Toughening of Crosslinked Polystyrene with Liquid Rubber

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ABSTRACT: The optimum conditions for preparing poly(styrene-*co*-divinylbenzene) were determined and the variation of the mechanical properties of the networks with the crosslinking density was evaluated. The molecular weight between crosslinks was in the 800–12,000 range. The flexural modulus and flexural strength were 5000 and 110 MPa, respectively, for the more crosslinked materials. When liquid rubber (hydroxyl-terminated polybutadiene) was incorporated into the glassy matrix, these values dropped to 2500 and 70 MPa, respectively, but the impact resistance increased to 70 J/m. These values were comparable to some commercial grade high impact polystyrene resins. The particle size of the dispersed rubber phase was on the nanometer scale, and attempts to increase its dimensions should provide further improvement in the impact properties. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2098–2105, 2001

Key words: crosslinked polystyrene; toughening; liquid rubber

INTRODUCTION

High impact polystyrene (HIPS) is obtained by the polymerization of a styrene monomer in which rubber is dissolved in bulk or bulk-suspension processes. The rubber, usually polybutadiene (PB), is dispersed in the styrene as particles. The particle size and its distribution, which are important for the degree of reinforcement, depend on the shear rate imposed by stirring. Phase inversion occurs after a certain degree of polymerization for styrene is attained, and the PS that is formed is the continuous phase.[1,2]

The physical blending of the two polymers has also been used, but the product from the former process has better modulus and impact properties for the same rubber content. This is due to the chemical reaction between growing PS chains and the rubber, which form grafted chains that act as a polymeric emulsifier, stabilizing droplets that are formed as phase separation begins. Another characteristic of this reactive processing is the inclusion of the continuous phase inside the particles, which increases the effective volume of the rubber phase.[3,4] The reinforcement obtained in this process leads to the improvement of other properties as well, such as increasing the ultimate elongation, ductility, and aging. These characteristics are followed by losses in transparency, tensile stress, and modulus in comparison with the nonmodified polymer. However, HIPS is generally considered to be a much improved version of the regular PS and has a widespread range of technological applications from automobile parts to household appliances.

Theories explaining the micromechanisms of toughening consider that the rubber particles act as stress concentrators, relieve hydrostatic tension by cavitation processes, and produce more extensive matrix deformation by crazing or shear yielding.[5–7]

Crazing, shear banding, and cavitation generally occur prior to impact failure. Dispersions of toughening agents are used to nucleate whatever energy-absorbing mechanism is available, which is frequently crazing or shear banding in thermoplastics and multiple crack formation in thermosets. Specialized texts dealing with the deformation mechanisms in polymers can be found in various studies.[1,2,8–11]

Liquid rubbers are used to reinforce thermosets, particularly epoxy and polyester resins,[12–16] but to our knowledge no attempts to extend this approach to toughen PS have been made so far. In this article we report the obtainment of reinforced crosslinked PS by dispersing oligobutadiene (a liquid rubber) into PS during its polymerization process. This idea was based on the following: commercial liquid rubbers exist in a variety of molecular sizes, in particular hydroxyl-terminated PBs (HTPBs); the liquid state of the rubber allows its easy incorporation into the PS during the polymerization process with a controllable particle size.

EXPERIMENTAL

Materials

Solvents

Ethyl acetate, *n*-butyl acetate, acetone, chloroform, ethyl ether, isopropyl ether, and methanol (Fisher, ACS) were purified according to standard techniques.[17]

Monomers

Styrene (Fisher ACS) was washed free of inhibitor with 5% aqueous NaOH, dried over $CaCl_2$, and distilled under reduced pressure (65°C, 200 mmHg, lit. 67°C[18]) using sulfur in the distillation flask and a copper wire in the distillation column to inhibit polymerization. Divinylbenzene (DVB, Aldrich) was distilled under reduced pressure (43°C, 10 mmHg, lit. 195°C, 760 mmHg[18]).

The HTPB (Liquiflex P, Petroflex, Brazil) was treated and characterized as described in Vilar et al.[19] (number-average molecular weight of 2700 g/mol, number-average functionality of 2.2). Other chemicals were used without further treatment.

Polymerization Procedures

Poly(styrene-*co*-DVB) networks were prepared in bulk using benzoyl peroxide as an initiator (0.5% w/w). The crosslinker concentrations were 0.5, 1.0, 1.5, and 2.0% (w/w). The prepolymer syrup at about 20% conversion was poured into a vertical glass mold and cured at 100°C for 24 h. The HTPB was added during the prepolymer stage for the preparation of the modified networks.

Average Molecular Weight between Crosslinks

The average molecular weight between crosslinks (M_c) was determined by means of equilibrium swelling measurements using the Flory–Rehner theory as described elsewhere.[20]

Determination of Optimum Cure Conditions

The polymerizations were monitored by measuring the material glass-transition temperature by differential scanning calorimetry at intervals of 24, 48, 72, 96, 190, and 240 h for reactions run at 85°C. The thermograms were recorded after heating the samples to 150°C and quenching with liquid nitrogen to −150°C. The glass transitions were determined according to ASTM D 3418 in the range of −150 to +150°C under a continuous nitrogen flow.

Mechanical Behavior

The hardness was evaluated with a Shore D durometer using a 5-kg load and an accommodation time of 15 s. The flexural strength and flexural modulus were measured with a Universal Instron machine at a crosshead rate of 11.5 mm/min and
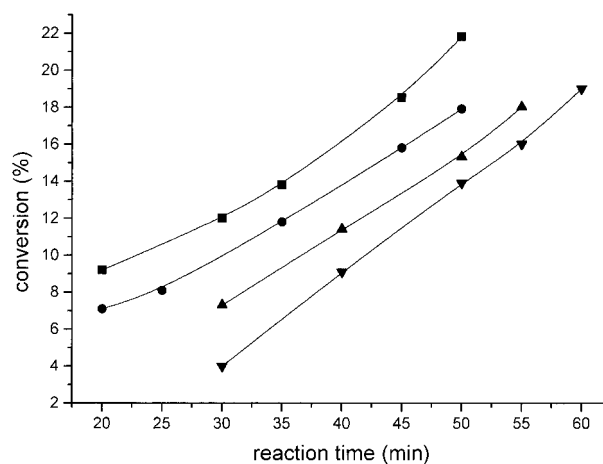

Figure 1 Conversion curves for the bulk copolymerization of styrene and divinyl benzene (DVB): (▼) 0.5% DVB, (▲) 1.0% DVB, (●) 1.5% DVB, and (■) 2.0%.
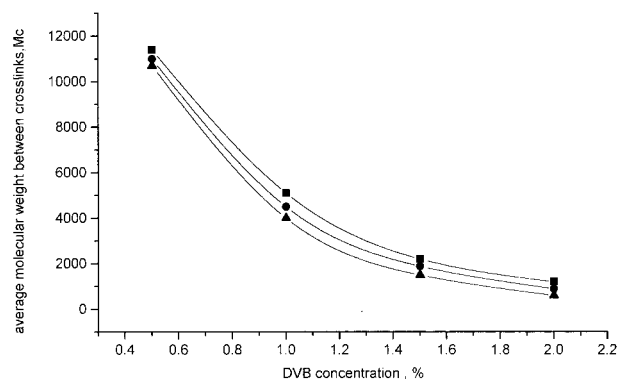
Figure 2   The crosslinking density of poly(styrene-*co*-divinylbenzene) determined by swelling measurements. The solvents were: (▲) ethyl acetate, (●) acetone, and (■) methyl ethyl ketone.

Figure 4   The variation of the crosslinking density of poly(styrene-*co*-divinylbenzene) with cure time for (■) 0.5% DVB, (●) 1.0% DVB, (▲) 1.5% DVB, and (▼) 2% DVB.

a load of 100 kg according to ASTM D 790-71. The impact resistance was determined in an Izod testing machine according to ASTM D 256-78.

The cryogenic fractures were sputter plated with gold using a Baltec SCD 005 apparatus and observed in a Phillips XL30 microscope for scanning electron microscopy (SEM). The metallic layer was approximately 150 Å thick.

RESULTS AND DISCUSSION

To evaluate the effect of the rubber added to the PS matrix, it was necessary to characterize the nonmodified networks. The following parameters were studied for the different levels of crosslinker
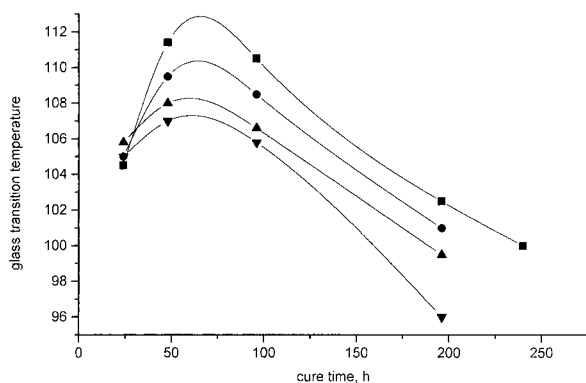
that were used: conversion, crosslinking density, optimal cure time, and mechanical properties.

Nonmodified Networks

Conversion

To minimize the gel effect and shrinking in the mold with consequent defect formation, it was necessary to find the point of maximum conversion with a workable viscosity. Figure 1 shows the conversion curves for DVB concentrations of 0.5, 1.0, 1.5, and 2.0. It was established that the reaction time that gave the best compromise between contraction in the mold and the viscosity should

Figure 3   The variation of the glass-transition temperature of poly(styrene-*co*-divinylbenzene) with cure time for (▼) 0.5% DVB, (▲) 1.0% DVB, (●) 1.5% DVB, and (■) 2.0% DVB.
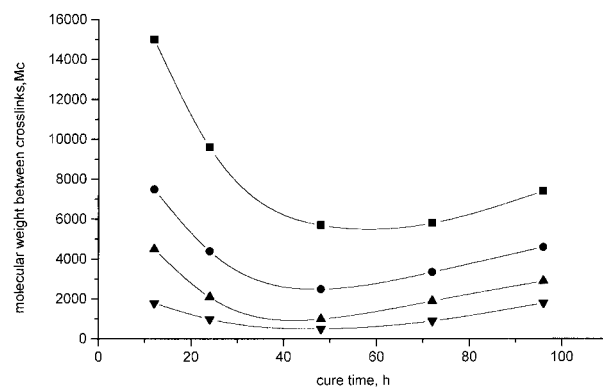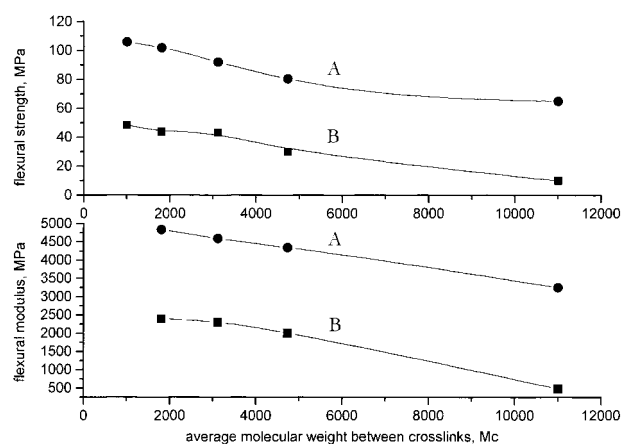

Figure 5   The flexural properties of poly(styrene-*co*-divinylbenzene). (●) nonmodified networks (A curves) and (■) networks modified with the addition of 10% HTPB (B curves).
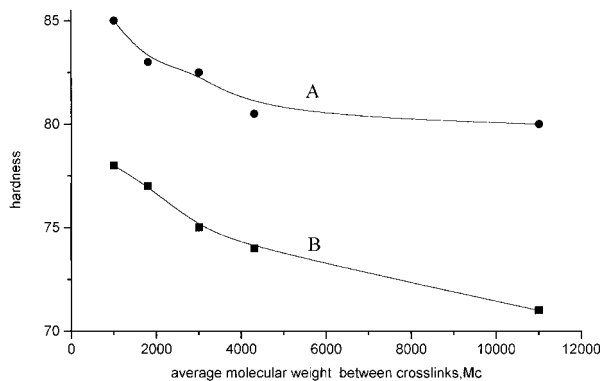
Figure 6 The variation of the hardness Shore D of poly(styrene-*co*-divvinylbenzene) networks with crosslinking density: (●) nonmodified networks (A curves) and (■) networks modified with the addition of 10% HTPB (B curves).

be no longer than that corresponding to a conversion of approximately 20%.

Crosslinking Density

Figure 2 shows the variation of the M_c with the DVB concentration. The solubility parameter of

the polymer used to calculate the M_c was 9.1 $(cal/mL)^{1/2}$.[21,22] The best results were obtained with ethyl acetate, acetone, and methyl ethyl ketone and are shown in Figure 2. The good agreement of the results for the three solvents is noteworthy.

Cure Time

In principle the optimum cure time is the one that permits maximum conversion, reducing the number of free radicals in the final material to the lowest possible value. In bulk polymerization the complete conversion is difficult to achieve because of the high viscosity in the last stages of polymerization and some entrapped radicals usually remain. As a result, long cure times are needed to assure that all monomer is converted. On the other hand, a cure time that is too long can result in chain breaking, leading to degradation. The ideal cure time was determined by monitoring the glass-transition temperature variation with time for cure cycles at 85°C. Figures 3 and 4 show that the maximum glass-transition temperature that corresponds to a minimum M_c was obtained with a 48-h cycle for the four crosslinking levels used.
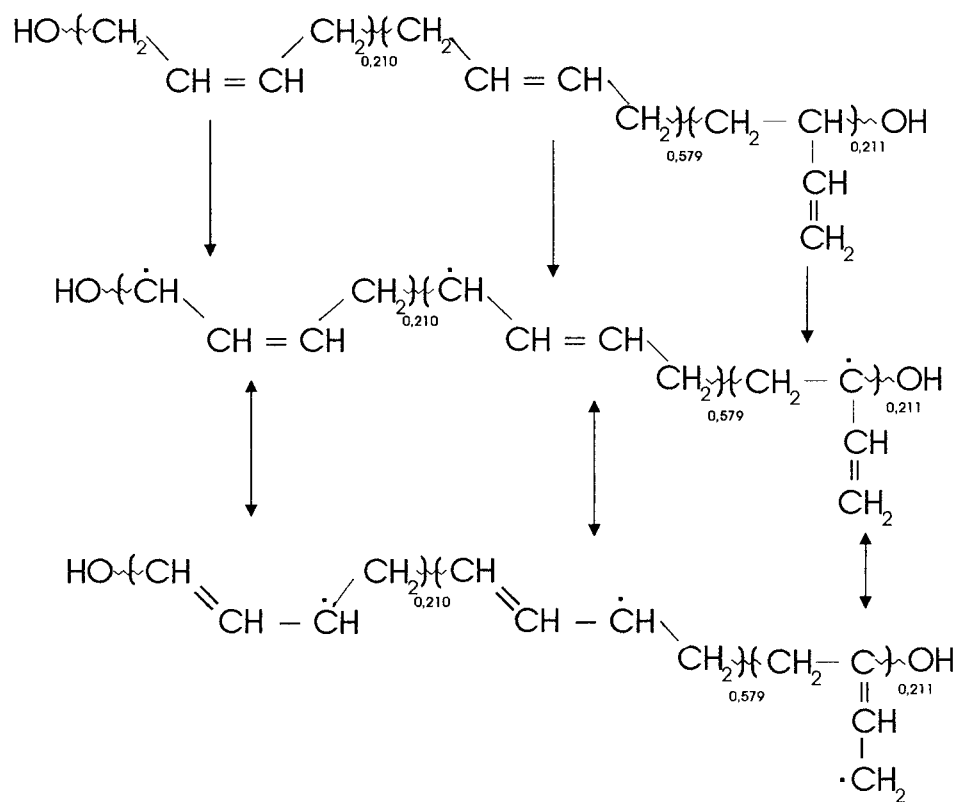
Scheme 1 The HTPB microstructure and most probable reactive sites.
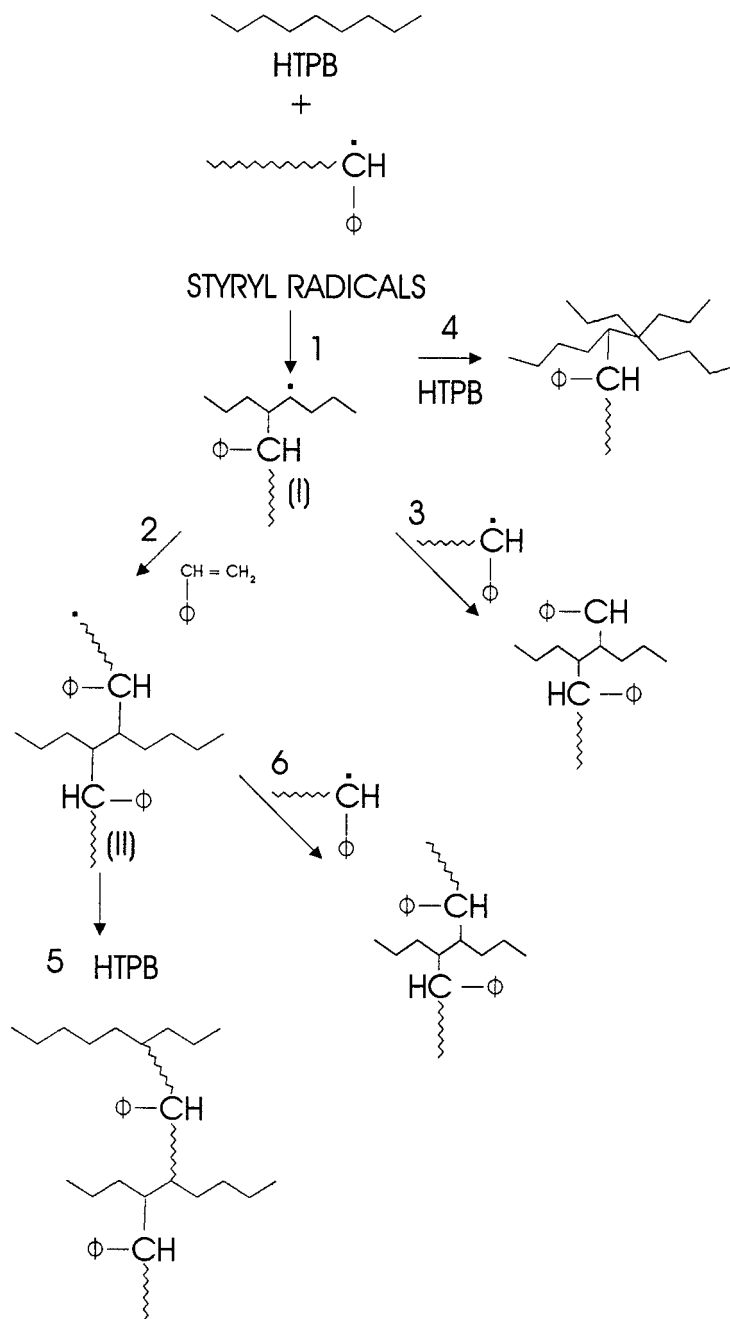
Scheme 2   The steps involved in the reactions of HTPB with growing styryl radicals.

Mechanical Properties

Flexural tests showed a significant increase in flexural strength with the crosslinking density (Fig. 5, curves A). The hardness showed a less pronounced variation (Fig. 6, curve A). The flexural characteristics of the materials were in the range of commercial grades of HIPS.[2]

Rubber Modified PS

The liquid rubber was added in the first step of the polymerization and the mixture was cured with the same conditions used for the nonmodified PS networks. In these conditions the propagating styryl radicals can react with the rubber double bonds, giving rise to grafted and
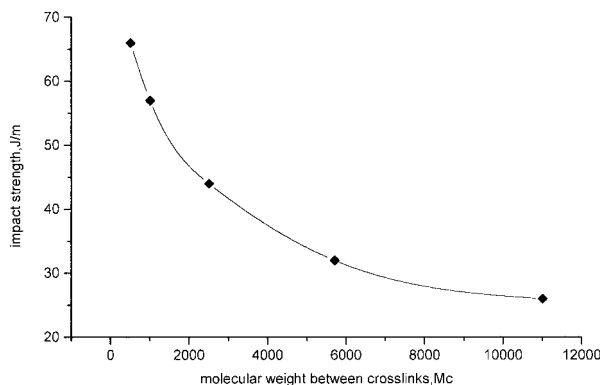
Figure 7 The variation of the Izod impact strength with the crosslinking density of poly(styrene-*co*-divinylbenzene) networks modified with 10% HTPB.

crosslinked rubber chains on the PS backbone. This is particularly desirable because good adhesion between the rubber particles and the matrix

can result from the emulsifying effect of the *in situ* formed copolymer. Schemes 1 and 2 depict some possible chemical reactions between HTPB and the growing polystyryl chains. The most probable HTPB free radicals are those formed in the allylic and vinylic positions in relation to the double bonds. The microstructural determination was made by NMR according to two sources.[19,23]

The maximum amount of rubber incorporation without macroscopic phase separation was 10% HTPB, and this level was maintained in all experiments. The effect of HTPB incorporation into PS networks was evaluated by comparing the results for modified and nonmodified materials.

Figure 5 (curves B) shows the variation of the flexural strength and flexural modulus with the degree of crosslinking. These properties increased with crosslinking as noted before, but the values for the modified materials were lower than those for the nonmodified materials. The same was ob-
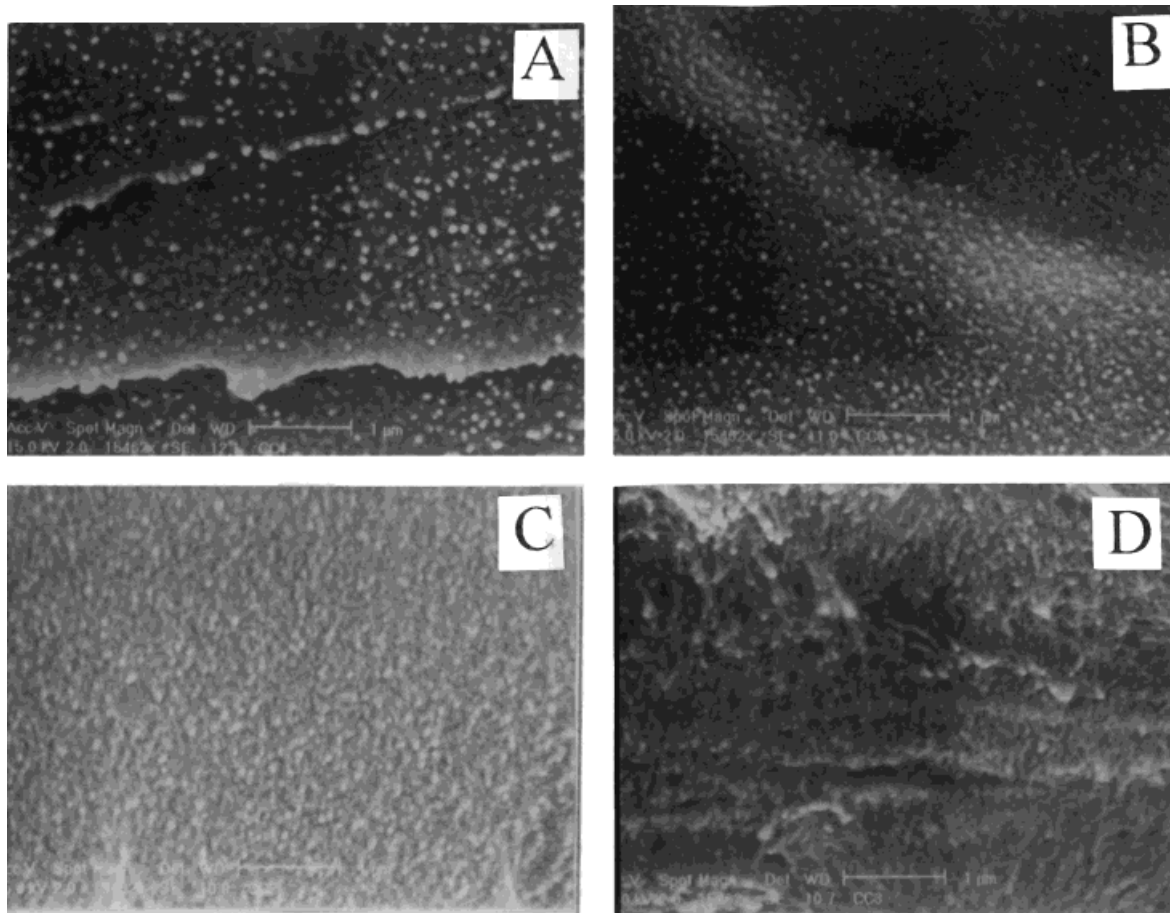

Figure 8 Photomicrographs of the modified networks: (A) 0.5% DVB, $d = 80$ nm; (B) 1.0% DVB, $d = 60$ nm; (C) 1.0% DVB, $d = 45$ nm; and (D) 2.0% DVB, $d = 35$ nm.

served for the hardness as shown in Figure 6 (curve B).

Figure 7 shows the results of the impact tests for the different crosslinking levels. This property was notably increased in the rubber modified PS, going from approximately 10 J/m for M_c values of around 11,000 to about 70 J/m for the highest crosslinked sample.

The results reported here show that the toughening effect of HTPB on PS networks permitted the acquisition of medium impact materials with good flexural properties. Some turbidity was a consequence of the dispersed rubber particles in the materials.

Studies of the impact strength of HIPS showed that this property increases with rubber phase volume.[1,24] At constant rubber concentration an increasing particle size can produce tougher materials; very small particles are inefficient compared to the same volume of larger particles. Studies of the mechanical properties of HIPS as a function of particle size showed that particles with 0.6–3.5 μm diameters typically showed Izod impact results from 48 to 100 J/m.[25] Generally, PS toughening requires rubber particles over 1 μm.[1] The maximum in toughness associated with an optimum particle size in HIPS was 2–5 μm.[1,26,27] One strategy for enhancing the toughness included the use of a multimodal particle size distribution.[2]

The SEM examinations of HTPB reinforced, crosslinked PS showed a dispersed phase with sizes on the nanometer scale and average diameters (d) of 80, 60, 45, and 35 nm for DVB concentrations of 0.5, 1.0, 1.5, and 2.0%, respectively (Fig. 8). These figures are below the desired particle sizes for the full development of the HTPB reinforced materials, and better properties can be anticipated with increases in HTPB particle sizes. Because of its liquid state, variations in the degree of dispersion could be achieved in principle by varying the shear rate during the prepolymer step. The effect of the resulting morphology on the material performance is currently under investigation, and the results will be reported in the near future.

CONCLUSIONS

It was demonstrated that the incorporation of liquid rubber into PS matrices can be used as a means to impart better impact properties. Fur-

ther work is still required to improve the particle size of the dispersed rubber for the full development of the mechanical performance of these materials.

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