

Characterization of Rubber Phase in Acrylonitrile–Butadiene–Styrene Polymers

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Received 5 August 2008; accepted 2 March 2009

DOI 10.1002/app.30371

Published online 29 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The performances of rubber-toughened polymers like acrylonitrile–butadiene–styrene (ABS) are strongly affected by the type and amount of rubber phase. Characterization of rubber phase is an effective method to predict and control the physical and mechanical behaviors of ABS materials. In this work, different methods have been employed to determine the amount of rubber phase in ABS polymers. The first method was based on thermogravimetry using a particular step degradation of the polymer. In the second method, characteristic absorption bands in the Fourier transform infrared spectra were used to make a calibration curve to determine the rubber con-

tent of unknown ABS samples. The third method was based on variation of heat capacity of ABS polymers with increasing the rubber phase content. In the fourth method, a two-step solvent extraction followed by centrifuging was used to separate the rubber particles of different ABS samples. Separation of hardened rubber particles was used to study the size and size distribution of rubber particles. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1908–1913, 2009

Key words: ABS; rubber content; step degradation; heat capacity; SHRP; particle size distribution

INTRODUCTION

It is well established that the impact toughness of glassy polymers can be appreciably enhanced by incorporation of grafted rubber particles. Two specific examples are high-impact polystyrene, consisting of rubber particles in polystyrene, and acrylonitrile–butadiene–styrene (ABS) polymers. The elastomeric component, e.g. polybutadiene (PB), exists as a discrete phase dispersed in the thermoplastic component, e.g. a copolymer of styrene and acrylonitrile (SAN). Grafting of SAN onto the elastomer permits the presence of a distinct rubber phase in a sufficiently compatible state.

Rubber content is one of the important factors determining the physical and mechanical properties, and rheological behavior of ABS polymers. For this reason, determination of rubber content of ABS polymers has been the subject of various papers. The use of Wijs reagent is an old method suggested by Kemp and Peters.¹ This method was based on iodine titration for determination of unsaturation degree of the materials like fats or oils. The test involves the addition of iodine to the existing double bonds using a solution of iodine monochloride in glacial acetic acid. Gesner studied the solvent extraction method.² He examined several solvents

to extract different phases from ABS. The most satisfactory separation was done with xylene, cyclohexane, and acetone. He could successfully separate free rubber, SAN copolymer, grafted or crosslinked rubber, antioxidants and rosin soap. Treatment of the isolated graft terpolymer with ozone has been employed to cleave the unsaturated elastomeric substrate from grafted SAN.³ Turner used ethyl acetate, hexachlorobutadiene, and their mixture for extraction of the grafted and ungrafted components.⁴

Giaconi et al. proposed a stereological approach, which consisted of analyzing transmission electron microscopy pictures from material slices having different thicknesses and then reconstruction the bulk situation.⁵ Sun et al. characterized various ABS core-shell modifiers and studied the effect of grafting degrees on dispersion mechanisms of rubber particles and morphology of ABS/poly(butylene terephthalate) blends using scanning electron microscopy (SEM).⁶ Šlouf et al. studied the morphological behavior of rubber particles in polypropylene/ABS blends. They proposed a new microscopic and image analysis technique that converted qualitative information from SEM to semi-quantitative structure descriptors.⁷

Jelinski et al. used ¹³C-nuclear magnetic resonance spectra for determination of rubber phase content of the ABS polymers.⁸

Nandan et al. employed some methods including differential scanning calorimetry and thermogravimetric analysis for the characterization of the polymer blends of ABS.⁹

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Contract grant sponsor: NPC-RT.

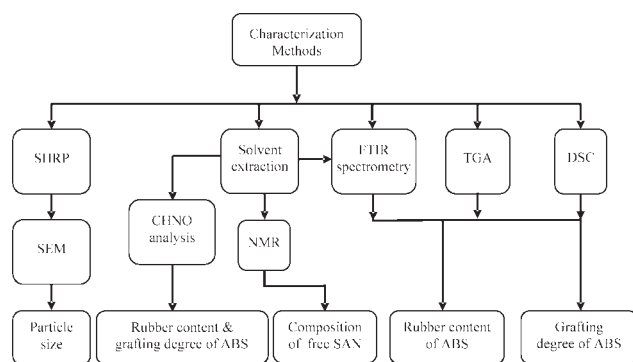


Figure 1 The different steps carried out to measure the rubber content, degree of grafting, and particle size of ABS samples.

Kuhn et al. studied the properties of a bimodal graft-ABS. These properties included degree of grafting and grafting efficiency, acrylonitrile content of the grafted chains, average particle diameter, and particle diameter distribution, molar mass distribution of the ungrafted chains, chemical distribution of the ungrafted chains, molar mass distribution of the SAN resin matrix, chemical distribution of the SAN resin matrix.¹⁰

Bair et al. analyzed ABS by differential scanning calorimetry, mechanical analysis, and gel permeation chromatography. They found that the magnitude of glass transition temperature for the rubber phase decreased as the ratio of SAN grafted to polybutadiene was increased.¹¹

In this work, the amount of rubber component in ABS polymers was determined by three different methods including thermogravimetry, Fourier transform infrared spectroscopy, and differential scanning calorimetric analysis. The results were compared with those obtained from the extraction method. The size and size distribution of rubber particles were evaluated by studying the scanning electron micrographs of separated hardened rubber particles (SHRP).

EXPERIMENTAL

Materials

The materials used in this study were a PB consisting of 2.5% vinyl, 4% trans, and 93.5% cis isomers, obtained from Arak Petrochemical (Arak, Iran), a SAN copolymer consisting of 74 wt % styrene and 26 wt % acrylonitrile, supplied by Tabriz Petrochemical (Tabriz, Iran), and two graft-ABS polymers which contain 50–60 wt% PB grafted by SAN chains: ABS-TP, supplied by Tabriz Petrochemical (Tabriz, Iran), and ABS-GP, supplied by Ghaed Basir Petrochemical (Golpayegan, Iran). Acetone, cyclohexane,

propanol, and benzene were supplied by Merck (Darmstadt, Germany).

Methods

ABS-M samples were prepared by melt compounding PB with SAN in a Brabender W-50-EHT internal mixer (Germany). The numbers after “M” show the rubber content of these samples. Initial temperature of mixing was set at 215°C and rotors specialized for thermoplastics mixing were selected.

ABS-C films were prepared by dissolving different amounts of PB and SAN, in a constant total mass, in benzene at 80°C. Then the solutions were cast on plates and dried in a vacuumed oven. The numbers after “C” show the rubber content of these samples. The obtained films were used to prepare a calibration curve for Fourier transform infrared spectroscopy.

The size and size distribution of the rubber particles were studied by SHRP method. In this method, the rubber particles were rapidly cross-linked in a 1 wt % solution of OsO₄ in cyclohexane and before swelling, the matrix was etched from the sample using acetone. By centrifuging (at 5000 rpm for 20 min), the rubber particles were separated from solution. After washing the particles by cyclohexane in a Maxwell ultrasonic bath (Turkey) for 15 min, the grafted chains on rubber particles were cleaved by means of the ultrasonic cleaner in the presence of propanol. This test was performed on ABS-TP and ABS-GP samples.

To obtain the percent of grafting by solvent extraction, the graft-ABS which contains PB-g-SAN, ungrafted PB, and free SAN, was dispersed in cyclohexane. The ungrafted PB forms a stable dispersion in cyclohexane but the PB-g-SAN/free SAN mixture precipitates. The dispersion of PB in cyclohexane

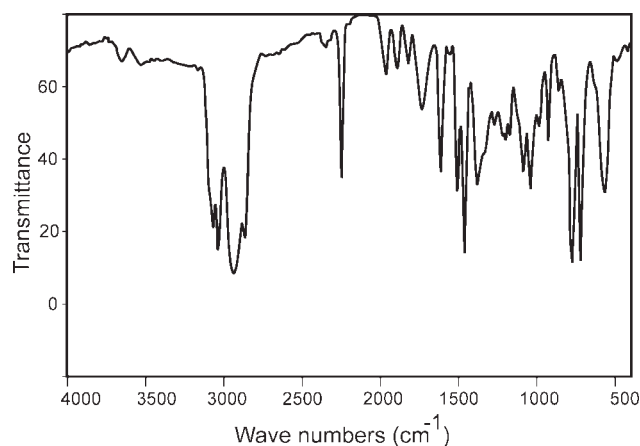


Figure 2 Fourier transform infrared spectrum of a thin film cast from solution of free SAN (of ABS-TP) in acetone.

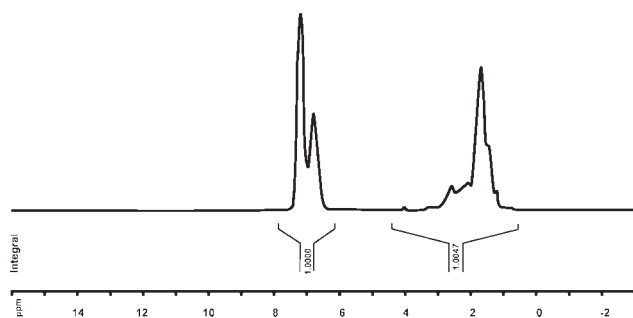


Figure 3 ^1H -nuclear magnetic resonance spectrum of the free SAN (of ABS-TP).

was separated from precipitated components by a Buchner funnel and dried in an oven with nitrogen atmosphere at 80°C for 24 h. The weight of ungrafted PB was determined by gravimetry. The free SAN was separated from PB-g-SAN/free SAN mixture by dissolving the mixture in cold acetone and centrifugation in an ultracentrifuge.

Apparatus and methodology

The different steps carried out to measure the rubber content, degree of grafting and particle size of ABS samples are summarized in Figure 1. Fourier transform infrared spectroscopy was carried out with a Unicam Matson 1000 spectrometer, in the wave number range $400\text{--}4000\text{ cm}^{-1}$.

To determine the degree of grafting and rubber content of graft-ABS, ungrafted PB was removed from graft-ABS (ABS-TP and ABS-GP) by dissolving the graft-ABS in refluxed cyclohexane for 1.5 h. The remaining material from filtration (PB-g-SAN and free SAN) was dissolved in the cold acetone for 2 h and then was centrifuged at -5°C and 10,000 rpm. In the obtained mixture, the solution contained free SAN and the settled material was PB-g-SAN component. The composition of PB-g-SAN obtained from solvent extraction was determined by a Thermo Finnigan Flash EA 1112 CHNO elemental analyzer. The ^1H -nuclear magnetic resonance spectra were recorded in CDCl_3 on a Bruker Spectro Spin-400 MHz spectrometer.

Thermogravimetric/differential thermal analysis and differential scanning calorimetric analysis were performed using a Pyris Diamond thermogravimetric/differential thermal analyzer and a Mettler

TABLE I
Results of CHNO Elemental Analysis of PB-g-SAN of Two Different Graft-ABS polymers (ABS-TP and ABS-GP)

Element	N (wt%)	C (wt%)	H (wt%)
ABS-GP	1.36	88.69	9.95
ABS-TP	2.14	88.01	9.85

TABLE II
Compositions of ABS-TP and ABS-GP Samples

	PB (wt%)	SAN (wt%)
ABS-GP	60.10	39.9
ABS-TP	55.57	44.43

Toledo differential scanning calorimeter, respectively. Scanning electron micrographs were obtained using a CamScan (MV2300) microscope.

RESULTS AND DISCUSSION

Figure 2 shows the infrared spectrum of a thin film prepared from free SAN (of ABS-TP) solution in acetone. The lack of characteristic absorption band of PB (the band occurring at 970 cm^{-1}) shows that the separation of SAN from PB-g-SAN of ABS-TP has been successful.

The ^1H -nuclear magnetic resonance spectrum of separated SAN is shown in Figure 3. The signal appearing around 7 ppm is related to styrene aromatic proton and the signals appearing between 1 and 3 ppm are related to the aliphatic protons of SAN. The mole ratio of acrylonitrile to styrene in the SAN can be calculated from the nuclear magnetic resonance spectrum.

Sediment grafted component obtained by centrifugation (PB-g-SAN obtained from ABS-TP and ABS-GP samples) was analyzed by elemental analysis and the results for two different graft-ABS are presented in Table I. By gravimetry of the separated components and the results of elemental analysis, total compositions were calculated (Table II).

Fourier transform infrared spectroscopy

Quantitative analysis by infrared spectroscopy has some problems. However, comparing the spectra

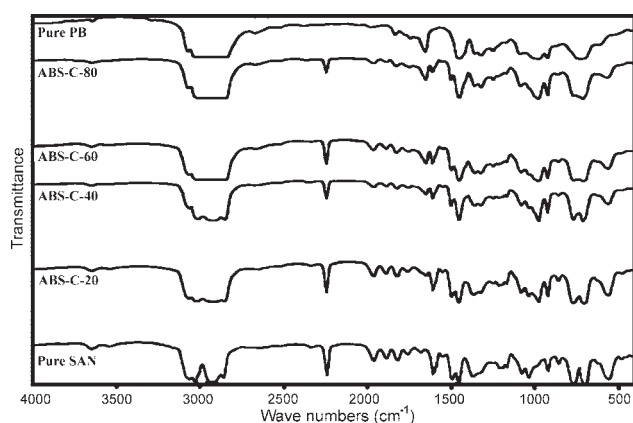


Figure 4 Fourier transform infrared spectra of the films prepared from ABS-C samples having different rubber contents.

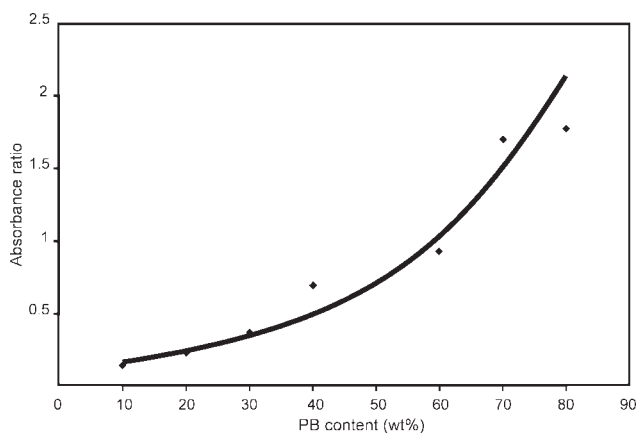


Figure 5 Calibration curve obtained from Fourier transform infrared spectra of ABS-C samples.

obtained from specimens having different amounts of one component can help to determine the content of that component in an unknown specimen. For this purpose, several thin films of ABS-C samples with different rubber contents were prepared. The infrared spectra of the samples are shown in Figure 4.

The absorbance bands appearing at 520, 570, 1453, and 2243 cm^{-1} are related to acrylonitrile and those appearing at 540, 690, 1450, 1490, 1610, 2960, and 3070 cm^{-1} indicate the presence of styrene. The absorbance bands occurring at 708, 916, 970, 1649, 2950, and 3070 cm^{-1} are related to PB.¹²

The ratios of absorbance peaks at 1649 and 1610 cm^{-1} , the characteristic peaks of PB and styrene, respectively, were selected to calculate the percent of each phase. The absorbance ratio versus PB content has been drawn in Figure 5 to obtain a calibration curve for determination of rubber content of unknown ABS specimens. By adding the absorbance amount of acrylonitrile at 2243 cm^{-1} in denominator

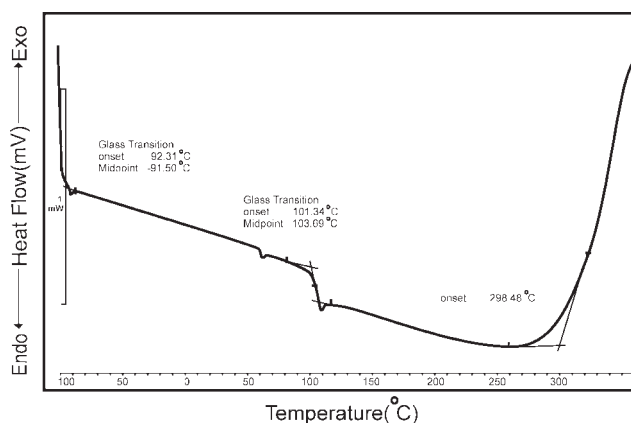


Figure 6 Differential scanning calorimetric thermogram of an ABS-M sample containing 20 wt % PB at a heating rate of 5°C/min.

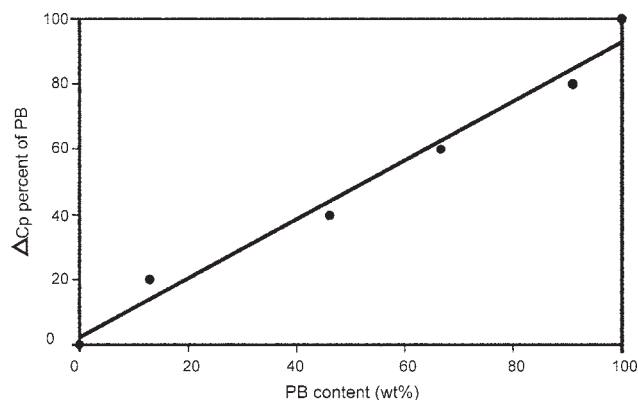


Figure 7 Variation of ΔC_p fraction of PB versus PB content in ABS-M samples.

of absorbance ratio, the effect of SAN composition can be eliminated from the calibration curve. The rubber content of an unknown ABS sample can be determined using this calibration curve and its infrared spectrum.

Variation of heat capacity

Figure 6 shows a differential scanning calorimetric thermogram of an ABS-M-20 sample. The changes in the base line of thermograms at -91°C and 103°C (T_g s of PB and SAN, respectively) are attributed to heat capacity variation (ΔC_p) when transition from rubbery to glassy states occurs.

For both components, ΔC_p decreases with decreasing the concentration of corresponding component. Differential scanning calorimetric analysis for ABS-M samples having 0, 20, 40, 60, 80, and 100 wt % of rubber was performed and ΔC_p values at glass transition temperatures of PB and SAN were calculated. The percent of ΔC_p for rubber phase ($100 \times (\Delta C_p)_{\text{PB}} / ((\Delta C_p)_{\text{SAN}} + (\Delta C_p)_{\text{PB}})$) is curved versus PB content in

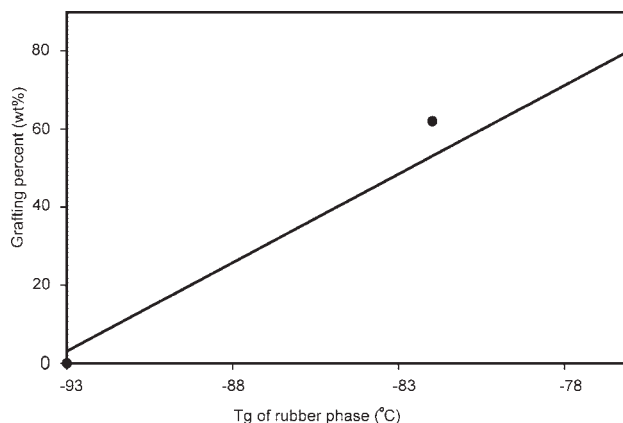


Figure 8 Variation of T_g of rubber phase versus grafting percent in ABS samples (ABS-M-60, ABS-TP, and ABS-GP).

TABLE III
Temperature Program for the Degradation of Different Components in ABS-M Samples

Step	Initial temperature (°C)	Final temperature (°C)	Heating rate (°C/min)	Holding time (min)
1	40	300	50	0
2	300	365	10	0
3	365	365	0	25
4	365	460	50	0
5	460	460	0	25
6	460	600	50	0

Figure 7. Rubber contents of unknown samples can be determined using this curve and measuring the ΔC_p of PB component from differential scanning calorimetric thermogram.

In ABS polymers, the T_g of rubber phase is affected by structural parameters like crosslinking in PB, density of the grafting on PB surface, and molecular weight of grafted SAN.¹³ The reduction of ΔC_p with increasing graft level appears to be caused by the reduced number of configurational changes that can occur in grafted polybutadiene molecules at T_g .¹¹ Variation of T_g for rubber phase was studied for three specimens (ABS-M-60, ABS-TP and ABS-GP) with 0, 62, and 75 percent of grafting (which is defined as the weight of PB-g-SAN divided by total weight of ABS) and is portrayed in Figure 8.

Step degradation

In ABS polymers, each phase begins to degrade in a certain temperature zone. These different degradation temperatures can be used to determine the concentration of each phase, if an appropriate step-wise heating program is applied. This heating program is shown in Table III.

Degradation of SAN and PB is completed in two different stages on heating at 365 and 460°C, respec-

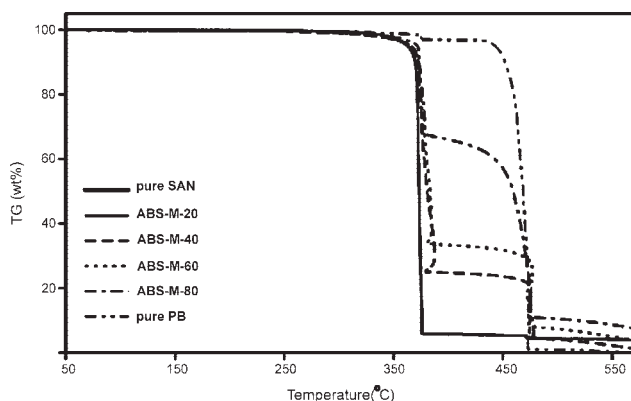


Figure 9 Thermograms of ABS-M samples with different rubber contents obtained by two-step degradation temperature program.

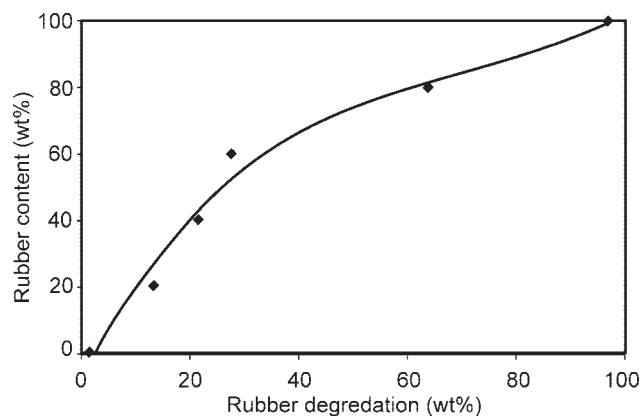


Figure 10 Variation of rubber content versus rubber degradation percent of ABS-M samples.

tively, for 25 min. Degradation of grafted component begins at 300°C; therefore, the temperature was increased from 300 to 365°C with a slower rate because of good detection of grafted component.

Figure 9 shows the thermograms of six ABS-M samples having 0, 20, 40, 60, 80, and 100 wt % of rubber. Figure 10 illustrates the variation of rubber content versus rubber degradation percent (the weight loss of rubber phase divided by total weight loss $\times 100$).

Figure 11 illustrates the thermograms of three ABS samples (ABS-TP, ABS-GP, and ABS-M-60) having a same PB/SAN ratio but different percent of grafting. As shown, during heating at temperatures about 300–365°C, the samples exhibited a different degradation behavior, and the shapes of the thermograms change with percent of grafting. The first step degradation of grafted samples begins at lower temperatures and continues with a slight slope to complete the first step degradation. On contrary, for ungrafted ABS sample (PB/SAN physically blend), the onset of first step degradation appears at higher temperatures, but continues with a sharp slope.

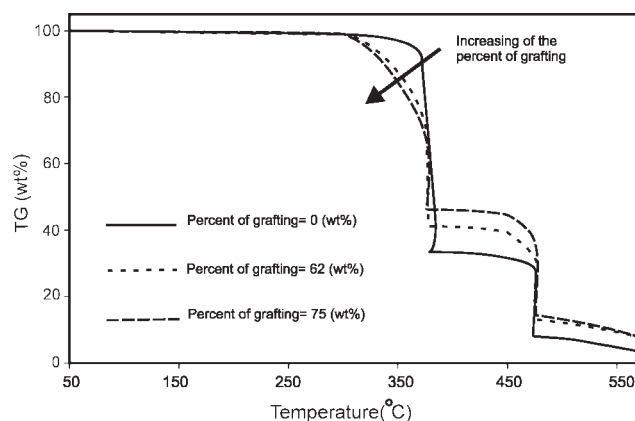


Figure 11 The thermograms for ABS specimens (ABS-GP, ABS-TP, ABS-M-60) having different percents of grafting.

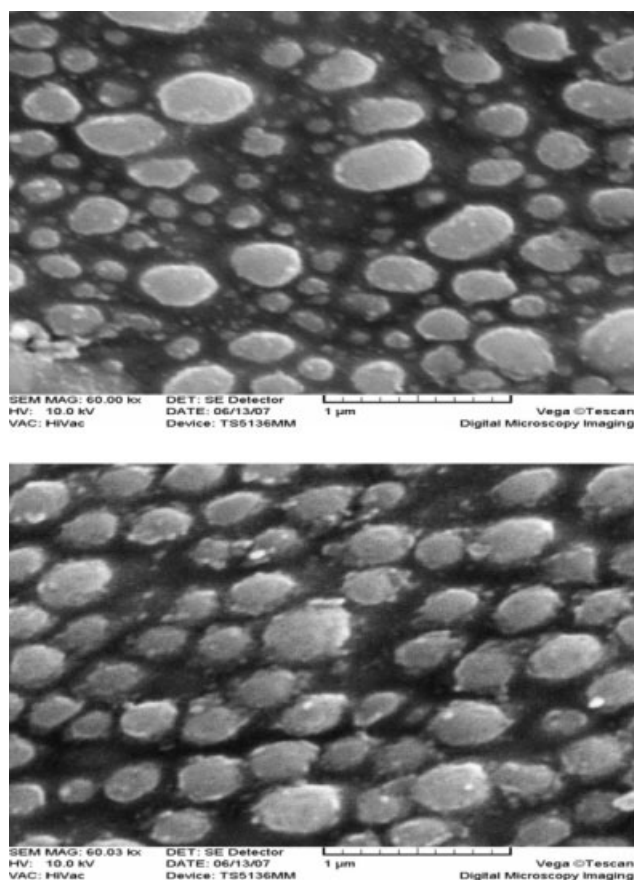


Figure 12 Scanning electron micrographs of ABS-TP and ABS-GP samples prepared by SHRP method indicating (a) a monomodal particle size distribution, and (b) a wide monomodal particle size distribution.

Determination of rubber particle sizes

SHRP enables determination of size and size distribution of rubber particles. In SHRP method, rubber particles were rapidly crosslinked by OsO_4 and before swelling of the particles, the matrix was etched using acetone. By centrifuging, the rubber particles were separated from solution. Grafted chains on rubber particles were cleaved by means of an ultrasonic cleaner in the presence of propanol. After gold coating of the separated particles, the particle size and size distribution are studied from scanning electron micrographs. Two kinds of ABSs (ABS-GP and ABS-TP) containing 48 wt % rubber

with different particle size distributions were evaluated by this method (Fig. 12). While the micrograph of Figure 12(a) indicates a monomodal distribution, a wide monomodal particle size distribution can be seen in scanning electron micrograph of Figure 12(b).

CONCLUSIONS

Four methods to characterize the dispersed and continuous phases in ABS plastics were studied. These methods included two-step degradation, measuring heat capacity variation, Fourier transform infrared spectroscopy, and solvent extraction. The latter method was used to evaluate the results of the three former methods. Measurement of heat capacity variation exhibited closer results to solvent extraction results. T_g s of ABS polymers were measured by differential scanning calorimetric analysis and the amount of shift in T_g of rubbery phase gave useful information about the grafting ratio of SAN on rubber particles. Separation of hardened rubber particles enabled studying the size and size distribution of rubber particles.

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