Structural Modification of Expandable Polystyrene. III. Copolymerization with Siloxane-Based Macroinitiator

Isa Taşkıran[1,2]

[1]R&D Center, Petkim Petrochemical Holding, Inc., 41470 Körfez, Kocaeli, Turkey
[2]Civil Aviation College, Kocaeli University, 41285 Arslanbey, Kocaeli, Turkey

ABSTRACT: Conventional expandable polystyrene (EPS) was chemically modified by preparing copolymers containing 0.1%, 0.2%, and 0.5% siloxane-based macroinitiator. This was used to enhance the surface and thermal properties of EPS particles. Copolymeric expandable polystyrene samples were characterized with various techniques including ^{1}H-NMR, gel permeation chromatography, differential scanning calorimetry, scanning electron microscopy, and contact angle measurement. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4826–4831, 2006

Key words: polystyrene; modification; synthesis; polysiloxones; structure–property relations

INTRODUCTION

Expandable polystyrene (EPS) is one of the important industrial plastic commodities and has interesting properties that lead to its use in a wide spectrum of applications, especially in the packaging and construction of commodities such as hot drink cups, ice chests, and sheets for thermal insulation. Expanded PS beads, composed of small spherical-shaped particles containing about 98% air, are commonly used in the cellular plastics and polymer industries. EPS, being comparatively inexpensive and lightweight, is a cost-effective solution for moderately heavy, fragile items such as artifacts, photographic equipment, audio and video electronic products, and instruments.

The polymerization of EPS occurs in the presence of suspension stabilizers and styrene-soluble polymerization initiators. Suspension polymerization can be thought of as water-cooled substance polymerization. High viscosity is not a problem in this reaction because of water is used as the suspension medium. The monomer droplets, in the presence of suspension stabilizers, are prevented from clumping or agglomerating by agitation during polymerization, especially in a higher exothermic cycle. The blowing agent is introduced into the closed suspension reaction vessel during the final stage of polymerization,[1] following which pentane is impregnated into the polystyrene beads while they are still suspended. The impregnated beads are then centrifuged and dried at low temperature.

Bead size and distribution, one of the most important parameters in suspension polymerization, can be controlled by special techniques.[2–4] The suspending agent also can affect the particle size and distribution of the product.[5–8]

The chemical and physical properties of polymer surfaces have attracted attention. It would be very expensive to change the properties of the whole polymer; treatment of the polymer surface is preferred. The materials keep their excellent bulk properties, and only the surface is modified to meet specific requirements. The surface properties of polymers are usually modified through the use of specific additives during processing or by various surface-coating techniques such as chemical grafting, the atom transfer radical polymerization (ATRP) process.[9–11] To change the physical properties of both components is important. Graft copolymers are one of the classes of polymers that have the ability to exhibit the physical properties of both components.[12–15] Blending is the simplest method of polymer surface modification. Surface-active copolymers may be blended with a base polymer such as polypropylene or high-density polyethylene.[16,17] The surface enrichment of polydimethylsiloxane (PDMS) in the blends specifically depends on PDMS chain length.[18] PDMS chains reside in the side chain of the molecule and accumulate on the polymer surface.[19–21] PDMS polymers are extremely hydrophobic and usually show water-contact angles well above 100°.[21–23]

The surface properties of polysiloxanes play important roles in determining the wettability and adhesion, friction and wear, gloss and scratch resistance, printability, biocompatibility, UV radiation, low surface energy, high gas permeability, and antistatic properties.[24–26]

The purpose of this study was to modify the surface and thermal properties of EPS by using PDMS containing macroinitiator. In the first article of this series we reported copolymerization with α-methylsty-

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Correspondence to: I. Taşkıran (taskiranisa@yahoo.com).

rene.[27] In the second article we aimed to improve the surface properties of styrene with silicone acrylate prepolymer.[28] In the third article of this work, copolymerization with silicone-based macroinitiator is reported. The structures of the copolymers were characterized using spectroscopic techniques. Thermal and surface properties and the molecular weight and distribution of the samples also were examined.

EXPERIMENTAL

Materials

Polymerization-grade (99.9%) styrene monomer was provided by Petkim Petrochemical Co. (Kocaeli, Turkey) and used with the inhibitor *tert*-butylcatechol (10 ppm). Polyvinyl alcohol (PVA) was purchased from Kuraray (Osaka, Japan), tricalcium phosphate and calcium stearate were obtained from Chemische Fabrik Budenheim (Mainz, Germany), calcium chloride (77%) was supplied by Kemira Kemi (Helsingborg, Sweden), *n*-pentane was purchased from Riedel de Haën A.G. (Seelze, Germany), and linear alkyl benzene sodium sulphonate (LABSS) was supplied by Cognis (Kocaeli, Turkey). Initiator dibenzoyl peroxide (DBPO; 75%) was obtained from Peroxide Chemie GmbH (Munchen, Germany), and initiators tertiary butyl perbenzoate (TBP) and dicumyl peroxide were supplied by Interchim (Wörgl, Austria). α-ω-Dihydroxy polydimethylsiloxane (PDMS; Tegomer H-Si 2311, $M_n = 2500 \pm 250$ g/mol) was obtained from Goldschmidt A.G. (Essen, Germany).

Analysis and tests

Syntheses were carried out in a Buchi Glassuster 5-L metal reaction vessel equipped with an adjustable mechanical stirrer, a thermostat (Haake N3), a temperature indicator and controller, vacuum and nitrogen lines, and a pentane inlet line. GC measurement was performed on a Chrompack CP 901 model instrument with a setup consisting of CD-WAX packed columns and a column flow of 2 mL/min. The analyses were carried out between 50°C and 210°C. A Normandie Labo Cannon Fenske SR.200 (E 346) viscometer was used to measure the viscosity of the samples. ^{1}H-NMR spectra of all the samples were obtained on a Bruker AC (200 MHz). Gel permeation chromatography (GPC) measurement was performed with a setup consisting of a Waters pump (model 600E) and three ultrastyrogel columns with porosities of 10^4, 500, and 100 Å. Detection was achieved with a Waters differential refractometer (model 410). All the samples were characterized by GPC analyses. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL/min. Molecular weight was calculated with polystyrene standards. The thermal characteristics of the samples were measured with a Shimadzu TA-501 DSC-5 model machine. Scanning electron microscopy (SEM) micrographs were taken on a JEOL JXA-840 model electron microscope. The samples were prepared by precise cutting of the beads and subsequent application of a gold coating of approximately 200 Å. The average particle size (D_{50}) and particle size distribution (D_{50}/D_{84}) were calculated through sieve analyses.[9] Sieve analyses were made with an EML model shaker, and seven test sieves (Retsch) with a mesh size between 300 and 1400 μm were used. The static water-contact angle of the copolymer films was measured with a Kernco model G-111 contact angle meter (El Paso, TX) at room temperature, using deionized and triple-distilled water. The volume of water droplets was 20 μL.
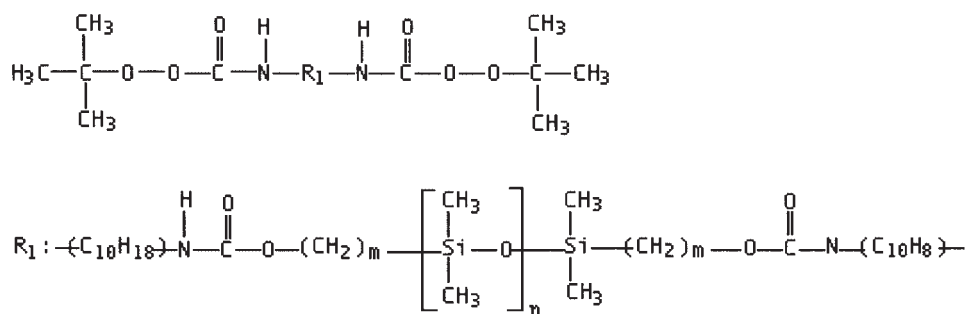
Syntheses of eps and copolymeric expandable polystyrene (CEPS)

Synthesis of EPS

The synthesis details of EPS were outlined in a previous report.[27]

Preparation of macroinitiator (MI)

The silicone-based macroinitiator used had already been prepared by a procedure previously described in the literature.[20] The structural formula of MI is:

$$5 < m < 10, \qquad n = 20$$

TABLE I
Synthesis Conditions of EPS

Sample	Styrene (%)	Macroinitiator (%)
EPS.01	100.0	0.0
EPS.02	99.9	0.1
EPS.03	99.8	0.2
EPS.04	99.5	0.5

$$5 < m < 10, \; n = 20.$$

Synthesis of CEPS

An experimental procedure previously described in the literature was applied to the copolymerization of styrene with MI.[8,20] MI was fed to the reactor at the beginning of polymerization along with styrene monomer. The conditions of the synthesis of the styrene homopolymerization and copolymerization are given in Table I.

Characterization

The residual monomer content after low- and high-temperature cycles was determined by GC analysis. GC also was used to determine the pentane content of the samples after the pentane impregnation and expansion stages of the samples. The solution viscosity of the polymers was determined according to the ASTM D-445 standard. Solutions (8%) of the expandable polymer beads in toluene were prepared. The viscosity of the samples was estimated in cSt units with a Cannon–Fenske viscometer. Sieve analysis were performed according to the ASTM D-1921 test method.

After expansion of the beads, all the samples were qualitatively characterized by FTIR. The film samples (20 μm) were prepared by the molding method. ^{1}H-NMR analyses were performed for a standard EPS and for a silicone-based macroinitiator/styrene copolymeric sample. GPC analysis of the samples was performed to determine molecular weight. The T_g values were determined from the second derivation of the differential scanning calorimetry (DSC) curves in the related temperature zones in the thermograms, so that a precise estimation could be made for the observation of very small changes in the T_g values. In all the experiments, the heating rate was 10°C/min. SEM micrographs were taken of cross sections of the samples (both inner and outer surfaces). Contact angle measurement of water droplets on the copolymeric films was performed at room temperature.

RESULTS AND DISCUSSION

In the preparation of styrene/silicone-based copolymer (CEPS), the residual styrene content was reduced at the end of the low-temperature cycle compared to the styrene homopolymerization (EPS). As shown in Table II, the conversion was increased and the residual monomer content was relatively reduced if there was an increase in the amount of silicone-based macroinitiator used. CEPS spherical bead particle size was measured as smaller than that of the homopolymer EPS particles. The macroinitiator affected the conversion, dynamic and kinematic viscosity, average molecular weight, and, indirectly, breakup coalescence of the particles during synthesis. Particle size also has been evaluated by several other investigators.[3,4,29] Particle size distribution (D_{84}/D_{50}) values, shown in Table II, was found to be nearly the same in all CEPS samples, a value that was lower than that of the homopolymer EPS, which showed enhancement of the particle size distribution of the copolymers. MI also affected the physical properties of the copolymers. After expansion density increased as the MI content increased in the copolymeric samples because of the reduction of the residual content of styrene monomer in the polymers and easy diffusion of the pentane through the pores formed during the expansion process of the beads containing the blowing agent, pentane. Because of the silicon-based MI, siloxane accumulation on the surface of the beads was observed. This phenomenon resulted in easy fractionation of the CEPS beads during a sieving process and increased the density of the CEPS samples after expansion, shown in Table II.

TABLE II
Experimental Results After *n*-Pentane Impregnation Stage

Sample	Conversion (%)	Residual monomer content (%)	After pentane impregnation			After expansion density (g/cm^3)
			D_{50} (μm)	D_{84}/D_{50} (μm)	Pentane (%)	
EPS.01	99.4	0.59	960	2.1	5.9	11.0
EPS.02	99.6	0.38	800	1.8	5.9	11.7
EPS.03	99.6	0.45	690	1.9	5.7	12.3
EPS.04	99.7	0.32	680	1.7	5.8	12.5
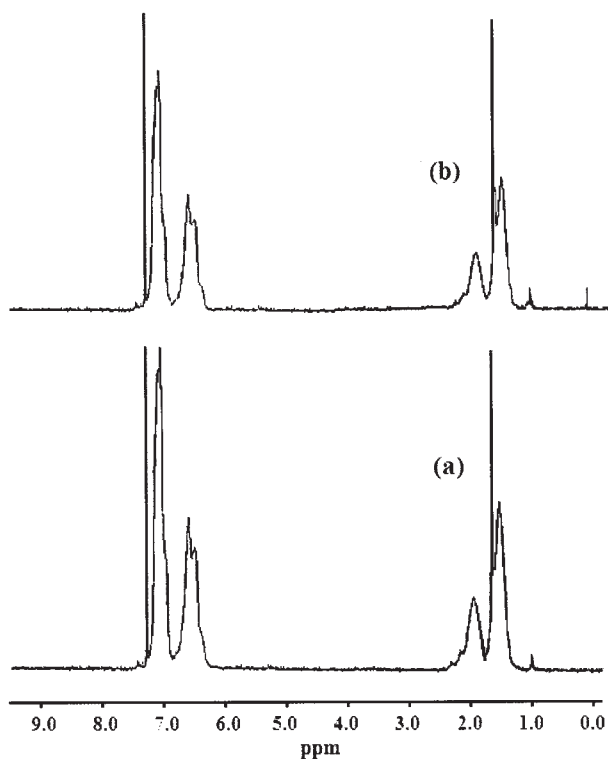
Figure 1 ^{1}H-NMR spectra of (a) sample EPS.01 and (b) sample EPS.04.

Figure 2 DSC thermograms of (a) sample EPS.01, (b) sample EPS.02, (c) sample EPS.03, and (d) sample EPS 04.

Percent conversion, shown in Table II, indicated that the EPS and expandable poly(silicone-based macroinitiator-*co*-styrene) samples were prepared at an adequate yield. Standard and modified EPS samples were characterized by ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra of samples EPS.01 and EPS.04 are presented in Figure 1(a,b), respectively, which shows there were two main peaks, at 6.25–6.83 ppm for protons closer to the main chain of polystyrene and at 6.83–7.20 ppm for protons farther from the main chain of polystyrene. These were the characteristic peaks of polystyrene. Sample EPS.01 [Fig. 1] showed a peak at 1.25 ppm because of the CH_3 group in the polymer. Because no proton splitting occurred in this single peak, there must have been a neighboring proton in the CH_3 group. This indicated that the homopolystyrene contained styrene homologue impurities such as
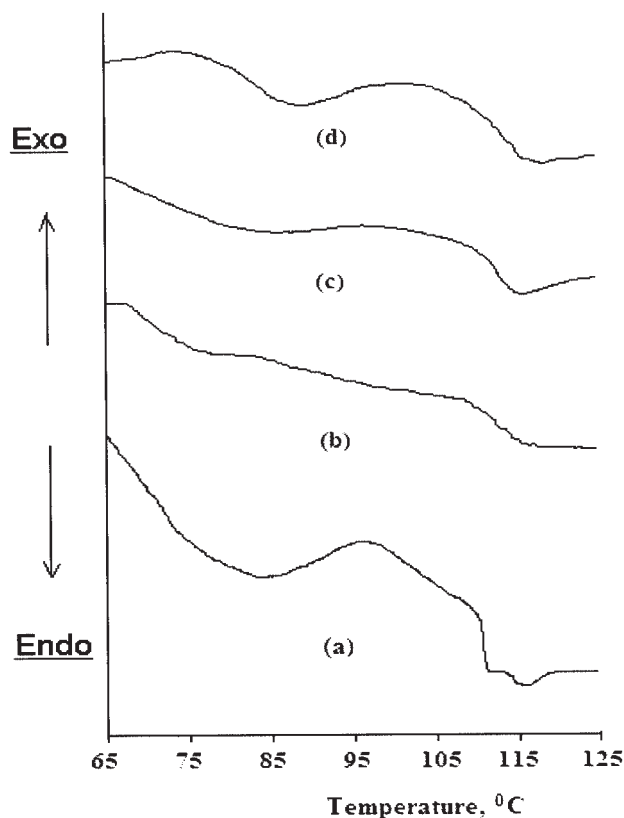
α-methylstyrene. The percent impurities from the styrene monomer were calculated from the areas under the curves from the peak at 1.25 ppm to the peak coming from phenyl protons between 6.26 and 7.20 ppm. The results obtained were 99% pure homopolystyrene. Similarly, the impurities from the homologous styrene were observed in the NMR spectra of the 0.5% MI containing EPS (EPS.04). In addition, a peak at 0.063 ppm belonging to the silicone group of the MI was observed. The silicone content of this sample could not be estimated qualitatively because of the high molecular weight of CEPS with a small amount of siloxane in the sample. Molecular weights of the EPS and CEPS samples are given in Table III, from which it can be seen that molecular weights of CEPS
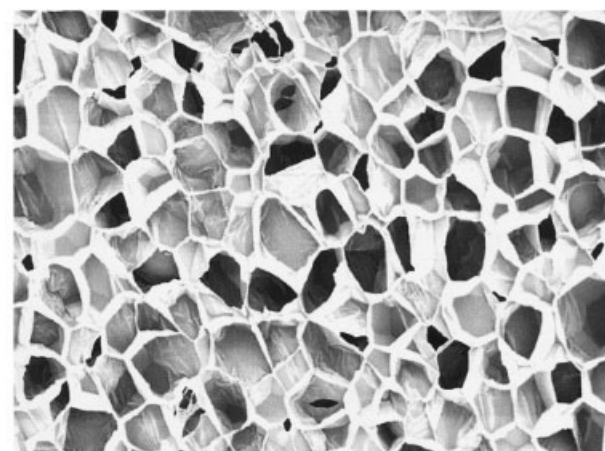
TABLE III
Characterization of EPS Samples

Sample	M_n	M_w	Polydispersity (M_w/M_n)	Kinematic viscosity (cSt)	T_g (°C)
EPS.01	91,000	152,000	1.67	8.7	110.5
EPS.02	96,000	155,000	1.61	9.0	112.6
EPS.03	96,000	159,000	1.66	9.0	112.4
EPS.04	110,000	166,000	1.51	9.2	115.0

M_n, number-average molecular weight; M_w, weight-average molecular weight.
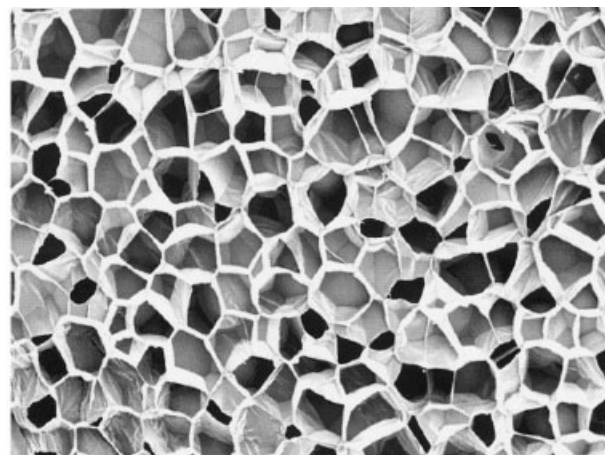
Figure 3 Scanning electron micrographs of inner part of (a) sample EPS.01 (magnification × 150) and (b) sample EPS.04 (magnification × 150).

samples were higher than those of EPS samples because of the initiator used in the synthesis.

The DSC thermograms of the samples are shown in Figure 2(a–d). The T_g of the standard homopolymer [Fig. 2(a)] was 110.5°C, and the T_g values of the 0.1%, 0.2%, and 0.5% silicone-based macroinitiator-containing samples [Fig. 2(b–d)] were 112.6°C, 112.4°C, and 115.0°C, respectively. The T_g's of the CEPS samples were higher than that of standard EPS. Table III shows all the T_g values. Of all the samples from both our previous and current studies, the highest T_g was found in the 0.5% MI-containing CEPS samples.[27,28]

SEM micrographs of cross-sectional views and of the outer surfaces of the samples are shown in Figures 3 and 4, respectively. Cross-sectional views of samples EPS.01 and EPS.04, shown in Figure 3(a,b), respectively, indicate that the styrene homo- and copolymers had similar cell structures. Cell size and homogeneity of cell size also were nearly the same in both micrographs [Fig. 3(a,b)]. Cross-sectional surface views of

the MI-containing sample (EPS.04) indicated that the best surface modification had occurred in this sample compared with modification with α-methylstyrene and V-Si 2250–containing CEPS samples.[27,28] Cell size and cell distribution were perfectly homogenous, and the typical polyhedron closed cell can be observed in Figure 3(b). In the micrographs the outer surface of the EPS showed roughness [Fig. 4(a)]. In contrast, the outer surface of the CEPS [Fig. 4(b)] appeared smoother and glossier than that of the standard EPS. These ideal structural units (pentagonal dodecahedron cell structure) of expandable PS were distinguishable in the modified samples.

The SEM results were proven by contact angle measurements, the results of which were reproducible at ± 1°, as shown in Table IV. The contact angles of copolymeric films exceeded 23%–28% with respect to PS because of the siloxane accumulation on the surface depending on the siloxane content of the CEPS samples.
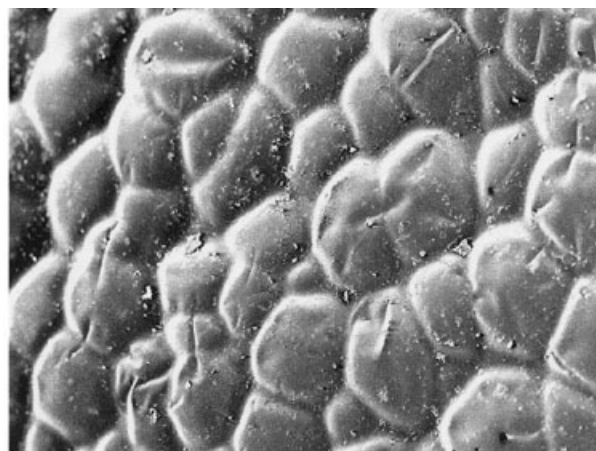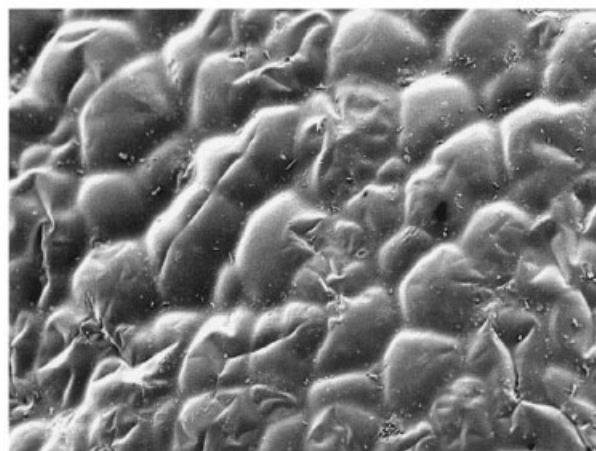
Figure 4 Scanning electron micrographs of outer surface of (a) sample EPS.01 (magnification × 200) and (b) sample EPS.04 (magnification × 200).

TABLE IV
Contact Angles of EPS Samples

Sample	Styrene (%)	Macroinitiator (%)	Contact Angle, θ (°)
EPS.1	100.0	0.0	78
EPS.2	99.9	0.1	96
EPS.3	99.8	0.2	96
EPS.4	99.5	0.5	100

CONCLUSIONS

From the results presented above, the following conclusions can be drawn: (1) three expandable CEPS samples were prepared by using siloxane-containing macroinitiator by suspension polymerization; (2) thermal modification also was achieved in this way; (3) outer surface smoothness and gloss were attained by siloxane; (4) because of the surface smoothness and siloxane accumulation on the surface of the beads, it was observed that sieve analyses was easier to conduct and blocking in pre-expender was prevented.

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