Effect of Acrylic Core–Shell Rubber Particles on the Particulate Flow and Toughening of PVC

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ABSTRACT: Different types of acrylic core–shell rubber particles with a poly(butyl acrylate) (PBA) core and a grafted poly(methyl methacrylate) (PMMA) shell were synthesized. The average size of acrylic core–shell latex particles ranged from 100 to 170 nm in diameter, having the core gel content in the range of 35–80%. The melt blending behavior of the poly(vinyl chloride) (PVC) and the acrylic core–shell rubber materials having different average particle sizes and gel contents was investigated in a batch mixing process. Although the torque curves showed that the particulate flow of the PVC in the blends was dominant, some differences were observed when the size and gel content of the particles varied. This behavior can be attributed to differences in the plasticizing effect and dispersion state of various types of core–shell rubber particles, which can vary the gelatin process of the PVC in the mixing tool. On the other hand, the highest toughen- ing efficiency was obtained using core–shell rubber par- ticles with the smallest particle size (i.e., 100 nm). The results showed that increasing the gel content of the core– shell impact modifiers with the same particle size improved the particle dispersion state in the PVC matrix. The toughening efficiency decreased for the blends containing 100 and 170 nm rubber particles as the gel con- tent increased. Nevertheless, unexpected behavior was observed for the blends containing 140 nm rubber par- ticles. It was found that a high level of toughness could be achieved if the acrylic core–shell rubber particles as small as 100 nm had a lower gel content. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2590–2597, 2009

Key words: acrylic core–shell particles; dispersion state; gel content; impact toughness; PVC; melt blending

INTRODUCTION

Rubber modification of brittle and semiductile ther- moplastics with core–shell rubber particles has been commercially improved for several past decades.[1–4] Poly(vinyl chloride) (PVC) is a typical example of semiductile thermoplastics that can be toughened by both methacrylate–butadiene–styrene rubber materi- als and all-acrylic impact modifiers (AIMs), all con- sisting of structured core–shell latex particles.[5–8] Butadiene-based rubber particles, that is, methacry- late–butadiene–styrene, are composed of a partially crosslinked poly(butadiene-*co*-styrene) core and a grafted plastic shell such as poly(methyl methacry- late) (PMMA), whereas acrylate-based rubber par- ticles, AIMs, having an acrylic rubber core such as poly(butyl acrylate) (PBA) and a PMMA shell are another type of core–shell impact modifiers.[9–12] Acrylic core–shell tougheners are usually used for interior applications, which offer increased environ- mental resistance. Using the acrylic type rubber impact modifiers is particularly critical for polymers that are used in making skin compounds for auto- motive instruments and door panels to display excellent heat and ultraviolet resistance, although their toughening efficiency is usually lower than that of the butadiene-based types.[13,14]

The toughening efficiency of the core–shell rubber particles in a polymer matrix depends substantially on the matrix and the particle properties, which can crucially affect the blend morphology and proper- ties.[15,16] In particular, the effect of particle size, shell thickness, and the grafting degree of butadiene- based core–shell rubber particles on their toughening efficiency has been investigated by numerous authors.[4–8,14–20] Breuer et al.[5] showed that increasing the grafting degree of core–shell rubber particles as well as the blending temperature improved particle dispersion state in the PVC matrix, but reduced the impact strength and stress-whitening of the blends.

The effect of butadiene-based core–shell rubber particles on the melt rheological behavior and impact toughness of PVC has been studied in a few research works.[17,21–23] Nevertheless, much less atten- tion has been paid to the acrylic core–shell impact modifiers used for the toughening of PVC.

In this research work, the effects of particle size and gel content of acrylic core–shell rubber particles on the particulate melt flow and impact toughness

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TABLE I
Recipes for Preparation of PBA Seed and Poly(butyl acrylate) (PBA)/PMMA Core–Shell Latex Particles

Ingredients	Recipe (g)		
	1	2	3
Core[a]			
Butyl acrylate (BA)	25(B)	25(SB)	25(SB)
DDI	75	75	75
$K_2S_2O_8$	0.06	0.06	–
t-BHP	–	–	0.06
SFS	–	–	0.06
SDS	0.12	0.12	0.12
ALMA	Variable	Variable	Variable
Core-Shell[b]			
PBA(Solid 25 wt%)	71	71	71
MMA	7	7	7
DDI	21	21	21
$K_2S_2O_8$	0.02	0.02	0.02
SDS	0.05	0.05	0.05
TDM	0.03	0.03	0.03

[a] The monomer, surfactant, and initiator used in the first-stage polymerization were added via both batch (B) and semi-batch (SB) processes.
[b] The seeded emulsion polymerization was carried out in a batch process.

of PVC are investigated. For this purpose, various types of acrylic core–shell impact modifiers having different particle sizes and gel contents were used to melt blend with PVC.

EXPERIMENTAL

Materials

Butyl acrylate and methyl methacrylate both from Merck Co. were distilled under vacuum to remove their inhibitors. Allyl methacrylate (ALMA) from Aldrich and tertiary dodecyl mercaptan (TDM) from Fluka were purchased as crosslinking agent and chain transfer agent, respectively. Sodium dodecyl sulfonate (SDS), *tert*-butyl hydroperoxide (*t*-BHP), sodium formaldehyde sulfoxylte (SFS), and potassium persulfate (KPS) all from Merck Co. were prepared. Tetrahydrofuran (THF), toluene, and benzene, all analytical grades, were purchased from Merck Co. Distilled deionized water (DDI) was prepared in the laboratory of the author.

A suspension grade of PVC (Poliran 6558, NIPC) (K65) and 10 phr acrylic core–shell rubber particles, also containing 1.5 phr liquid tin stabilizer (801DX, Argus chemical), 1.5 phr processing aids (1 phr Paraloid K-120 and 0.5 phr Paraloid K-175, Rohm & Hass), 0.5 phr external lubricant (Lubriol E 190, Rohm & Hass), and 1 phr internal lubricant (calcium stearate, Synpro, Ferro) were used to prepare PVC

specimen and its blends with acrylic core–shell rubber particles.

Core and core–shell synthesis

Several types of acrylic core–shell rubber particles with different average particle sizes and gel contents were synthesized via a two-stage seeded emulsion polymerization. Acrylic rubbery core and core–shell polymers were made in a 200-mL three-neck glass reactor equipped with a reflux, inlet nitrogen, and a magnetic stirrer. The reactor was held in a bath with thermostatic control. First, PBA seed latices were synthesized at 250 rpm for 3.5 h according to the emulsion recipes listed in Table I. The monomer, surfactant, and initiator used in the first-stage polymerization were added via both batch (B) and semi-batch (SB) processes. In the latter process, the above-mentioned ingredients were divided into several parts to be fed in to the reaction reactor. PBA core latices were synthesized using KPS initiator at 80°C except for the C3 core latex which was prepared using *t*-BHP initiator at 90°C. Although the emulsifier contents in all the recipes are equal, applying various addition modes of ingredients and polymerization temperatures resulted in acrylic core–shell latices with different mean particle sizes (Table II). Various amounts of the ALMA were also used to make rubbery PBA seed samples with different gel content levels. In the second stage, the methyl methacrylate (MMA) along with other ingredients was added to form the shell over the PBA seeds at 80°C and 200 rpm in a batch polymerization process for 3 h (Table I).

The synthesized acrylic core–shell rubber particles were designated with a common name (CS), a mean particle size in nm, and a gel content level: for example, acrylic core–shell rubber material with particle diameter close to 170 nm was indicated by CS170X in which X can be substituted by capital letters L, M, and H corresponding to low, moderate, and high gel content levels, respectively.

TABLE II
The Characterization of the Synthesized Core and Core–Shell Particles

Code	Recipe	Dia (nm)	Gel (%)	Gd (%)
CS170L	1	175	45.3	51.5
CS170M	1	168	62.1	42.8
CS170H	1	171	79.2	31.5
CS140L	2	142	42.9	59.8
CS140M	2	135	61.7	50.7
CS140H	2	139	78.9	39.9
CS100L	3	104	43.1	60.9
CS100M	3	108	59.3	56.3
CS100H	3	97	78.4	38.4

Gel content and grafting degree

The gel content of PBA seeds and grafting degree of PBA/PMMA core–shell particles were determined via solvent extraction method and gravimetrical measurements. The THF and toluene/benzene (70/30) were used for gel content and grafting degree measurements, respectively.

Core–shell particle size and size distribution

The size and size distribution of the core–shell latex particles were measured via dynamic laser light scattering with wavelength 632.8 nm and laser source light He and Ne gas. Light scattering measurements were performed using a Sematech SEM-633 stepper-motor-driven goniometer.

Melt blending

PVC and its blend samples with acrylic rubber particles were prepared in a Haake HBI90 internal batch mixer equipped with a Rheomix corotating twin screw. The control system of the mixer recorded automatically the torque values at 6-s intervals. The torque measurement provided an approximate characterization of melt viscosity variation for the PVC and its blends with various types of acrylic core–shell rubber particles during melt blending process at 180°C and 60 rpm.

Specimen preparation and impact testing

The PVC and blend samples prepared by melt mixing were cooled at room temperature and then chopped into small pieces. The pieces were placed into the rectangular cavities of the mold (3 × 12.7 × 63.5 mm³), preheated at 180°C for 5 min, and then compressed under 20 MPa at the same temperature for 15 min. Hereafter, the melted samples were cooled down to room temperature under the constant pressure mentioned earlier. A 2-mm-deep notch with a notch radius of 0.25 mm was sawed into the specimen. The notched Izod impact toughness of the samples was measured using an Izod impact tester. The notched samples were tested at room temperature according to the procedure outlined in ASTM D256. Before testing, the samples were conditioned at 45% relative humidity and room temperature for 48 h. The average of the measurements on 10 test specimens was taken to obtain a reliable average value.

Blend morphology

Dispersion state of the acrylic core–shell rubber particles in the blend specimens was studied by means of scanning electron microscopy (SEM) before testing. The surface of the samples were cut and

smoothed with a diamond knife on a Reichert OM3U ultramicrotome at −30°C and then etched by toluene for 3 h. Dissolving the PMMA shell of the dispersed phase in the blend samples by the solvent caused the rubber particles to leave out the PVC matrix. The etched surface specimens were dried and then gold-sputtered before microscopy.

Transmission electron microscopy Zeiss CEM 902A was also used to observe the dispersion state of the structured latex particles in the PVC matrix. Ultrathin sections of the blend samples were prepared and transferred onto the copper grids, mesh 400, and dried in open air. The sections were then stained by osmium tetroxide vapor (OsO_4) for 2 h before microscopy.

RESULTS AND DISCUSSION

The characteristics of the prepared core–shell particles consisting of poly(butyl acrylate) (PBA) core and a PMMA shell with core–shell ratio 70/30 (wt/wt) are given in Table II. As shown, by increasing the gel content of PBA cores, the grafting degree of the core–shell particles was deceased. Nevertheless, using a special kind of crosslinking agent in the first-stage emulsion polymerization, that is, allyl methacrylate, resulted in preparing core–shell particles with rather high grafting degree even for the high gel-containing particles (Table II).

Melt blending behavior

Figure 1 shows the variation of torque amount versus time for the PVC and its blend with CS100L
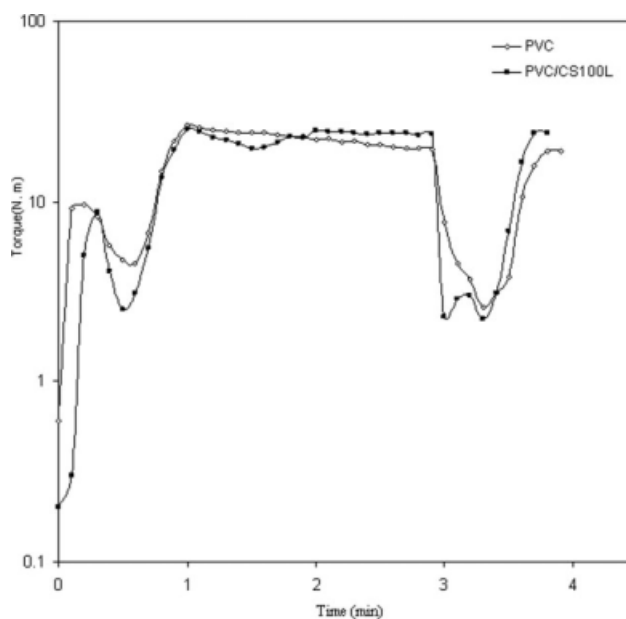
Figure 1 Haake torque responses for PVC and PVC/CS100L mixture during melt blending process at 180°C and 60 rpm.
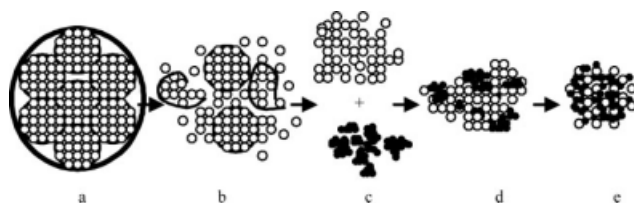
Figure 2 Schematic illustration of the melt blending process: (a) a PVC grain containing subgrains; (b) the breakdown of the grains into primary particles; (c) adding core–shell bulk particles; and (d, e) dispersion and distribution of the core–shell rubber particles in the matrix.

rubber particles in a melt blending process at 180°C. For the PVC, the amount of torque first increased to a maximum, but immediately decreased to a minimum value. In continuing, the torque increased again, reaching a peak value where the processing aids were added. After the peak, the amount of the torque lowered to some extent to get a constant amount in a so-called plateau region. This rheological behavior can be attributed to the particulate structure of the PVC, which varies by elapsed time of mixing. In the suspension grade of PVC, grains (120–150 μm) usually consist of subgrains (30–50 μm) containing a lot of primary particles (1 μm in diameter), which are formed during suspension polymerization.[21] This complex particulate structure can strongly affect the melt rheological behavior of the PVC during melt processing. At the beginning of the process, the PVC grains absorbed the liquid stabilizer and became sticky and flowed less freely inside the hot cavity. This caused the mechanical energy of the mixing tool and consequently the amount of the torque to increase (Fig. 1). Continuing the applied shear stress decreased immediately the torque value. The shear build-up in the hot cavity led to the breakdown of the grains and subgrains to their primary particles; hence, the amount of torque increased substantially, reaching a peak value where the processing aids were added. Adding the low-modulus processing aid materials caused the rigid PVC particles to flow more freely, and the amount of the torque lowered to a constant value in a plateau region. A balance between the rate of reagglomeration and agglomerate breakdown of the primary particles resulted in a constant amount of the torque in the plateau region (Fig. 1). Finally, adding the lubricants to the PVC paste decreased the amount of the torque intensively because of the melt slippage over the screws. By dissolving the lubricant into the PVC melt, the torque value increased again to a constant level where the mixing was stopped.

Melt flow behavior of the PVC mixed with CS100L rubber particles was different from the PVC (Fig. 1). For the blend, both the core–shell rubber particles and processing aids were added to the PVC

when the torque value reached the peak value. Adding the low-modulus core–shell bulk particles to the PVC paste lowered the torque value to some extent. The heat and shear stress field in the mixing tool caused the core–shell bulk particles to break into their original particle size, 100 nm in diameter. The melt blending process is shown in Figure 2. By distributing the rubber particles in the PVC matrix, the elasticity, and consequently the torque value of the melt blend increased. In comparison with the PVC melt, a new physical bond formation between the rubber particles and the PVC particles in the blend caused the torque value of the blend to increase. More interfacial adhesion between the rubber particle PMMA shell and the PVC particle increased the elastic melt property. Thereafter, the torque value of the blend decreased to a higher constant level when compared with the PVC in the plateau region. After adding the lubricants to the melt blend, a rather similar rheological behavior like that of the PVC melt was observed.

Figure 3 shows the melt flow behavior of the PVC blends with various types of the core–shell rubber materials having different gel contents, but with the same particle size close to 140 nm. As shown, adding the CS140L rubber material with the lower gel content to the PVC decreased the torque value more than the CS140H particles with higher gel content. The low gel content core–shell particles seemed to have a very good plasticizing effect to facilitate the particulate flow of the PVC particles in the mixer. On the other hand, a higher torque value in the
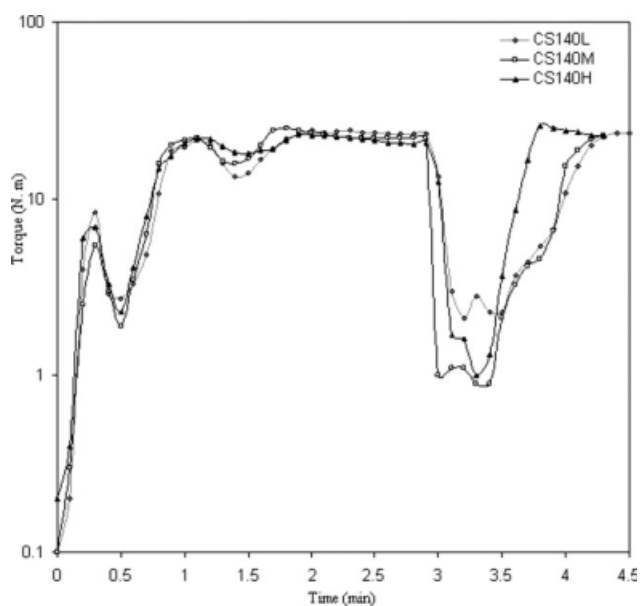
Figure 3 Haake torque responses for PVC mixed with the CS140 core–shell rubber materials having various gel content levels during melt blending process at 180°C and 60 rpm.
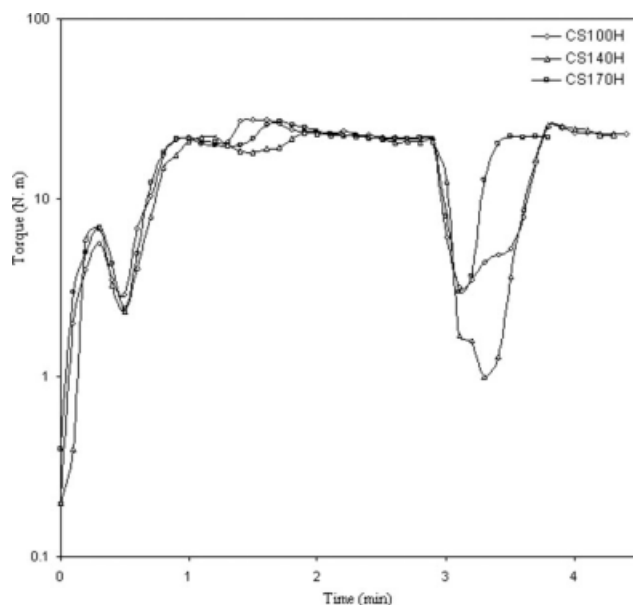
Figure 4 Haake torque responses for PVC mixed with the core–shell rubber materials having various average particle sizes but with same gel content level (78%).
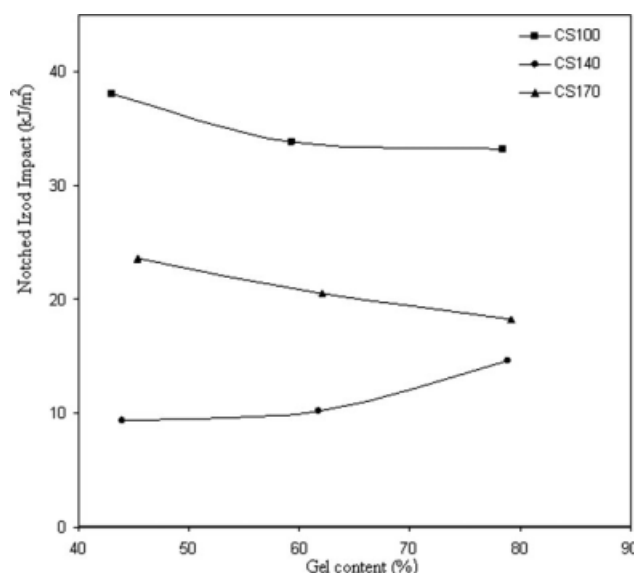
plateau region was observed for the blend containing the core–shell rubber particles with lower gel content. This behavior can be attributed to the higher grafting level of the rubber particles having lower gel content. The grafted PMMA chains of the acrylic core–shell particles interdiffuse into the outer layer of the PVC particles and improve the interfacial adhesion between the particles in the blends. Increasing the grafting degree of the rubber particles resulted in higher network elasticity. Nevertheless, the dispersion state of the core–shell particles in the matrix can also influence the torque value of the blend in the plateau region. A good dispersion of the core–shell particles in the PVC matrix can lead to a lower torque value when compared with coarse dispersion or connected particle morphology in the plateau region. In fact, the bulk particles containing

TABLE III
Plasticizing Time and Equilibrium Time and Torque Values of PVC and PVC Blended with Various Kinds of Acrylic Core–Shell Impact Modifiers

Code	Plast. time (s)	Eq. time (N m)	Eq. torque (s)
PVC	154	174	19.5
CS170L	66	150	20.5
CS170M	78	162	21.7
CS170H	78	168	21.5
CS140L	87	162	23.2
CS140M	84	159	22.2
CS140H	92	156	22.1
CS100L	90	168	23.7
CS100M	83	171	22.6

low gel content core–shell rubber particles need more intensive shear stress to break well to their original rubber particles. A similar gel content effect on the melt blending behavior was observed for the acrylic core–shell particles with other average particle size (not shown here).

The effect of acrylic rubber particle size on the melt blending behavior of the PVC was investigated. Figure 4 shows the torque variation versus time for the blends with various acrylic core–shell materials having rather the same high gel content (78 wt%), but with different average particle sizes ranging from 100 to 170 nm (Table II). At the peak of the PVC torque value, adding the core–shell rubber materials with different particle sizes decreased the torque values to some extent (Fig. 4). By dispersion of the CS100H with the lowest particle size (100 nm) in the PVC matrix, the torque increased to the highest amount when compared with CS140H and CS170H materials used in the blends. The smaller core–shell particles had a higher specific area, which can result in higher interfacial adhesion between the rubber and PVC particles and increase the melt elasticity. Nevertheless, the torque increment for the PVC blend with larger CS170H particles was higher than that of the blend containing smaller CS140H rubber particles (Fig. 4). By breakdown of the rubber particle aggregates in the plateau region, no substantial difference in the torque values for the aforementioned blends was observed. This behavior can be attributed to the rather same distribution state of the rubber particles, which were similar in elastic properties.

Figure 5 Effects of acrylic core–shell rubber particle size and gel content on the impact toughness of PVC.
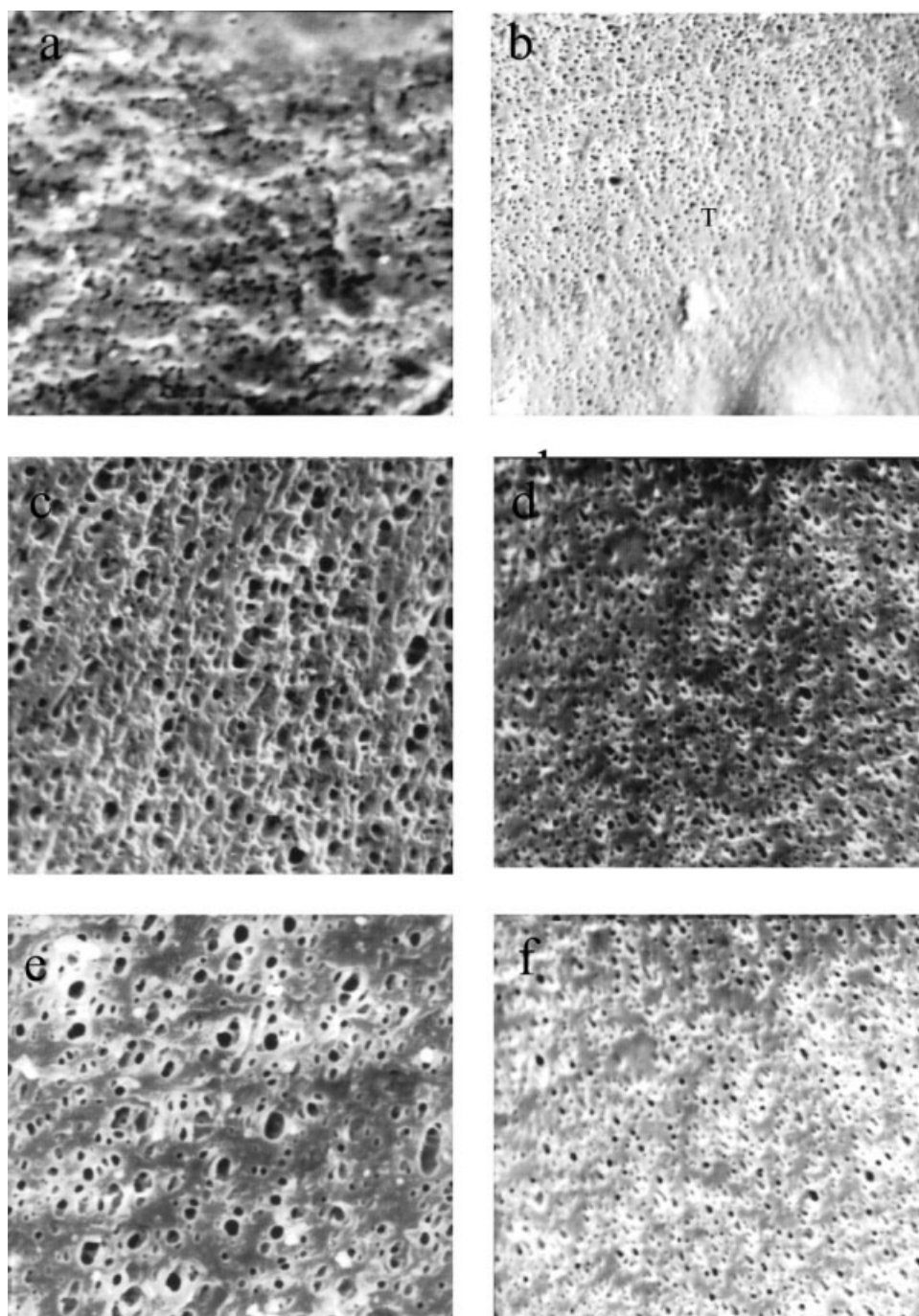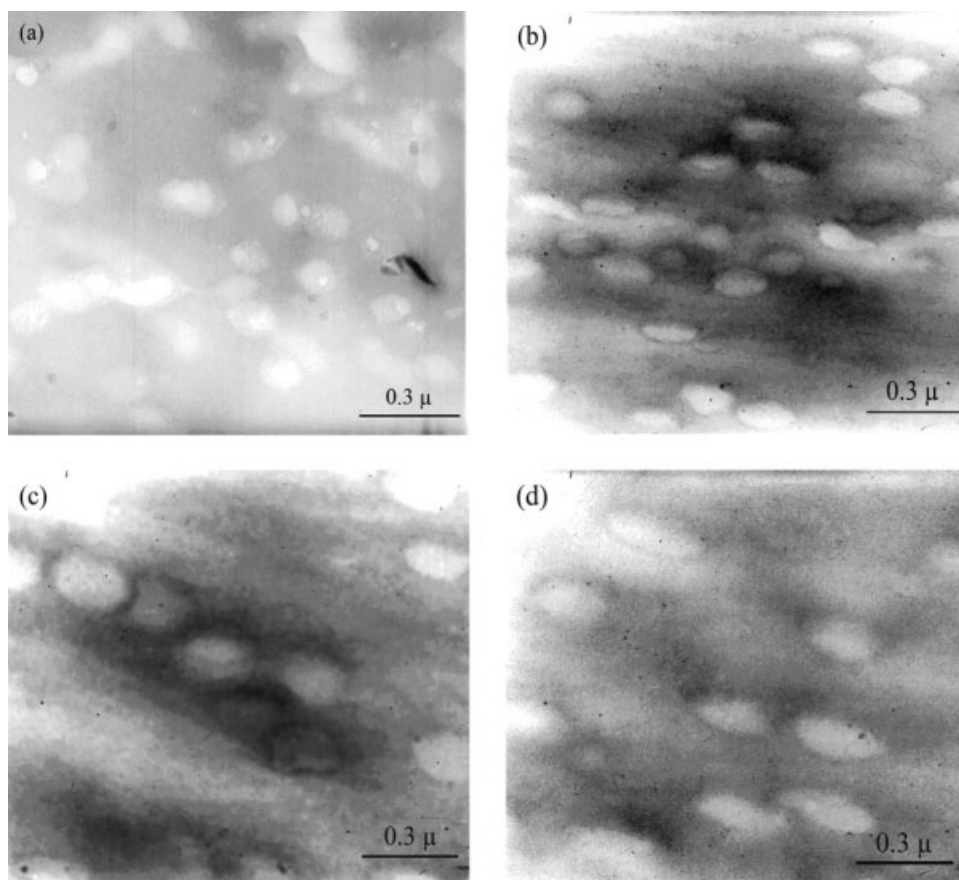
Figure 6 Scanning electron micrographs of PVC blends containing 10 phr different types of acrylic core–shell rubber particles: (a) CS100L; (b) CS100H; (c) CS140L; (d) CS140H; (e) CS170L; (f) CS170H. (The magnification of all micrographs is equal to 5000).

The final data such as plasticizing time and equilibrium time and torque values from Figures 1, 3, and 4 are listed in Table III. As shown, the core–shell particles could shorten the plasticizing time considerably, while increase the equilibrium torque in the plateau region on some extent. Although the equilibrium torque values in Table III represented that the particulate melt flow of PVC is dominant, some differences for PVC and its blends with the acrylic core–shell modifiers having different particle sizes and gel content levels are observed.

Impact toughness

The notched Izod test was carried out to study the effect of acrylic core–shell rubber particle characteristics on the impact toughness of PVC. The notch Izod fracture toughness of the PVC was measured

Figure 7 Transmission electron micrographs of PVC blends: (a) CS100L; (b) CS100H; (c) CS170L; (d) CS170H.

for comparison purposes. For the PVC, the fracture behavior was brittle because of its low fracture energy (7 kJ/m²). Adding the acrylic core–shell rubber materials having various elastic properties and particle sizes to the PVC showed different toughening efficiencies under similar impact test conditions (Fig. 5). The gel content effect of the acrylic rubber particles with the same particle size on the impact toughness of the PVC was investigated. Unlike the CS140 rubber materials, the impact toughness of the PVC blended with both CS170 and CS100 rubber particles decreased substantially as the gel content of the particles increased (Fig. 5). These differences in the impact energies of the blend specimens varying the gel content can be originated from the difference in the mechanical property and dispersion state of the rubber particles in the PVC matrix. In fact, increasing the gel content caused the cavitation resistance of the rubber particles to increase and their capability for rapid particle elongation and absorbing the impact energy in the PVC matrix to decrease. On the other hand, varying the gel content of the core–shell rubber particles caused the particle dispersion state in the PVC matrix to be changed. Figures 6 and 7 show the effect of gel content on the dispersion of rubber phase in the blend specimens

before impact testing. As shown in Figure 7, the acrylic core–shell rubber particles dispersed in the matrix are observed as bright phase, because conventional staining agents such as OsO_4 cannot stain neither PBA phase nor PMMA phase within the composite particles. Both scanning and transmission electron micrographs indicate improving dispersibility of the rubber particles in the matrix as the gel content of the particles increases. For the blend containing CS170L grafted copolymers, a bimodal dispersion state of rubber phase was observed [Fig. 6(e)]. By increasing gel content, though a better dispersibility of the CS170H particles was observed, the impact toughness decreased substantially (Fig. 5). Both CS100L and CS100H rubber particles were uniformly dispersed in the matrix. Nevertheless, the high gel-containing one for toughening of the PVC resulted in lower impact strength. Unexpectedly, the impact toughness of the blends containing CS140 particles was increased with increasing the gel content level (Fig. 5). A coarse dispersion of the low gel-containing CS140L rubber particles as particle microagglomerates decreased the impact toughness when compared with the blend containing high gel-containing CS140H particles with much fine dispersed rubbery phase in the matrix (Fig. 6c–d). In

other words, increasing the gel content of the CS140 modifiers increased the impact toughening of the blends owing to decrease in the size of the agglomerates in the matrix.

The effect of core–shell particle size on the toughening of PVC was compared for the blends over the same gel content range (Fig. 5). As shown, the rubber particle size is a crucial controlling factor for toughening of PVC. Obviously, decreasing the size of core–shell rubber particles from 170 to 100 nm in the blends caused the amount of fracture energy to increase to higher values over the entire gel content range. The acrylic core–shell rubber particles as small as 100 nm can be more effective toughening agents for the PVC. For these blends, the electron micrographs also revealed a row structure containing a number of connected core–shell rubber particles, which surrounded the PVC primary particles (1 μm). This structural morphology caused the impact strength to improve substantially when compared with other PVC blends with greater core–shell particle size.

Unexpectedly, decreasing the rubber particle size from 170 to 140 nm in the blends lowered the toughening efficiency. This impact behavior of the blends containing CS140 grafted rubber particles can be attributed to the course morphology of the dispersed rubbery particles as agglomerates in the matrix, which decreases the toughening efficiency (Fig. 6b, d).

CONCLUSIONS

Several types of acrylic PBA/PMMA core–shell impact modifiers with different average particle sizes and gel contents were synthesized. The effect of acrylic rubber particle size and gel content on the melt blending behavior of the PVC was investigated. The rheological measurements showed that although the particulate melt flow of the PVC in the blends was dominant, the melt torque curves indicated some differences when the above core–shell particle characteristics were varied. This behavior can be attributed to differences in the plasticizing effect and dispersion state of various types of core–shell rubber particles, which can vary the gelatin process of the PVC in the mixing tool. Decreasing the rubber particle size and gel content level in the blends increased the toughening efficiency. In fact, increasing the gel content caused the cavitation resistance of the rubber particles to increase and their capability for rapid particle elongation and absorbing the impact energy in the blends to decrease.

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