

Rheological Behavior and Thermal Properties of Poly(butyl acrylate-co-2-ethylhexyl acrylate)-Grafted Vinyl Chloride Resin

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Received 30 September 2003; accepted 8 June 2004

DOI 10.1002/app.21113

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

ABSTRACT: The rheological behavior and thermal properties of a poly(butyl acrylate-co-2-ethylhexyl acrylate) [P(BA-EHA)]-grafted vinyl chloride (VC) composite resin [P(BA-EHA)/poly(vinyl chloride) (PVC)] and its materials were investigated. The rheological behavior, thermal stability, and Vicat softening temperature (VST) of P(BA-EHA)/PVC were measured with capillary rheometry, thermal analysis, and VST testing, respectively. The effects of the P(BA-EHA) content and the polymerization temperature of grafted VC on the rheological behavior of the composite resin were examined. The weight loss of the composite resin and its extracted remainder via heating were analyzed. The influence of the content and crosslinking degree of P(BA-EHA) and the polymerization temperature of the grafted VC on VST of the materials was determined. The results indicated the pseudoplastic-flow nature of the composite resin. The flow property of the modified PVC resin was improved because of the incorporation of the acrylate polymer. The molecular weight of PVC greatly influenced the flow behav-

ior and VST of the composite resin and its materials. The flowability of the composite resin markedly increased, and the VST of its materials decreased as the polymerization temperature of the grafted VC increased. The initial degradation temperature of the composite resin increased as the P(BA-EHA) content increased. The VST of the samples was enhanced a little as the content of the crosslinking agent increased in P(BA-EHA). As expected, the composite resin, with good impact resistance, had better heating stability and flowability than pure PVC, whereas the VST of the material decreased little with increasing P(BA-EHA) content. Therefore, P(BA-EHA)/PVC resins prepared by seeded emulsion polymerization have excellent potential for widespread applications. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 419–426, 2005

Key words: degradation; poly(vinyl chloride) (PVC); rheology; thermal properties

INTRODUCTION

Poly(vinyl chloride) (PVC) is a general resin with many excellent properties and is widely applied in cable and wire jacketing and in the automotive, building, construction, and packaging industries. However, PVC has some deficiencies, such as a low notched-impact strength, poor processability, and bad thermal stability. Polymer blending is an important means of improving the mechanical properties, heat resistance,¹ and processability of the blended materials and lowering the cost of products. Therefore, a great number of additives can be compounded with PVC to obtain desired product properties. Sombatsompop and co-workers^{3,4} investigated the processability, rheology, and thermal, mechanical, and morphological proper-

ties of postconsumer PVC bottles and cables² and PVC/wood-sawdust composites.^{3,4}

Shah and Shertukde⁵ studied the effects of plasticizers on the mechanical, electrical, permanence, and thermal properties of PVC. The incorporation of plasticizers can improve the processability by lowering the melting and softening points and viscosity of the melts. Their high compatibility and solvency produce the fastest fusion during processing. However, the use of plasticizers beyond the threshold limit of a polymer results in increased softness. Because this weakens the bond holding the polymer molecules together, plasticizers greatly reduce the modulus. A migration of the plasticizers onto the surface is another undesirable property of this kind of product. On the basis of the aforementioned facts, adding a crosslinked rubbery polymer to a PVC resin is a conventionally used method for PVC modification.⁶ The thermal properties and rheological behavior of blends for hard PVC and its modifiers, including impact-resistant and processing aids, are studied currently in practice.^{4,7–9} A study on the melt rheology of this class of toughened plastics is evidently important to processors, who have to

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Contract grant sponsor: Major Program of Hebei Province in China; contract grant number: 01213074D.

know how heterogeneous blends behave in the melt state to obtain high impact levels in molded products.¹⁰ Hernández et al.¹¹ analyzed PVC/copoly(ester urethane) and PVC/ethylene vinyl acetate copolymer blends from the point of view of the effect of miscibility on the mechanical and rheological properties of PVC blends. Still, graft copolymerization is indispensable for the modification of polymers such as PVC. Therefore, research on composite resins prepared by graft copolymerization has the same importance. Very few articles have been published on the effects of rubbery polymers on the thermal properties and rheological behavior of elastomer-grafted vinyl chloride (VC) composites,¹² especially for composite emulsion resins.

In our previous work, composite emulsion resins {poly(butyl acrylate-*co*-2-ethylhexyl acrylate) [P(BA-EHA)]/PVC} were synthesized by the grafting of VC onto crosslinked P(BA-EHA) latex, and the mechanical properties and structure characterization of P(BA-EHA)/PVC were reported in detail.¹³ Here, P(BA-EHA) was used as a rubber-toughened modifier. The rheological behavior and thermal properties of the P(BA-EHA)/PVC resin and its materials were investigated. The rheological behavior, thermal stability, and Vicat softening temperature (VST) of P(BA-EHA)/PVC and its materials were measured with capillary rheometry, thermal analysis, and VST testing to determine the effects of the main synthesis factors on these properties. With this research, we sought to confirm whether our synthesized P(BA-EHA)/PVC resin with good impact resistance also had improved thermal properties and rheological behavior in comparison with neat PVC compounds.

EXPERIMENTAL

Materials

The monomers *n*-butyl acrylate (BA), 2-ethylhexyl acrylate (EHA), and 1,4-butylene glycol diacrylate (BDA) were industrial products. All the monomers were supplied by the Beijing Dong Fang Chemical Plant (Beijing, China) and were freshly distilled *in vacuo* and stored at -10°C before use. Sodium dodecyl sulfate (SDS), chemically pure, was used as an emulsifier. Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), chemically pure, was recrystallized with distilled water at 35°C and used as an initiator. Tetrahydrofuran, analytically pure, was used as a solvent. VC, greater than 99.99 wt % pure, was supplied by the Tianjin Chemical Plant (Tianjin, China).

Synthesis of the P(BA-EHA)/PVC composite resin¹³

Synthesis of the P(BA-EHA) latex

Distilled water (200 mL), 0.50 g of SDS, 12.9 g of BA, 5.6 g of EHA, 0.28 g of BDA, and 0.15 g of $\text{K}_2\text{S}_2\text{O}_8$ were

charged into a 500-mL, four-necked glass flask. The mixture was stirred and purged under nitrogen over 20 min. Then, 37 mL of an $\text{Na}_2\text{B}_4\text{O}_7$ solution (concentration = 0.03 g/mL) was added to control the pH of the reaction system between 8 and 9. Next, the reaction vessel was heated to 80°C . The copolymerization was carried over 1.5 h under an N_2 atmosphere and was stirred thoroughly.

In the second stage, a monomer mixture of 51.6 g of BA, 22.4 g of EHA, 1.11 g of BDA, and 0.30 g of $\text{K}_2\text{S}_2\text{O}_8$ dissolved in 20 mL of distilled water was added dropwise over 1.5 h. The reaction was then maintained at 80°C for an additional 2 h.

Preparation of the P(BA-EHA)/PVC emulsion resin

A mixture of 900 mL of deionized water, 2.20 g of SDS, and 0.70 g of $\text{K}_2\text{S}_2\text{O}_8$ was charged into a 2-L, stainless steel autoclave, and a certain amount of P(BA-EHA) latex as the seed was added. A 5 wt % sodium hydroxide solution was used to adjust the pH of the reactive mixture between 9.5 and 10.5. After the autoclave was closed and the air was removed, 400 g of the VC monomer was gradually added to the reactor with stirring. The polymerization was continued at $50 \pm 0.3^{\circ}\text{C}$ until the pressure dropped to 0.35 MPa, and the seeded emulsion copolymerization was short-terminated. After cooling, the unreacted monomer was removed. The resin was isolated from the emulsion via freezing at -20°C . The product was filtered, rinsed with deionized water, and dried under reduced pressure at 50°C .

Remainder [P(BA-EHA)GPVC] after P(BA-EHA)/PVC extraction

The P(BA-EHA)-grafted VC composite resin was substantially a mixture composed of the homopolymer of PVC, crosslinked P(BA-EHA), and the P(BA-EHA) grafting of the VC copolymer. Thus, the P(BA-EHA)/PVC resin was extracted with tetrahydrofuran to remove PVC not grafted onto P(BA-EHA), but the crosslinked P(BA-EHA) and its grafting of the VC copolymer were left. In the experiment, a weighed amount of the sample was sealed in a special paper bag, placed in a Soxhlet thimble, and extracted with tetrahydrofuran for 24 h. The undissolved polymer was dried, weighed, and again extracted with tetrahydrofuran for additional hours until no further weight loss was observed. The final remainder [P(BA-EHA)GPVC], in which the homopolymer of PVC was not contained, was dried under reduced pressure to test the heat-resistant stability. A solution of nongrafted PVC dissolved in tetrahydrofuran was used for the determination of the PVC molecular weight.

Determination of the molecular weight of PVC

Here viscometry was used to determine the molecular weight of PVC. The aforementioned tetrahydrofuran solution (15 mL) of nongrafted PVC was added slowly to a viscometer with a 0.49-mm capillary diameter, which was placed in a water bath at a constant temperature of $20 \pm 0.1^\circ\text{C}$. After 15 min, the time at which the solution passed between the scales of the capillary was determined twice. The average value of the time was recorded twice, but the absolute error between both had to be less than 0.2 s. The absolute viscosity (η) of the PVC solution was calculated with the following equation:

$$\eta = Rdt$$

where R is the viscometer constant, d is the specific gravity of the PVC solution, and t is the time at which the solution passes between the scales of the capillary.

The average degree of polymerization of nongrafted PVC was determined according to GB5761-86.

Preparation of the composite samples

The P(BA-EHA)/PVC resin was mixed with a determined quantity of additives.¹³ All the components were first mixed in a high-speed mixer at room temperature and were then milled on a laboratory two-roll mill between 170 and 175°C for 7 min. Four-millimeter-thick plates were pressed at $180\text{--}185^\circ\text{C}$. The plates were cooled under a cooling press. All samples for the determination of VST were cut from the plates.

Rheological behavior of the composite resin

The rheological behavior of P(BA-EHA)/PVC was investigated with an XLY-II flow tester (capillary rheometer) (Jinlin University Science and Educational Instrument Plant, Changchun, China). The fixed-temperature method was used. The nozzle diameter was 1 mm, and the nozzle length was 40 mm. The experimental specimens were prepared as follows: 100 parts of the P(BA-EHA)/PVC resin was mixed with 2.5 parts of organotin. The weight of the tested specimen was 2.5 g. The operation temperature was fixed at 183°C , with experimental loads of 360, 400, 440, 480, and 520 kg/cm^2 .

The apparent shear stress (τ_w), apparent shear rate ($\dot{\gamma}_w$), and apparent viscosity (η_a) were calculated with following equations:

Effective shear stress at wall of nozzle:

$$\tau_w = \Delta PR/2L$$

where ΔP is the applied pressure (kg/cm^2), R is the nozzle radius (cm), and L is the nozzle length (cm). The efflux rate (Q) is given by

$$Q = S \cdot h/t \text{ (cm}^3/\text{s)}$$

where h is the downward displacement of the plunger (cm), S is the area of the plunger cross section (cm^2), and t is the effluent time of the melt (s). For a Newtonian liquid, $\dot{\gamma}_w$ at the wall of the nozzle can be calculated as follows:

$$\dot{\gamma}_w = 4Q/\pi R^3 \text{ (s}^{-1}\text{)}$$

η_a is given by

$$\eta_a = \tau_w/\dot{\gamma}_w = \Delta P\pi R^4/8QL$$

For a non-Newtonian liquid, the corrected apparent shear rate ($\dot{\gamma}_{wc}$) is given by

$$\dot{\gamma}_{wc} = (3n + 1)\dot{\gamma}_w/4n$$

where n is an index of a non-Newtonian liquid. Then, the corrected apparent viscosity (η_{ac}) is

$$\eta_{ac} = \tau_w/\dot{\gamma}_{wc}$$

Thermogravimetric analysis of the P(BA-EHA)/PVC resin

The P(BA-EHA)/PVC resin was fully dried *in vacuo*. The thermogravimetric analysis of the P(BA-EHA)/PVC resin and its extracted remainder was performed under a nitrogen atmosphere with a TA-2000 thermal analyzer (DuPont Co., New Castle, DE) at a heating rate of $20^\circ\text{C}/\text{min}$ from room temperature to 600°C .

Determination of the VST

All the samples were $12 \times 13 \times 4\text{ mm}^3$. The determination of VST was performed with an XWB-300F tester (Hebei Chengde Testing Machine Co. Ltd., Chengde, China) of the heat distortion and Vicat softening point. According to GB1633-79, VST of the samples, into which a needle-press head with a section area of 1 mm^2 was pressed to a depth of 1 mm, was measured at a fixed heating rate of $50^\circ\text{C}/\text{h}$ and with an experimental load of 9.81N. The VST value of each sample was the average value of two parallel samples.

RESULTS AND DISCUSSION

Rheological behavior of the composite resin

The melt-flow behavior of a multiphase polymeric system is controlled mainly by the structure and par-

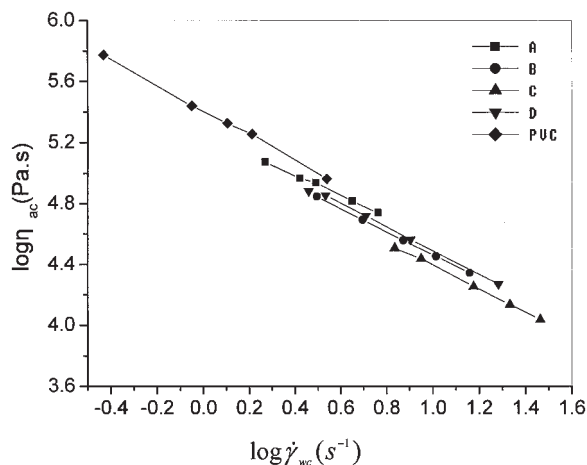


Figure 1 Rheological behavior of composite resins with different P(BA-EHA) concentrations: (A) 4.2, (B) 6.3, (C) 8.5, and (D) 13.8%.

ticularly by the size and shape of the dispersed phase domains and the interfacial tension between the phases.¹⁰ Logarithms of η_{ac} plotted as a function of logarithms of $\dot{\gamma}_{wc}$ are given in Figures 1 and 2. The P(BA-EHA) concentrations (wt %) of the samples in Figure 1 were 4.2, 6.3, 8.5, and 13.8%, and the experiments were labeled A–D. η_{ac} decreased with an increasing shear rate in all cases. The values of the flow behavior index (n) were less than one. The flow behavior of this melt mixture was pseudoplastic. As explained earlier, the applied force disturbed the long-chain polymer from its equilibrium position, and the macromolecules became disentangled in the direction of the force; this caused a reduction in the viscosity.¹⁴

Figure 1 shows that the flowability of the composite resin gradually increased with increasing P(BA-EHA) content. The flowability of pure PVC was the worst, and the flowability of the composite resin with 8.5% P(BA-EHA) was the best. This may have occurred because the formation of the grafting copolymer between PVC and P(BA-EHA) weakened the strong interaction between the neat PVC macromolecules when there was less P(BA-EHA). Therefore, the flow property of the modified PVC resin was improved by the addition of polyacrylate (ACR). Furthermore, when the P(BA-EHA) content in the composite resin was increased continually or too much, the flowability of the composite resin began to decrease, as shown in Figure 1(D). This was due to very interactive forces between PVC and P(BA-EHA) and the difficult melting of the crosslinked P(BA-EHA) itself and its grafting copolymer. Because the crosslinked particles were difficult to melt and less deformable in the melt mixture, the strong interaction and high entanglement between the crosslinked P(BA-EHA) and PVC macromolecules increased with increasing P(BA-EHA) content. Meanwhile, the interfacial compatibility between

them was increased. Therefore, the morphology was highly stable, and the direction of the polymer chains was not easy. The melt system showed a higher viscosity.

As shown in Figure 2, the flowability of pure PVC was very bad. The flowability of the synthesized pure PVC under a polymerization temperature of 50°C was much worse than that of the composite resin with a 6.3 wt % P(BA-EHA) synthesized under 47°C. It is not difficult to understand that the flowability of pure PVC prepared under 47°C was worse than that of pure PVC synthesized under 50°C. The reason is given later.

Figure 2 shows that the flowability of the composite resin markedly increased as the grafting polymerization temperature of VC increased. This result showed that the flowability of the composite resin was greatly influenced by the polymerization temperature of VC. This reason was that the molecular weight of the PVC matrix was greatly affected by the polymerization temperature. Therefore, it influenced the rheological behavior of the composite resin. Especially for the VC monomer, the chain-transfer constant was greater than that of other common monomers and greatly increased with the polymerization temperature. When the polymerization temperature was increased, the molecular weight of PVC decreased, as shown later in Figure 9. Then, the flowability of the modified PVC was enhanced. This high molecular weight accounted for the high viscosity of the melt sample. Hence, it was possible that the degree of polymerization of PVC and the flowability of the composite resin were regulated through the polymerization temperature under the condition that the demand for the mechanical strength of the materials was ensured.

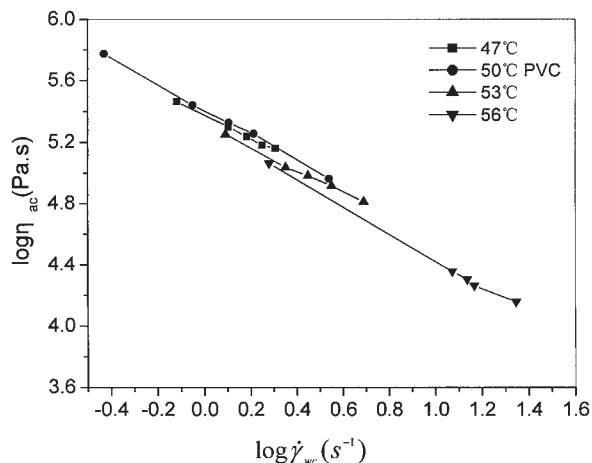


Figure 2 Influence of the polymerization temperature on the rheological behavior of the P(BA-EHA) composite resin (concentration = 6.3 wt %).

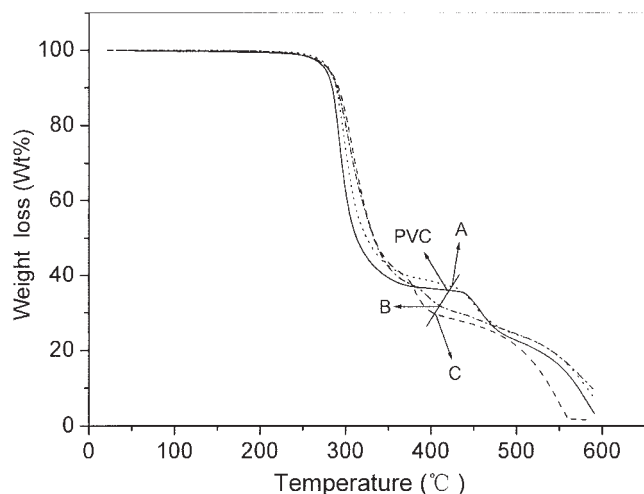


Figure 3 Weight-loss curves of composite resins with different P(BA-EHA) concentrations: (A) 4.2, (B) 6.3, and (C) 10.8%.

Thermogravimetric analysis

Thermogravimetry is an important means of evaluating the thermal stability of resins or plastics. The degradation of PVC usually proceeds in a two-stage process. The first stage corresponds to the step-by-step elimination of HCl with some benzene traces. The second stage corresponds to the formation of conjugated unsaturation that results from the elimination of HCl from adjacent carbon atoms; this resembles a polyacetylene structure, which gradually reticulates and becomes more stable than that of PVC.⁵

As shown in Figure 3, all the composite resins underwent a two-stage degradation process like PVC. The curves for PVC and sample A have very similar shapes. The result is reasonable because a small amount of the P(BA-EHA) copolymer would not affect the degradation behavior of PVC much. However, the degradation profile of the composite resin during the second stage was distinctly different from that of PVC with an increase in the P(BA-EHA) content. As shown in Table I, the degradation temperature during the second stage, during which the weight loss accelerated sharply, gradually decreased with increasing P(BA-EHA) content because the degradation mechanism of P(BA-EHA) differed from that of PVC. From

about 400°C, a weight loss was observed that was attributed to polyacetylene cracking.

In comparison with the PVC resin, weight-loss curves of the P(BA-EHA)/PVC resin gradually shifted to a higher temperature with increasing P(BA-EHA) content. The initial degradation temperature of the composite resin began to increase, as shown in Table I. Moreover, Table I shows the degradation temperatures at 10 and 50% weight losses for the composite resin and PVC. The same effect was observed. Furthermore, we processed differential analyses for all the curves in Figure 3 to obtain the maximum degradation temperature, which is listed in Table I. From the data, we can see that the maximum degradation temperature increased with increasing P(BA-EHA) content. In other words, the heating stability of the composite resin became better with the incorporation of P(BA-EHA). This was due to the fact that ACR has excellent heating stability and weather resistance. This is just the reason that ACR is very welcome. As an impact-resistant modifier for thermoplastic polymers such as PVC and polystyrene, ACR is superior to chlorinated polyethylene (CPE) and methyl methacrylate-butadiene-styrene copolymers (MBS).

The interaction mechanism that led to improved thermal stability for the composite resin may have been the formation of hydrogen bonds between carboxylic ester groups of the ACR chains and hydrogen chloride. The hydrogen chloride was produced through the structural deficiency (e.g., tertiary carbon structure) of PVC chains, which were formed in the synthesized PVC as a head-head combination of chain structural units, and through degradation or elimination during the processing and use. We speculate that a six-membered ring or an octatomic cyclic structure may have been formed among the α -hydrogen atoms, carbonyl groups in the ACR, and active chloride and hydrogen atoms in PVC. The heating decomposition action of PVC may have been suppressed by the stable structure, and this led to an interruption of the so-called unzipping and self-catalytic process involved in HCl elimination.¹⁵ The probable interaction mechanism is schematically shown in Figure 4.

Figure 5 presents a plot of the weight losses of pure PVC, the remainder [P(BA-EHA)GPVC] of the com-

TABLE I
Progressive Degradation Temperatures (DTs) of Composite Resins with Different P(BA-EHA) Contents

Sample	Initial DT (°C)	10% weight-loss DT (°C)	50% weight-loss DT (°C)	DT at the second stage (°C)	Maximum DT (°C)
PVC	278.7	285.0	313.4	439.8	292.4
A	282.0	287.8	324.4	434.1	297.9
B	284.2	291.4	333.5	389.3	303.4
C	286.0	292.3	334.0	373.9	309.0

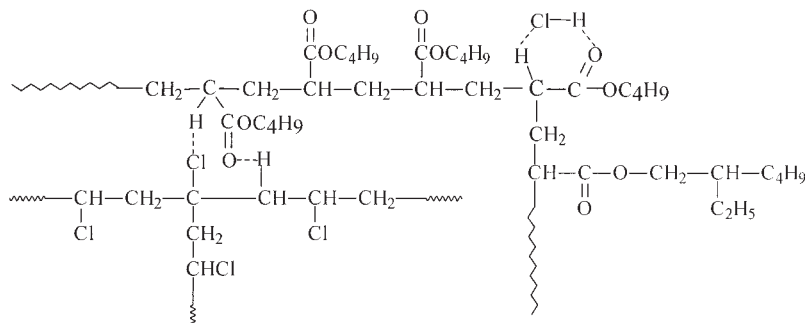


Figure 4 Speculative mechanism of the interaction between the P(BA-EHA) and PVC macromolecules.

posite resin extracted with tetrahydrofuran, and pure P(BA-EHA) with increasing temperature. Their thermal stability studies were performed on the basis of thermogravimetric measurements. The degradation curves of these samples are generally of a similar two-step type, as shown in Figure 3. However, the degradation of the remainder during the second step accelerated sharply with increasing P(BA-EHA) content until the degradation profile of pure P(BA-EHA) almost presented a one-stage process.

In comparison with pure PVC, P(BA-EHA)GPVC (i.e., the remainder) had a higher initial degradation temperature or better heat stability. However, its initial degradation temperature was lower than that of pure P(BA-EHA). When the weight losses of the samples reached 20% of the total weight, the initial degradation temperatures of pure PVC, P(BA-EHA)GPVC 1 and 2, and pure P(BA-EHA) were 294, 318, 328.5, and 363.5°C, respectively. This showed that the heat stability of the samples was enhanced with increasing P(BA-EHA) content. As expected, the observed results were similar to those shown in Figure 3. The effect was

attributed to the incorporation of the acrylic polymer into PVC. After the weight losses of the samples reached 70% of the total weight, the decomposition of PVC slowed, the degradation speed of pure P(BA-EHA) increased, and the degradation speed of P(BA-EHA)GPVC was between them. The residual weights of the samples decreased with increasing P(BA-EHA) content at about 450°C. This result was associated with the different decomposition mechanisms of PVC and P(BA-EHA) because the degradation of PVC usually proceeded by a dehydrochlorination process, which resulted in the formation of long conjugated double bonds or polyene sequences, causing a color change.³ Then, the remains may have been long carbon-carbon chains. When the temperature was enhanced continually, the weight loss of the remains became more difficult. After heating over 500°C, the remaining residue stayed more or less stable. For a char-forming polymer, the formed char in the case of PVC serves as a much more effective insulator.¹⁶ However, the degradation mechanism for P(BA-EHA) was chiefly a scission degradation of the P(BA-EHA) macromolecules at a higher temperature. Degradation by scission process led to the formation of either only monomer or a mixture of monomer and oligomers. Finally, the residual weight of P(BA-EHA) was almost zero over 500°C, as curve 4 in Figure 5 shows.

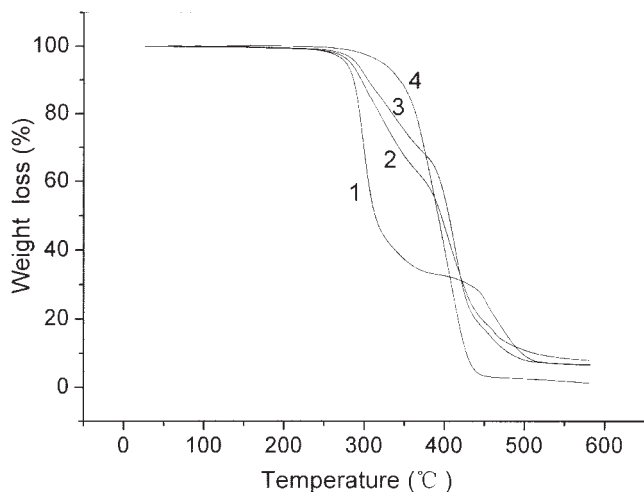


Figure 5 Thermogravimetric analysis of (1) PVC, (2) P(BA-EHA)GPVC with 53.4% P(BA-EHA), (3) P(BA-EHA)GPVC with 59.8% P(BA-EHA), and (4) P(BA-EHA).

VST of the P(BA-EHA)/PVC composite samples

Influence of the P(BA-EHA) content on VST of the samples

Figure 6 shows the relationship between the P(BA-EHA) content and VST of the samples. VST of the composite samples decreased slightly with increasing P(BA-EHA) content. The reason was that the dispersed phase of P(BA-EHA)-grafted VC materials was an elastomer with a low modulus. Then, the matrices of the materials gradually led to a brittle-ductile transition with an increase in the P(BA-EHA) content. The rigidity and hardness of the materials decreased with it. Therefore, VST of the composite samples decreased

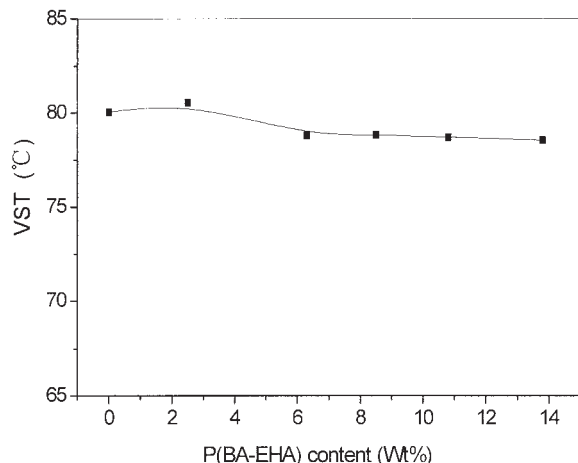


Figure 6 Influence of the P(BA-EHA) concentration on VST.

with increasing P(BA-EHA) content. Because the P(BA-EHA) content in the samples was less within the range of the added amount of P(BA-EHA) covered in these experiments, the rubbery polymer was a separating phase, and intensive interaction could occur between PVC chains and P(BA-EHA) chains, especially for the sample with 2.5% P(BA-EHA). Therefore, it could not cause an obvious reduction of VST of the matrix PVC.

Influence of the content of the crosslinking agent in P(BA-EHA)

When the content of the crosslinking agent in the P(BA-EHA) was increased, the degree of crosslinking in P(BA-EHA) increased. The interactions between the rubbery polymer molecules and PVC macromolecules were enhanced. The elastic modulus of the rubbery polymer increased. When the degree of crosslinking in P(BA-EHA) was increased to a great extent, the rubbery polymer transformed into a nonelastomer or rigid particles. Then, the P(BA-EHA) particles could not easily initiate the formation of crazing and shear bands.¹⁷ The toughening effect of the P(BA-EHA) particles decreased, and the impact properties of the samples began to decrease obviously. However, the modulus of the P(BA-EHA) dispersed phase increased with an increasing amount of the crosslinking agent. The rigidity and modulus of the P(BA-EHA)/PVC material increased, and its toughness decreased. Therefore, VST of the samples was enhanced a little with an increasing content of the crosslinking agent, as shown in Figure 7. According to the aforementioned results, selecting an appropriate degree of crosslinking was necessary for a modified impact-resistant resin.

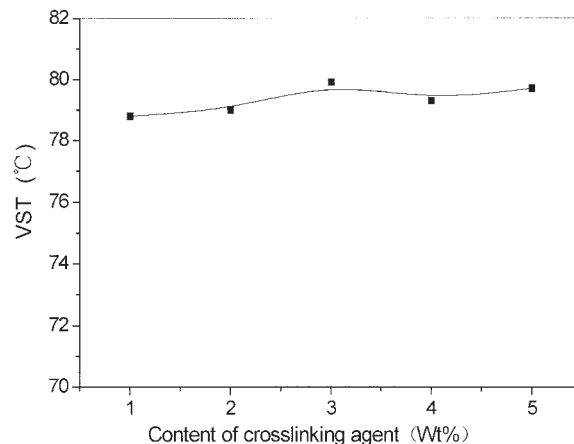


Figure 7 Influence of the crosslinking agent concentration in P(BA-EHA) on VST [P(BA-EHA) concentration = 6.3 wt %].

Influence of the graft copolymerization temperature of PVC

As shown in Figure 8, VST of the samples was evidently influenced by the polymerization temperature of grafting VC. The VST values of the samples gradually decreased with an increasing grafting polymerization temperature. As mentioned previously, the molecular weight of the PVC resin intensively depended on the polymerization temperature. When the polymerization temperature was enhanced, the chain-transfer constant of VC, which was usually greater than that of other common monomers, greatly increased with it. Then, the molecular weight of the synthesized PVC decreased, as Figure 9 shows. The hardness and modulus of the composite resin materials decreased, and its toughness increased because of the reduction of the molecular weight of the PVC matrix. Hence, VST of the composite sample gradually decreased with it.

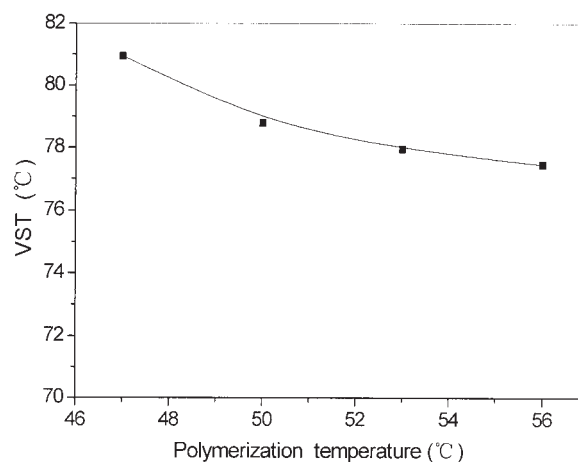


Figure 8 Influence of the polymerization temperature on VST [P(BA-EHA) concentration = 6.3 wt %].

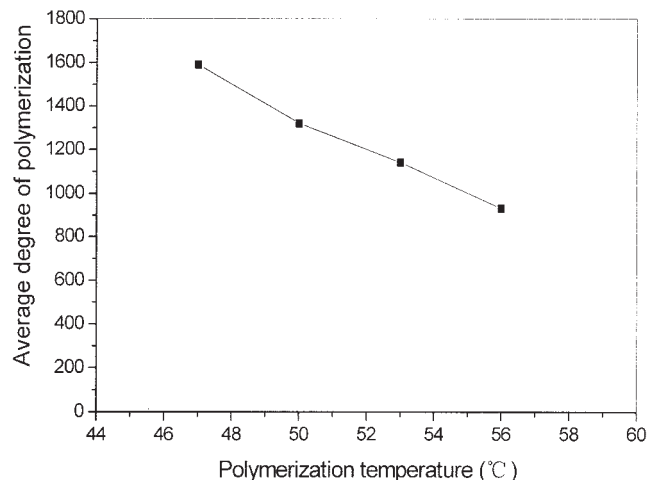


Figure 9 Influence of the polymerization temperature on the average degree of polymerization [P(BA-EHA) concentration = 6.3 wt %].

CONCLUSIONS

The rheological behavior of the composite resin showed a pseudoplastic flow nature. Its rheological behavior was obviously affected by both the P(BA-EHA) content and the grafting polymerization temperature of VC. The influence of the latter was greater than that of the former. The flow property of the modified PVC resin was improved by the incorporation of the ACR polymer and was optimum with the proper P(BA-EHA) content. The flowability of the composite resin markedly increased with an increasing polymerization temperature of the grafted VC as the polymerization temperature was increased, and the average molecular weight of the PVC matrix decreased. The initial degradation temperature of the composite resin increased with increasing P(BA-EHA) content. VST of the samples was enhanced a little with

an increasing content of the crosslinking agent in P(BA-EHA).

As expected, the composite resin had better thermal stability and flowability than pure PVC. The notched impact strength of the composite sample was greatly enhanced, as reported in a previous article,¹³ whereas its VST decreased little. In a word, P(BA-EHA)-grafted VC resin prepared by seeded emulsion polymerization has excellent prospects for wide application in the near future.

References

1. Yang, L. T.; Sun, D. H.; Li, Y. F.; Liu, G. D.; Gao, J. G. *J Appl Polym Sci* 2003, 88, 201.
2. Sombatsompop, N.; Sungsanit, K. *J Appl Polym Sci* 2003, 89, 2738.
3. Sombatsompop, N.; Chaochanchaikul, K.; Phromchirasuk, C.; Thongsang, S. *Polym Int* 2003, 52, 1847.
4. Sombatsompop, N.; Phromchirasuk, C. *J Appl Polym Sci* 2004, 92, 782.
5. Shah, B. L.; Shertukde, V. V. *J Appl Polym Sci* 2003, 90, 3278.
6. Peng, J.; Wei, G. S.; Zhang, Y. D. *J Appl Polym Sci* 2003, 88, 2478.
7. Gao, J. G.; Yang, L. T.; Li, Z. T.; Ren, L. *J Appl Polym Sci* 1996, 59, 1787.
8. Gao, J. G.; Yang, L. T.; Deng, K. L.; Yao, Z. H. *Polymer* 1997, 38, 1139.
9. Gao, J. G.; Li, Z. T.; Shan, Z. Q.; Yao, Z. H. *Polymer* 1995, 36, 1269.
10. Kozłowski, M.; Bucknall, C. B. *Pure Appl Chem* 2001, 73, 913.
11. Hernández, R.; Peña, J. J.; Irusta, L.; Santamaría, A. *Eur Polym J* 2000, 36, 1011.
12. Zhang, X. C.; Wang, L. L.; Qian, B. G. *Angew Makromol Chem* 1993, 209, 1.
13. Pan, M. W.; Zhang, L. C. *J Appl Polym Sci* 2003, 90, 643.
14. Oommen, Z.; Thomas, S.; Prenalatha, C. K.; Kuriakose, B. *Polymer* 1997, 38, 5611.
15. Zhou, Z. M.; Zhu, M.; Wu, X. D.; Qian, D. Z. *Polymer* 1994, 35, 2888.
16. Du, J. X.; Wang, D. Y.; Wilkie, C. A.; Wang, J. Q. *Polym Degrad Stab* 2003, 79, 319.
17. Pan, M. W.; Zhang, L. C.; Wan, L. Z.; Guo, R. Q. *Polymer* 2003, 44, 7121.