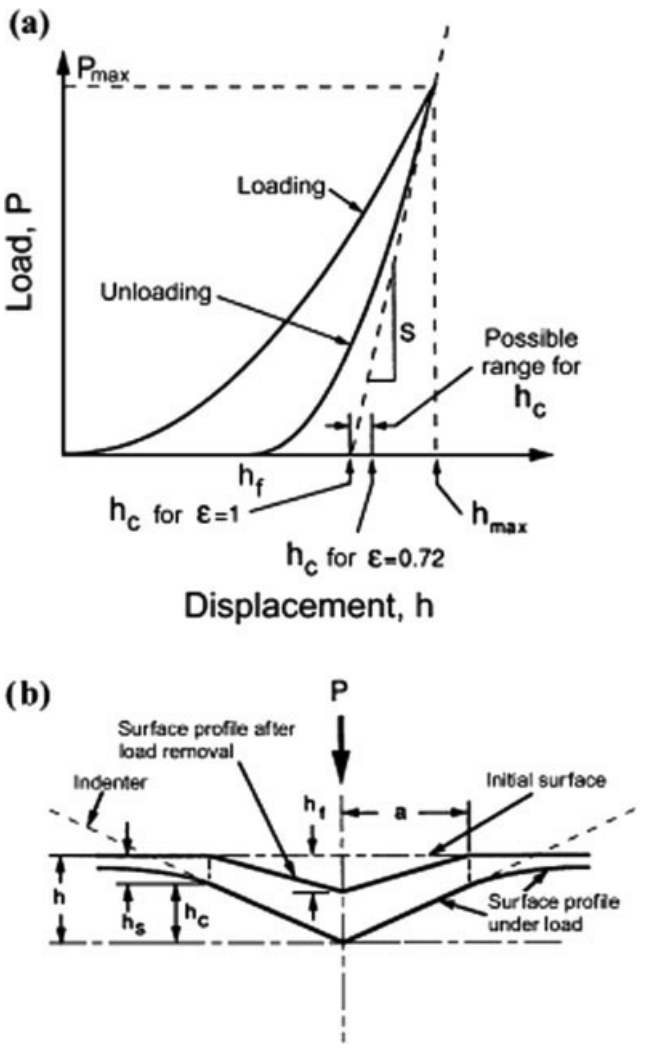

Figure 1 (a) Typical load–penetration curve and (b) illustration of the unloading process showing the parameters characterizing the contact geometry. h_f, depth of the residual indent area.

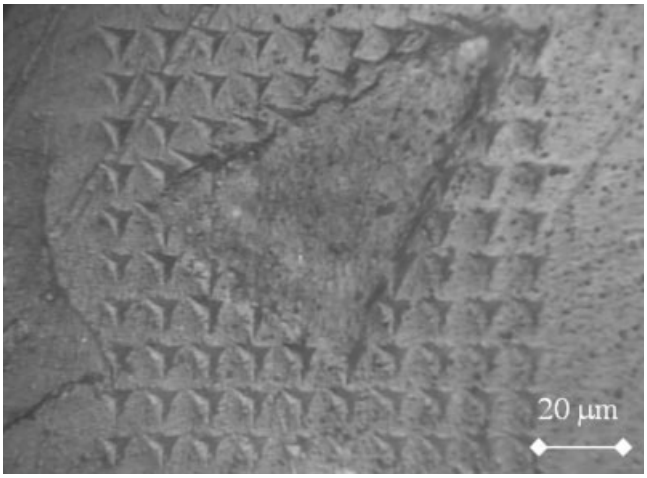

Figure 2 Indentation matrix in a PC/rubber blend.

load was held at maximum value for 60 s; and finally, the indenter was withdrawn from the surface at the same rate as the loading until 10% of P_{max} was reached.

Nanoindentation experiments were performed as indentation matrices on PC sheets, PC blends, and PC/rubber blends. In the case of PC/rubber blends, indentations were carried out on both sides of the PC/rubber-particle interface. Other indentations were conducted on PC and at the center of rubber particles to assess the mechanical characteristics of the two elements of the blends. Figure 2 shows an indentation matrix in a PC/rubber blend. This figure shows the indentation position around a rubber particle in the case of a 10 × 10 matrix with 10 μm between each indentation.

Only samples showing stable nanomechanical properties were preserved to avoid heterogeneities in the blend depth.

RESULTS AND DISCUSSION

Indentations in PC

Figure 3(A,B) shows results from tests performed on pure and recycled PC with the nanoindenter. This figure shows the modulus or hardness evolution according to the indentation displacement into the sample surface. A Poisson's ratio of 0.35 was used in all modulus calculations.

Grinding and reprocessing do not show significant effects on the modulus and hardness of PC as probed by nanoindentation. Similar results were obtained from classical tensile tests of standard test samples.

In Table I, the modulus and hardness values obtained for the different PC samples are shown. The values are averaged for an indentation depth of 1000–1500 nm from a minimum of 30 indentations. We can compare these results with literature values. Good agreement is found with Hochstetter et al.'s[16] values (3.20 vs 3.18 GPa for the neat PC modulus). The modulus and hardness of the PC sheet are significantly lower than those of PC lenses reported by Charitidis et al.[15] (3.20 vs 3.70 GPa for the modulus and 0.22 vs 0.27 GPa for the hardness). However, these values obtained by nanoindentation present an overestimation of 25% in comparison with compression values (3.20 vs 2.50 MPa for the PC modulus[22]). According to Briscoe and Sebastian,[23] we can interpret these results as an effect of the high hydrostatic pressure generated beneath the Berkovitch indenter.

We have plotted in Figure 4(A,B) the evolution of the Young's modulus and hardness as functions of the depth for the PC matrices in PC/untreated-rubber, PC/flamed-rubber, and PC/washed-rubber blends. As shown in Table I, a slight decrease in the mechani-

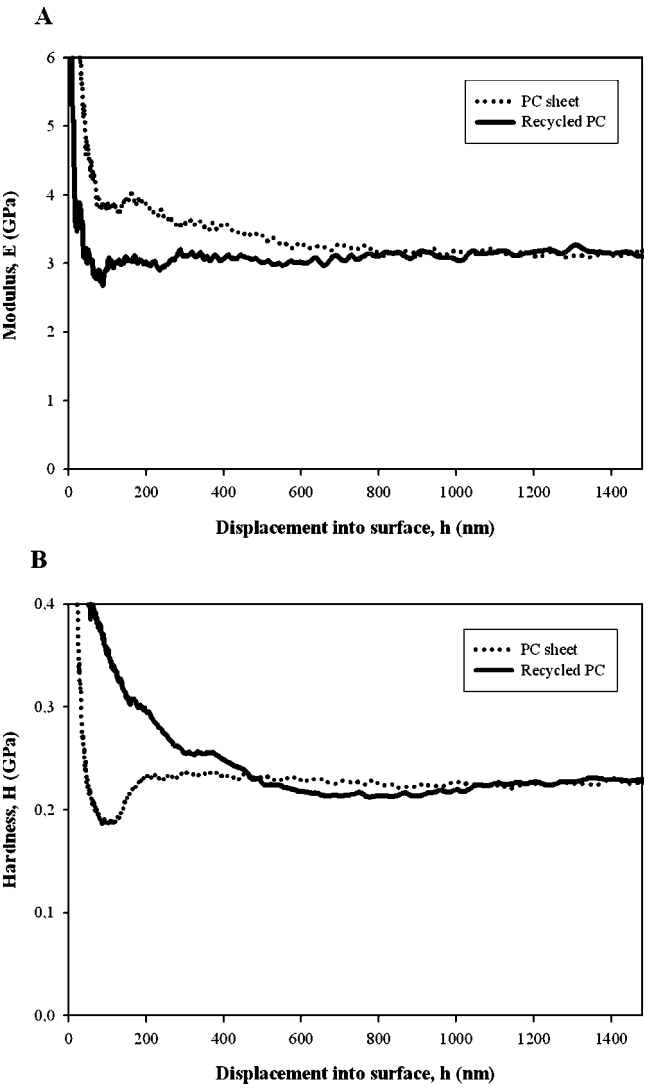

Figure 3 (A) Modulus and (B) hardness profiles of the PC sheet and recycled PC.

TABLE I
Summary of the Modulus and Hardness Values of PC Sheets, Recycled PC, and PC Matrices in PC/Rubber Blends

Sample	Modulus (GPa)	Hardness (GPa)
PC sheet	3.20 ± 0.097	0.223 ± 0.010
Recycled PC	3.19 ± 0.155	0.222 ± 0.013
PC matrix in a PC/untreated-rubber blend	2.98 ± 0.197	0.203 ± 0.013
PC matrix in a PC/flamed-rubber blend	2.01 ± 0.092	0.165 ± 0.019
PC matrix in a PC/washed-rubber blend	2.79 ± 0.147	0.183 ± 0.022

cal properties between the PC matrix in PC/untreated-rubber blends and PC sheets and recycled PC can be observed. We can suppose that untreated rubber particles induce a slight plastification of the PC matrix probably caused by a diffusion of rubber free chains out of the crosslinked particle network. It has been estimated that 10% of the rubber free chains can be extracted by a solvent treatment, yielding a decrease in the PC mechanical properties.

This decrease is more significant for the PC matrix with washed rubber particles, and the PC mechanical properties show an abrupt decrease for PC/flamed-rubber-particle blends. The diffusion of free chains seems to be favored by washing and even more by flaming. Flaming enables the creation of polar functions on rubber chains at the surface of the particles and also chain breakage. By the way, these polar functions induce greater miscibility and therefore mobility of rubber free chains because of the important affinity between the polar function and PC chains. Thus, the diffusion of rubber free chains is greater with flamed particles. The effect of methanol washing on rubber chain diffusion is unclear, but an oxidation process can also be assumed.

Indentations on rubber particles

Figure 5(A,B) illustrates the modulus and hardness profiles for untreated, washed, and flamed rubber particles. A Poisson's ratio of 0.49 was used in all modulus calculations.

In Table II, the modulus and hardness values obtained for the different rubber particles are indicated. The values are averaged for an indentation depth of 1000–1500 nm from a minimum of 30 indentations. Indentations were carried out in the center of different rubber particles. The hardness values obtained for untreated rubber can be compared with literature values. Mina et al.[12] performed microindentation tests on PMMA/rubber blends. In rubber particles, they obtained hardness values between 110 and 170 MPa versus 10 MPa for our samples. These values are different, but the experimental conditions are not similar either. Indeed, Mina et al. performed microindentation and not nanoindentation; the tip and dimensions of the shape were not the same, and the rubber crosslinking density was different. Hochstetter et al.[16] showed that different tip shapes induced different results for the same material. Moreover, the crosslinking density of the rubber may induce large differences in the results.

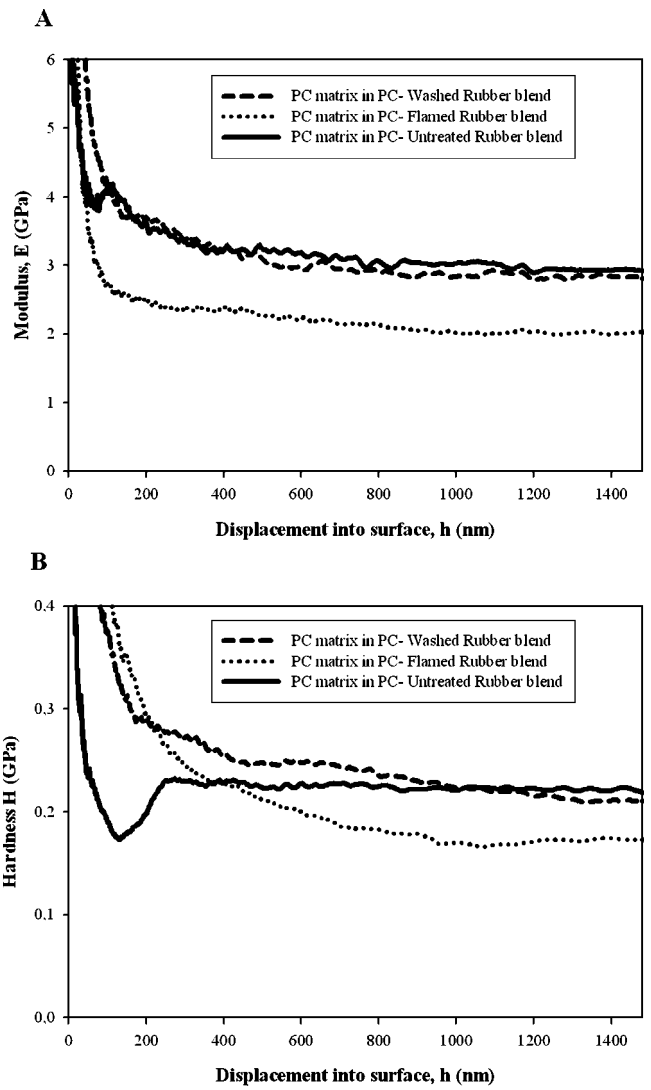

Figure 4 (A) Modulus and (B) hardness profiles of the PC matrix in washed, untreated, and flamed rubber particles.

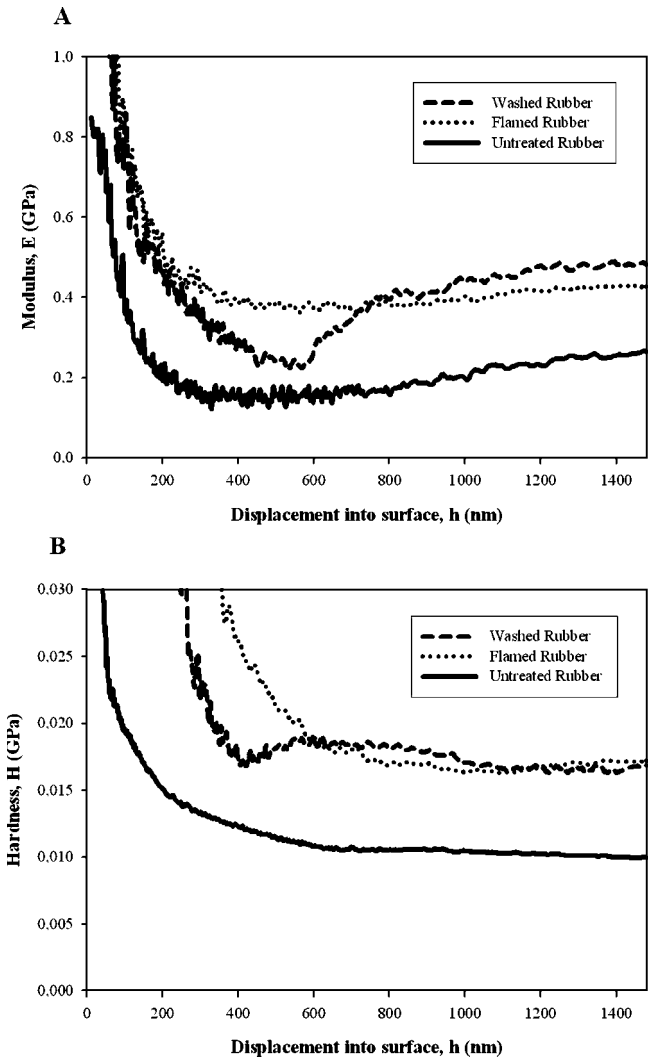

Figure 5 (A) Modulus and (B) hardness profiles of washed, flamed, and untreated rubber particles.

We can now compare the values obtained for untreated and treated rubber particles. The modulus and hardness of flamed rubber are close to the mechanical properties obtained with washed rubber. On the other hand, the values of the untreated rubber are clearly lower, indicating that the treatments induce an important increase in the rubber stiffness. These results prove that flame and solvent treatments modify the properties of the rubber particles.

Pastor-Blas et al.[24] showed that an oxygen-plasma treatment of vulcanized rubber particles modifies the surface morphology of the rubber. This treatment produces surface cleaning by the removal of some surface heterogeneities and creates a morphology similar to ribbons.

Oxygen-plasma treatment also induces a migration of waxes and zinc stearate to the surface. We can suppose that the same phenomenon could occur with a flame treatment. The migration of waxes can produce a significant modification of the hardness and modulus values of rubber particles. A chemical or physical aging process due to the flame or methanol treatment can also explain this increase in the hardness. Moreover, the enhancement of the surface crosslinking can also be achieved with the flame treatment, whereas the methanol treatment can remove wax and other impurities from the surface of the particles.

Indentations at PC/rubber-particle interphases

Figure 6 shows the modulus and hardness values measured as functions of the distance from the interphase for untreated, washed, and flamed rubber particles. A value of 0 indicates the interphase position evidenced by optical microscopy on the nanoindenter. The hardness and modulus values increase with the distance up to a plateau, which corresponds to the values of the PC matrix.

The curve profiles are different according to the treatments. In the case of flamed or untreated particles, we have observed an abrupt increase in the mechanical properties, which highlights a low interphase width between the rubber particle and the matrix. On the contrary, the evolution of the hardness and modulus of washed rubber particles is much smoother with the distance from the interphase.

From the profiles of the modulus and hardness shown in Figure 6, the interphase region has been estimated to be between 5 (for flamed and untreated particles) and 10 μm (for washed particles). In a previous work, Zhu et al.[11] investigated a PVC/SBR blend interphase with nanoindentation tests. The interphase region was estimated to be about 5 μm. This value is consistent with our results.

These results validate the existence of a variable interphase region between the two components of the blend according to the particle treatment. Moreover, Figure 6 shows that the shape of the interphase is asymmetrical. The hardness and modulus evolve more strongly on the PC side than on the rubber side. The interdiffusion that takes place during the melt-mixing process favors rubber chain diffusion out of the particles rather then the PC ones.

TABLE II
Summary of the Modulus and Hardness Values of Untreated, Washed, and Flamed Rubber Particles in PC/Rubber Blends

Sample	Modulus (GPa)	Hardness (GPa)
Untreated rubber particles	0.245 ± 0.057	0.010 ± 0.006
Washed rubber particles	0.489 ± 0.076	0.017± 0.005
Flamed rubber particles	0.431 ± 0.0.084	0.017 ± 0.006

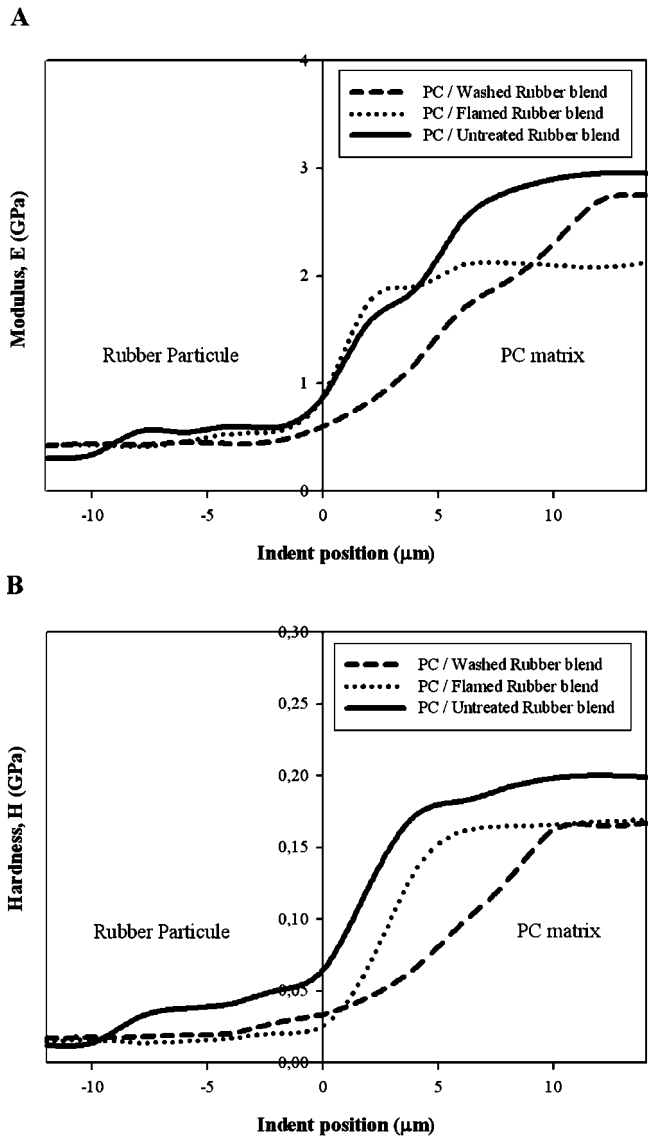

Figure 6 (A) Modulus and (B) hardness profiles at interfaces of PC/washed-rubber, PC/flamed-rubber, and PC/untreated-rubber blends.

The adhesion between PC and rubber particles is improved by chain interdiffusion and plastification. Therefore, washed rubber particles are expected to exhibit better adhesion with PC. Preliminary tensile results have shown the tensile strength at yield (23 ± 2 MPa vs 13 ± 1.5 MPa for a PC/untreated-rubber blend and 16.5 ± 2.5 MPa for a PC/flamed-rubber blend) and elongation at break (3.3 ± 0.3 vs 1.5 ± 0.2 for a PC/untreated-rubber blend or PC/flamed-rubber blend) to be better for PC/washed rubber. These results indicate that the matrix–particle interphase is optimized for this particle treatment.

This adhesion will be evaluated with complete macroscopic tensile and brittle tests in a forthcoming work.

CONCLUSIONS

In this work, we have studied the mechanical properties of recycled PC/rubber blends with nanoindentation. Nanoindentation is a powerful tool that can be used to show differences in the hardness or modulus at various locations on a sample and according to the rubber-particle treatment.

Indentation tests carried out with PC matrices and rubber particles have shown reproducible values and have evidenced differences between the samples. These results have led to the following main conclusions:

1. Reprocessing does not show a significant effect on the modulus and hardness of PC. PC is not much affected by moderate recycling, that is, grinding and subsequent melt mixing.
2. In PC/rubber blends, rubber acts as a plasticizer of the PC matrix, probably because of a diffusion of rubber free chains and additive desorption. This plasticizing effect is more important when flamed rubber particles are introduced into blends.
3. Flame and solvent treatments modify the morphology and surface chemistry of the rubber particles. These treatments produce a significant increase in the hardness and modulus values of rubber particles.
4. Nanoindentation tests performed at PC/rubber-particle interphases evidence an interphase region. A larger width is achieved with methanol-washed particles in blends.

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