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ORIGINAL CONTRIBUTION

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Preparation and properties of novel plastisols based on acrylic core-shell lattices

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Abstract A series of core-shell lattices comprising a core portion of rubbery acrylic homo- or copolymers and a surrounding shell portion of glassy methyl methacrylate (MMA) homo- or copolymers were designed as plastisols for automotive underbody coatings. The lattices were synthesized by a semi-continuous seeded emulsion polymerization and characterized by using differential scanning calorimetry (DSC) and scanning electronic microscopy (SEM). DSC investigations demonstrated that the incorporation of a hard segment of MMA into the core portion and strongly polar monomer methyl acrylic acid (MAA) or cross-linker allyl methacrylate (ALMA) into the shell portion resulted in an improvement of the glass transition temperatures. SEM micrographs verified that the latex particles were always spherical with regular structure throughout the polymerization stage. Novel plastisols were developed based on the abovementioned core-shell polymers with dioctyl phthalate (DOP) or tricresyl phosphate (TCP) plasticizers, whose core portions were compatible with the employed plasticizer and whose shell portions were incompatible with the plasticizer. Evaluation of the viscosity as a function of the storage time revealed that the storage stability of the plastisols could be obtained through incorporation of the strongly polar monomer MAA or the cross-linker ALMA into the shell portions. The mechanical properties of the plastigels were improved by incorporating MMA into the core portion or by incorporating MAA or ALMA into the shell portion of the lattices. A balance between the mechanical properties of plastigels and the storage stability of plastisols should be considered during selection of the monomers both for the core and shell.

Keywords Emulsion polymerization · Core-shell lattices · Plastisols · Storage stability · Mechanical properties

Introduction

To protect both the underbody and the lateral parts of every vehicle, a layer of elastic-rubber material is applied through a spray technique [1]. This layer, which has a consistent thickness normally between 600 and 1,000 μm, provides excellent resistance against abrasion, corrosion, and vibration, and heat insulation for the automotive underbody [2]. Plastisol-gel coating based on poly(vinyl chloride) (PVC) has been successfully applied to automotive underbodies [3]. Plastisol is a paste-like liquid mixture which contains a particulate polymer in a plasticizer and inorganic fillers. Plastisol can gel on warming to form a solid body [4]. PVC is predominantly used as the particulate polymer because it does not dissolve in the liquid plasticizer at room temperature even during long periods of storage [5]. On heating above 80°C, a solution of PVC in the plasticizer is created; this solution has the properties of a solid body because of the high concentration of polymer therein. On cooling to room temperature, the gel permanently retains its homogeneous quality. Unfortunately, this coating system does have many disadvantages, especially where environmental and toxicological problems connected to PVC are concerned [6, 7, 8]. It is environmental and legislative pressures that have driven industry to accelerate R&D activity on "green" polymers which have sophisticated composition and structure and are expected to exhibit performances at the same level as conventional PVC plastisol-gel systems [9].

Recent research has focused on testing a number of acrylic polymers instead of PVC-based coatings [10, 11, 12, 13, 14]. Acrylic homopolymers and copolymers do not have the aforementioned disadvantages of PVC, but they also do not have the particular advantages of the latter material in the gelling process [15]. PMMA and its copolymers can form stable plastisols with organic plasticizers. However, in many cases when the gel material is cooled to room temperature, the mixture proves to be unstable and bleeds the plasticizer in liquid form. This is particularly the case with plasticizers which are commonly used in technical applications because of their low price, for example, phthalic acid esters [16, 17, 18]. The compatibility of methyl methacrylate copolymers with phthalate plasticizers can be increased by using acrylic acid esters of methacrylic acid esters of higher alcohols as comonomers. The plasticized gel masses prepared with these copolymers do remain homogeneous for indefinite periods of time, but plastisols prepared in this manner become solid at room temperature within a few days (i.e., they have no storage stability). In the coating field, the storage stability of plastisol is one of the most important issues that should be considered for industrial purposes. To a small degree, storability can also be improved by the use of relatively coarse polymer particles. However, this improvement on storability is accompanied by the disadvantage that a longer time is required for the gelation process and by impaired film properties [19].

The goal of the present study was to find acrylic copolymer composites for preparation of plastisols which possess excellent physical and chemical properties and good storage stability. For this purpose, a series of acrylic core-shell copolymers were synthesized by seeded semi-continuous emulsion polymerization, and their thermal properties and morphology were investigated by using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The correlation between the thermal properties of the core-shell lattices and the storage stability of plastisols was established. The mechanical properties of plastigel films were also studied.

Experimental

Materials

Methyl methacrylate (MMA), *n*-butyl acrylate (BA), *n*-butyl methacrylate (*n*-BMA), *iso*-butyl methacrylate (*i*-BMA), methacrylic acid (MAA), and allyl methacrylate (ALMA) were of reagent grade and purchased from Aldrich Chemical Co., USA. All monomers were distilled at reduced pressure to remove inhibitor. The purified monomers were stored at 5°C before use. Potassium persulfate (KPS) initiator was supplied by Daejung Chemicals & Metals Co. Ltd., South Korea. Sodium dioctyl sulfosuccinate (OT-75) emulsifier was supplied by Cytec Industries Inc., USA. Plasticizers such as dioctyl phthalate (DOP) and tricresyl phosphate (TCP) were purchased from Oriental Chemical Industries Co. Ltd., South Korea. All other chemicals were of analytical grade and used as supplied. Distilled and deionized water was used.

Emulsion polymerization

Emulsion polymerization was carried out in a 1,000-mL five-necked flask equipped with an overhead Teflon stirrer, a reflex condenser, thermocouples, a calibrated dropping funnel, and a nitrogen inlet system. Distilled water (200 mL) and the emulsifier was charged into the flask and then heated to 80°C. The solution was purged with nitrogen gas. The polymerization was a two-step operation. The core-shell ratio (wt/wt) was set to 1:1 in all polymerizations. Initially, the polymerization started with the preparation of seed lattices by one batch process. The monomer mixture (30 wt% of total amount) of the core portion (Table 1) was charged into the flask and stirred for 0.5 h, and then some KPS, dissolved in distilled water (2.25 wt%), was added. The temperature was kept at 80°C for 1 h throughout the polymerization. The residual monomer mixture of the core portion and some KPS solution were added gradually through a dropping funnel by a delay process over a period of 1–1.5 h, and the polymerization was continued for a further 1 h. The second-stage polymerization was carried out in the same flask with a continuous feed of the monomer mixture of the shell portion (Table 1). The dropping process was carried out at a constant rate over a period of 3 h. The residual initiator solution was added, and then the temperature was maintained at 80°C for 2 h. After completion of polymerization, the lattices were cooled to room temperature. The solid particulate polymers were obtained by dropping the lattices into

Table 1 Composition of the core and the shell for emulsion polymerization, and DSC test results of the core-shell latex samples

Sample code	Core composition (wt%)				Shell composition (wt%)			T_{g1}(°C)	T_{g2}(°C)
	BA	*n*-MBA	*i*-MBA	MMA	MMA	MAA	ALMA		
1	50	–	–	–	50	–	–	−28.8	104.2
2	–	50	–	–	50	–	–	25.4	103.5
3	–	–	50	–	50	–	–	49.2	105.3
4	–	–	47	3	50	–	–	51.3	104.7
5	–	–	45	5	50	–	–	53.9	106.3
6	–	–	43	7	50	–	–	55.9	105.5
7	–	–	50	–	49	–	1	50.2	107.8
8	–	–	50	–	47	–	3	48.7	109.4
9	–	–	50	–	45	–	5	49.4	114.4
10	–	–	50	–	49	1	–	48.5	112.4
11	–	–	50	–	47	3	–	49.6	116.9
12	–	–	50	–	45	5	–	50.1	122.5

$MgSO_4$ coagulation solution; these were then filtered, washed with water, and dried under vacuum.

Characterization

Glass transition temperature (T_g) was determined by using a Perkin–Elmer differential scanning calorimeter-7C. All measurements were made under a nitrogen gas atmosphere between −30°C and 160°C at a heating rate of 10°C min^{-1}. In all case, the second heating cycle was carried out for the analysis to diminish the heat and process history. An Hitachi S-4300 scanning electron microscope was employed to study and record the morphology of all the latex samples and the tensile fracture surfaces of plastigels. For the scanning electron microscopy (SEM) measurements, the latex samples were diluted in water (1:100 v/v). A drop of the diluted latex was placed on the sample holder and dried at room temperature. The surfaces of samples for both the lattices and the tensile fracture surfaces were coated with a thin layer of gold–palladium; for this, the coating was carried out by placing the specimen in a high-vacuum evaporator and vaporizing the metal held in a heated tungsten basket. The average particle size of the polymerized latex was determined by using a particle size analyzer (Santa Nicomp 370) at a fixed scatting angle of 90°.

Preparation of plastisols

Plastisols were prepared by mixing the polymer powder and the plasticizer. A predetermined quantity of the polymer powder sample was charged into a beaker and mixed with the plasticizer (DOP or TCP) by using a homemade kneader for 0.5 h at room temperature. The weight ratio of the polymer to the plasticizer was 50:50.

Measurement of storage stability

The storage stability of plastisol was estimated by the viscosity variation. The viscosity of plastisol was measured with a Brookfield DV-II viscometer equipped with a #7 spindle at 20 rpm and 23°C according to ASTM D-1824.

Preparation of plastigel films

The samples from plastisols were coated as a 5-mm-thick layer onto an aluminum sheet, and then were evacuated in a vacuum desiccator for 1 h to get rid of the air entrapped in them. All prepared plastisol films were heated for 40 min in an air-circulating oven at 150°C to afford the 2-mm-thick plastigel films.

Measurement of mechanical properties

The tensile properties of the plastigel samples were determined with an Instron-4303 universal testing machine by using a 1,000-N-load transducer according to ASTM D-638. All the tests were done at room temperature and a minimum of five specimens were analyzed to ensure the accuracy for one sample.

Results and discussion

Differential scanning calorimetry investigation

The lattices synthesized in this study were designed as two-stage beads with a rubbery core (PBA or PMBA-based) and a glassy shell (PMMA-based). T_g plays a major role in optimizing monomers for both the core and the shell during the polymerization for plastisols, because it is one of the most important parameters controlling plastisol-gel performance. The advantage of selecting acrylic monomers is that one can get the desired product with the desired T_g of the copolymer, so that the prepared plastigels could have the desired mechanical properties and the good storage stabilities of plastisols. The T_g values of the core-shell polymers synthesized in the present study were measured by differential scanning calorimetry (DSC) and are listed in Table 1. For the core-shell structure, testing results show that there are two distinct T_gs, which suggests that the synthesized products are not random copolymers but particles with two separated phases (i.e., the core-shell structure). It has also been observed that in the core portion, P *i*-BMA exhibits a higher T_g of 49.2°C, whereas PBA possesses a low value of −28°C. The T_g increased with an increase in the percentage of MMA. This is due to the rigidity of the molecular chain of MMA. The T_gs of copolymers were found to be in good agreement with the theoretical T_gs calculated by the Fox equation [20]. PMMA is well suited as a shell material because of its high T_g of above 100°C. A similar observation was also noticed in the copolymer of the shell portion, whose T_g increased with addition of a strongly polar MAA monomer. ALMA is a monomer with bifunctional double bonds. When introduced into the copolymer of the shell portion, ALMA results in cross-linking of the copolymers, and thus an increase in T_g. The effect of T_gs of the core and the shell portions on properties of plastisols is discussed later.

Morphology of lattices

The morphology of latex depends on the properties of the employed monomers. Figures 1 and 2 display the SEM micrographs for the different core-shell lattices in the core and the shell polymerization stages. These micrographs show that the latex particles always retain a spherical and regular structure in all polymerization stages. The particles also keep growing with the polymerization time. The control of latex particle morphology has always been of prime importance both in academia and industry, as many properties of the finial products depend upon the composite structure of the latex particles. Although the latex particles may be prepared in two consecutive stages, a core-shell structure is not necessarily obtained [21]. In this study, the core-shell arrangement of the finial latex particle could be assured because MMA-derived shell materials are more strongly hydrophilic than the core materials (BA or BMA). As a result, it is impossible for the inverted

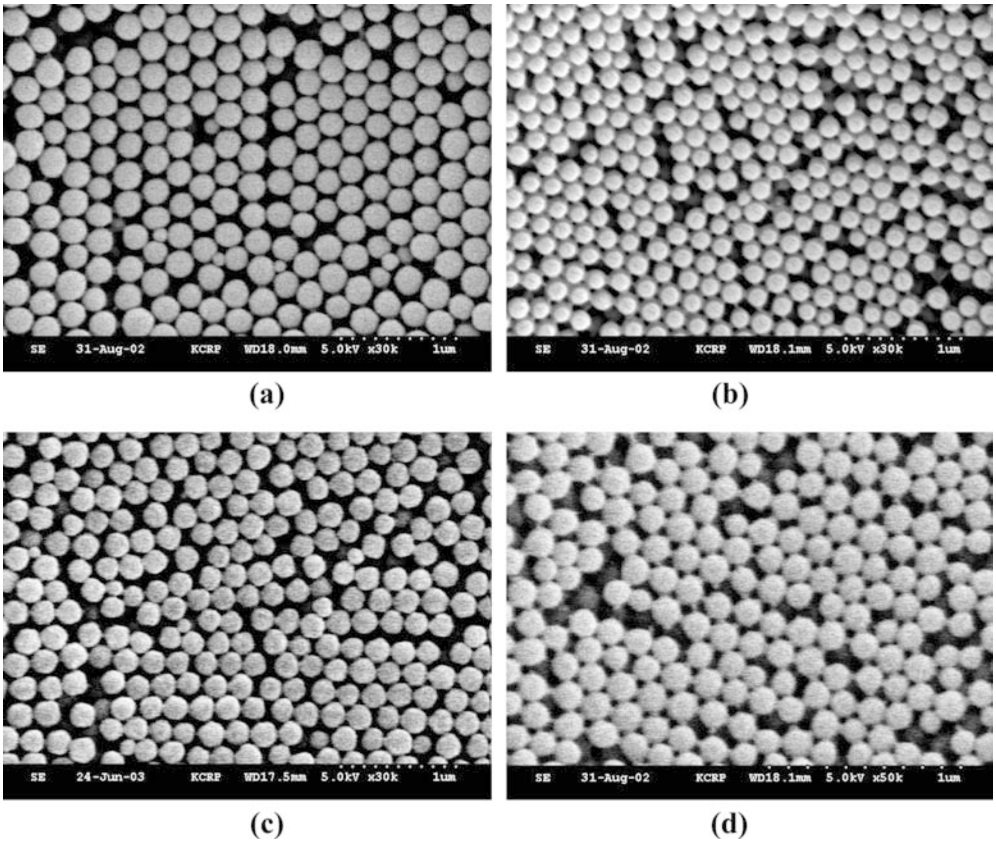


Fig. 1a–d SEM micrographs of the lattices at the end of the polymerization stage of the core: **a** PBA, **b** P *n*-BMA, **c** P *i*-BMA, **d** P(*i*-BMA-*co*-MMA)

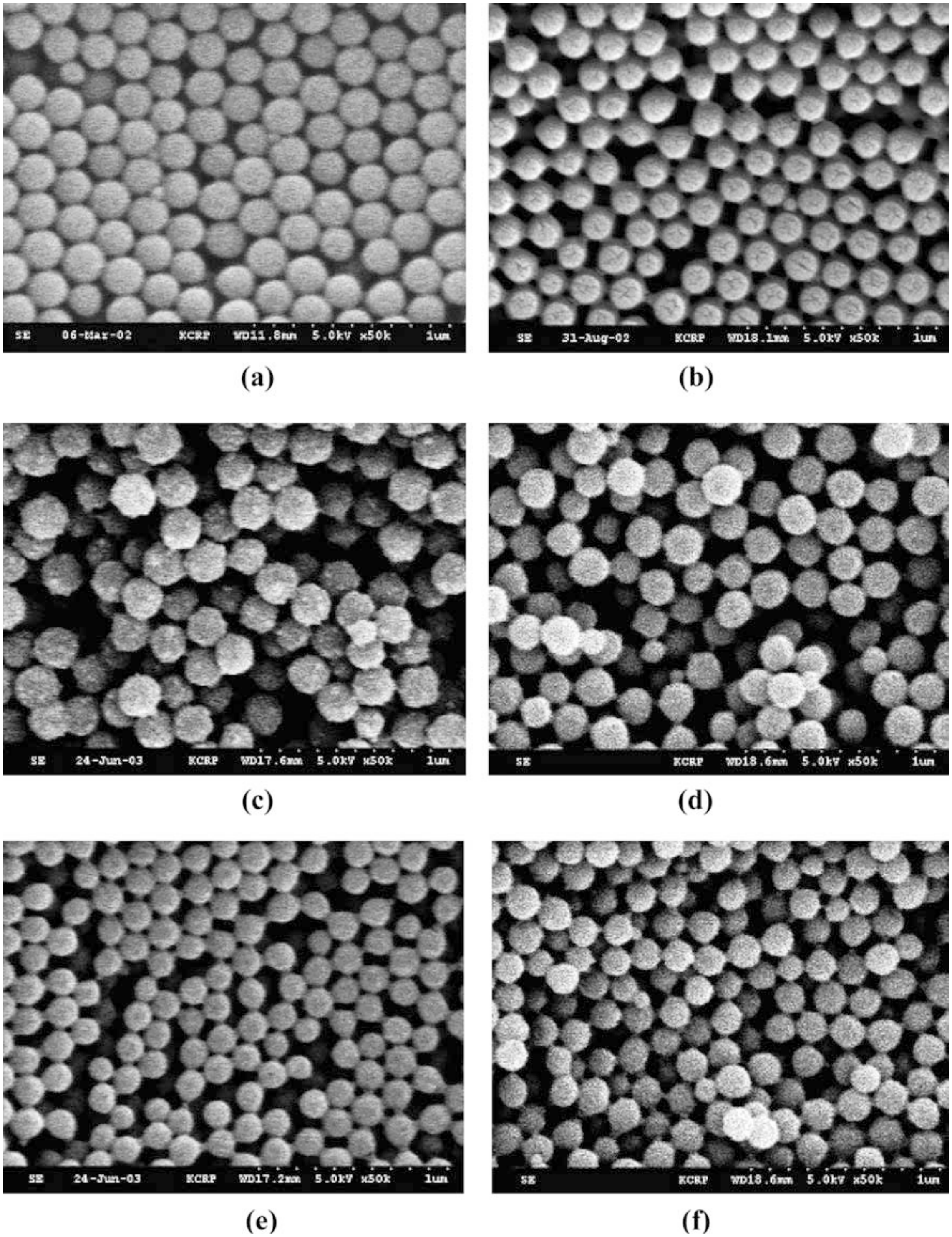


Fig. 2a–f SEM micrographs of the core-shell lattices (finial polymerization products): **a** sample 1, **b** sample 2, **c** sample 3, **d** sample 6, **e** sample 9, **f** sample 12

core-shell structure to occur [22]. The formation mechanism of the core-shell particles is explained briefly as follows: in the early stage of the polymerization, PBA domains are formed as the seed particle surface, and the absorbed BA monomers in the particle are predominantly located there. A PMMA-rich continuous phase is always fixed because the T_g of PMMA is about 100°C, which is higher than the polymerization temperature. Therefore, during the second stage of the polymeriza-

Table 2 Average particle diameters of the core and the shell of the lattices

Sample code	Average particle diameter (nm)	
	Core latex	Core-shell latex
1	173.53	235.75
2	154.26	226.58
3	158.54	214.32
4	147.39	197.65
5	156.41	215.32
6	152.73	210.74
7	149.42	190.42
8	167.21	176.53
9	155.21	154.16
10	159.86	195.33
11	156.19	203.94
12	158.68	206.27

tion, as the conversion of MMA increases, the PMMA domains, which are swollen with the MMA monomer, gradually contract and result in dents at the particle surface [23]. It is also observed in Figs. 1d, 2e, and 2f that the introduction of MMA into the core domains and MAA or ALMA into the shell domains does not influence the formation and the shape of the core-shell structure.

The average particle diameters of the core and the shell were measured and are listed in Table 2. The particle size of the core based on P *n*-BMA or P *i*-BMA was found to be smaller than that on PBA because of the high cohesion energy of PBMA. However, the effect on the particle size of the core is quite slight and negligible when PMMA is incorporated into the core copolymer. It is notable that the introduction of MAA or ALMA exhibits a significant influence on the particle sizes of the shell. Due to the strong hydrophilicity of MAA, the incorporation of MAA into the shell portion resulted in swelling of the shell in water medium and thus an increase of the particle size. On the other hand, when bifunctional ALMA was introduced into the shell materials, cross-linking of the shell copolymer occurred. As a result, the density of the shell copolymer increased. Therefore, the particle size of the shell decreased with an increasing amount of ALMA.

Storage stability

Storage stability of the plastisol is one of the most important issues that should be considered for industrial purposes, and this property can be evaluated by the viscosity change. The stability was judged to be sufficient when the viscosity change rate of the plastisols was kept at not more than 30% of the initial value even after 14 days at room temperature after preparation of the plastisols. For preparation of the plastisols, DOP and TCP were employed as plasticizers to be mixed with various core-shell lattices. The viscosities of the plastisols in DOP or TCP were recorded as a function of storage time and are shown in Figs. 3 and 4. Both in DOP and in TCP, the viscosities of the plastisols based on samples 1–3, which exhibited poor storage stability, were found to increase rapidly with increasing storage times. The core material for the above lattices is PBA, P *n*-BMA, or P *i*-BMA, which is characterized by good

Fig. 3 Plots of the viscosity versus the storage time for the plastisols based on various core-shell lattices with DOP: (■) sample 1, (▲) sample 2, (●) sample 3, (□) sample 4, (△) sample 5, (○) sample 6, (★) sample 7, (♦) sample 8, (▼) sample 9, (☆) sample 10, (◇) sample 11, (▽) sample 12

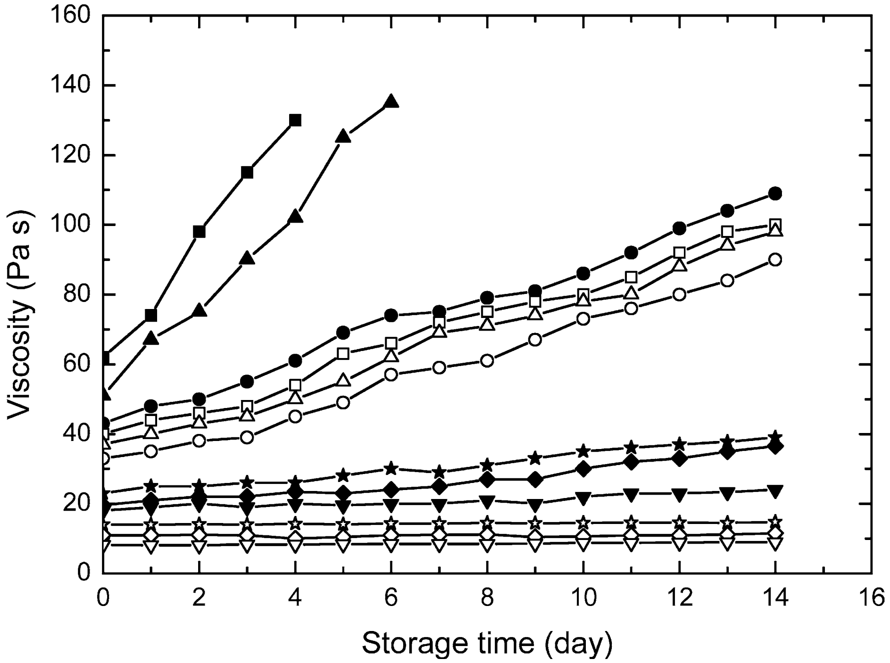
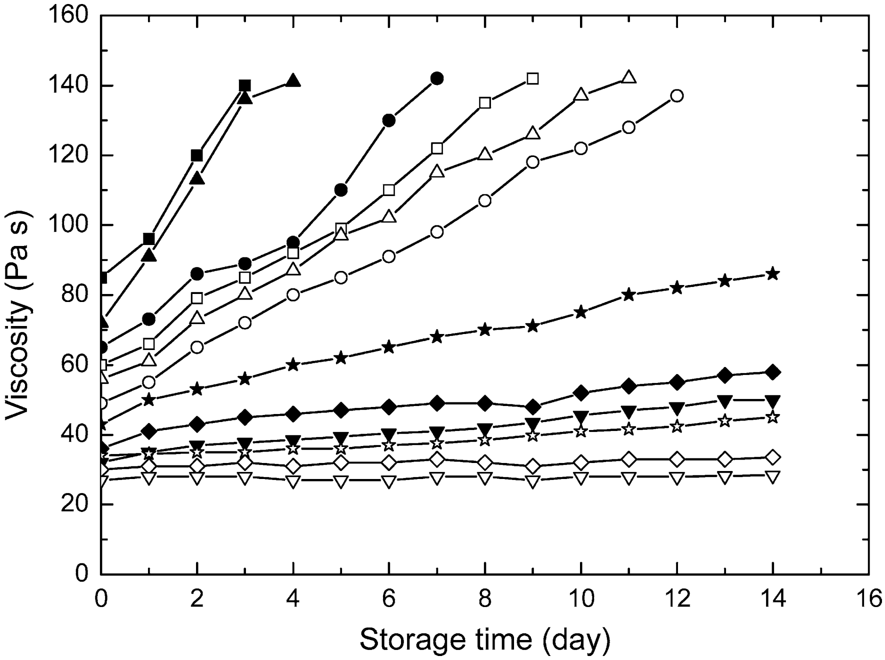


Fig. 4 Plots of the viscosity versus the storage time for the plastisols based on various core-shell lattices with TCP: (■) sample 1, (▲) sample 2, (●) sample 3, (□) sample 4, (△) sample 5, (○) sample 6, (★) sample 7, (♦) sample 8, (▼) sample 9, (☆) sample 10, (◇) sample 11, (▽) sample 12



compatibility with plasticizers, particularly also with phthalate plasticizers such as dioctyl phthalate. The core material alone would gel together with the plasticizer even at room temperature within several minutes. The lower the T_g of the core material, the softer its segments, thus the faster the gelation of its plastisol. When a hard segment of MMA was incorporated into the core portion, the compatibility of the core materials with plasticizers weakens due to the polarity of PMMA. As a result, the gelation time was prolonged.

The shell material is PMMA, which is resistant without limit to plasticizers at room temperature but which, after gelling and cooling, does not tightly retain the plasticizer in a homogeneous phase. During storage, the shell material affords sufficient protection against the premature gelation of the core material. If gelation has taken place at an elevated temperature, the plasticizer is so tightly bound by the core material that its incompatibility with the shell material no longer leads to demixing or separation. The compatibility of the core material with plasticizers is attributable to its content of acrylic acid alkyl esters having at least three carbon atoms in the alkyl portion, or of methacrylic acid alkyl esters having at least two carbon atoms in the alkyl portion. The affinity of homopolymers comprising these monomers toward plasticizers, particularly toward phthalic acid esters, is so great that the surrounding skin of shell material would not afford any lasting protection against gelation at room temperature if this affinity were not reduced by the presence of the strongly polar monomers. Therefore, the polarity of the shell materials was improved remarkably by introduction of MAA monomer. As a result, the storage stability of the plastisols based on these lattices was improved significantly. Moreover, the incorporation of ALMA into the shell portion resulted in a cross-linking of the shell materials, which also affords more sufficient protection against the premature gelation of the core material. Thus, the storage stability of the plastisols based on these shell materials was improved.

It is also notable in Figs. 3 and 4 that the increment of viscosity of plastisols based on the same latex in DOP is less than that in TCP. It is well known that compared with DOP, TCP is more compatible with the shell materials as a result of the stronger polarity of TCP, and it is easier for TCP to migrate into the core materials, which results in a disadvantageous effect on the storage stability of the plastisols.

Mechanical properties

The plastisols based on various core-shell lattices were subjected to processing plastigel films. The mechanical properties of these plastigels were measured, and the results are listed in Table 3. It is observed that the mechanical properties of the plastigels strongly depend on the T_g of the core or shell portion. For different core materials, the higher the T_g, the better the mechanical properties. Obviously, the higher T_g for the core portions is expected to impart good mechanical properties to the finial plastigel films [24]. Incorporation of MMA into the core materials could result in an increase of the T_g; therefore, the mechanical properties were also improved by the addition of MMA into the core materials. However, too much MMA caused the core materials to

Table 3 Mechanical properties of the plastigels based on various core and the shell of the lattices with DOP and TCP

Sample code	Tensile strength (MPa)		Elongation at break (%)	
	With DOP	With TCP	With DOP	With TCP
1	0.24	0.36	253	290
2	0.42	0.57	270	310
3	0.53	0.61	275	311
4	0.54	0.68	204	255
5	0.62	0.70	206	259
6	0.66	0.81	165	198
7	0.59	0.69	264	294
8	0.63	0.75	211	242
9	0.62	0.72	152	186
10	0.69	0.71	256	269
11	0.85	0.93	175	190
12	0.67	0.82	86	93

become brittle. As a result, the elongation at break of the plastigels deteriorated. It is also found in Table 3 that the tensile strength of the plastigels improved when the MAA was introduced into the shell portion of the lattices, and an optimum value was obtained with the content of 3 wt% MAA. But the elongation at break decreased with increased MAA content. This may be attributable to the rigidity of the plastigels caused by the strong polarity of MAA. However, excessive amounts of MAA resulted in a brittleness of the plastigels, and thus a decrease of mechanical properties. A similar phenomenon could be found regarding the introduction of ALMA into the shell portion, as shown in Table 3. This can be considered to be a result of the cross-linking of the shell materials, which enhance the strength of the plastigels. One may also find that, based on the same latex, the plastigel in TCP exhibits much better mechanical properties than those in DOP. Compared with DOP, TCP is more compatible with the shell portion. This makes it easier for TCP to migrate into the core portion and form more homogeneous plastisols.

Morphology of tensile fracture surfaces

The tensile fracture surfaces of the plastigels based on various core-shell lattices were observed with SEM and their micrographs are shown in Fig. 5. One can see that the fracture surfaces are not smooth but rippled with striations, and exhibit plastic shear deformation. There are many holes of different sizes on the fracture surface. An extensive plastic deformation of the matrix is evidenced by the appearance of numerous striations, cavitation, shear banding, and voids [25]. For samples with high MAA content and ALMA in the shell portion, some small particles were observed on the fracture surfaces of their plastigels. These particles were estimated to be the undiluted core-shell lattices. We concluded that high incompatibility of the shell portion with plasticizers

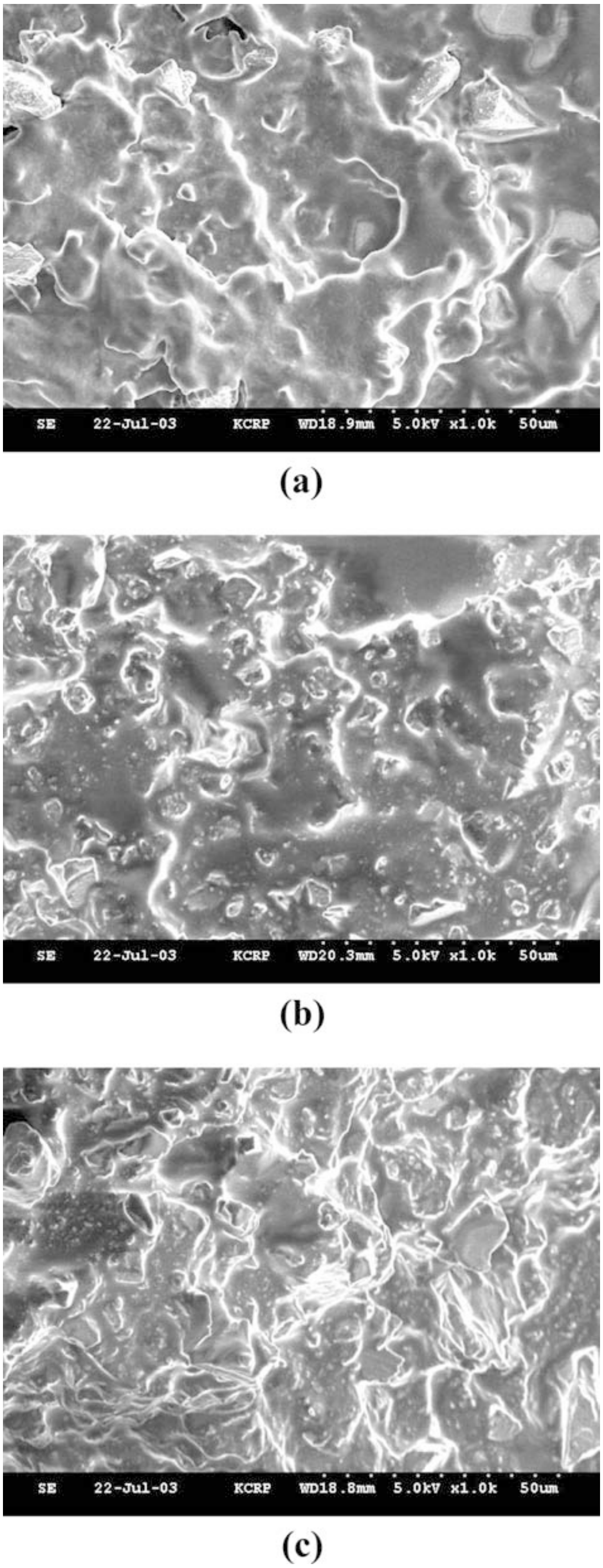


Fig. 5a–c SEM micrographs of the tensile fracture surfaces of the plastigels: **a** sample 3, **b** sample 9, **c** sample 12

has a disadvantageous effect on the dilution of the core-shell lattices, as does the high cross-linking of the shell materials by incorporation of ALMA.

Conclusions

A series of core-shell lattices comprising a core portion of rubbery acrylic alkyl ester homo- or copolymers and a surrounding shell portion of glassy MMA homo- or copolymers were designed as plastisols for automotive underbody coatings and synthesized by a semi-continuous seeded emulsion polymerization. Novel plastisols with use of DOP and TCP plasticizers were proposed based on these core-shell lattices, whose core portions were compatible with the employed plasticizers and shell portions were incompatible with the plasticizers. The storage stability of the plastisols could be obtained through incorporation of a strongly polar monomer MAA or a cross-linker ALMA into the shell portions. The mechanical properties of the plastigels depended on the T_g of the core materials as well as the incompatibility of the shell materials with the plasticizers. For industrial applications, a balance between the mechanical properties of plastigels and the storage stability of plastisols should be carefully considered during optimization of the monomers both for the core and the shell materials. The target of novel automotive underbody coatings should be pursued in terms of safety, performance, and cost.

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References

1. Tomalino M, Bianchini G (1997) Prog Org Coat 32:17
2. Tomalino M, Panfili M (1995) Int seminar ATA-FAST, Milan, Italy, pp 169–178
3. Funke W (1996) Prog Org Coat 28:150
4. Soucek MD (1996) Prog Org Coat 28:313
5. Mark HF (1971) In: Encyclopedia of polymer science and technology, vol 14. Wiley, New York, pp 370–413
6. Nakajima N, Sadeghi MR, Kyu T (1990) J Appl Polym Sci 41:889
7. Nakajima N, Daniels CA (1980) J Appl Polym Sci 25:2019
8. Rebrovic JA (2000) Metal Finishing 98:124
9. Johnson TL (1995) J Coat Technol 67:45
10. Boessler H, Quis P, Buechse J, Rauch H (1980) US Patent 4 199 486
11. Overend AS, Cooper DH, Padget JC (2002) US Patent 6 495 626
12. Nonoyama A, Torii H, Ito K, Ohashi Y, Takata A (2003) US Patent 6 559 153
13. Webster DC, Crain AL (2002) Prog Org Coat 45:43
14. Teng G, Soucek MD (2001) Polymer 42:2849
15. Hibino K, Kimura Y (2000) J Appl Polym Sci 77:1794
16. Loehden G, Belik P, Dorn K, Schickel N, Traebing M (2002) US Patent 6 498 209
17. Beck M, Jeromin L, Hoeltgen C, Ritter W (1998) US Patent 5 840 786
18. Kotaro S, Kazuyoshi S (2002) US Patent 6 489 023
19. Overend AS, Padget JC (1994) US Patent 5 324 762
20. Fox TG (1956) Bull Am Phys Soc 1:123
21. Yan C, Xu Z, Cheng S, Feng L (1999) J Appl Polym Sci 68:969
22. Scheinder M, Pita T, Lambla M (1996) J Appl Polym Sci 62:273
23. Hu R, Dimonie YL, El-Aasser MS (1997) J Appl Polym Sci 64:1123
24. Winnik MA, Feng J (1996) J Coat Technol 68:39
25. Pan M, Zhang L (2002) J Appl Polym Sci 90:643