Studies on Mechanical and Rheological Properties of Poly(Vinyl Chloride) Modified with Elastomers and Rigid Organic Particles

Jing Peng, Genshuan Wei, Yudong Zhang*

Institute of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

ABSTRACT: Chlorinated polypropylene (CPP) as rigid organic particles and chlorinated polyethylene (CPE) as elastomer were used to modify the properties of poly(vinyl chloride) (PVC) by melt blending. Both mechanical and rheological properties of the PVC blends were investigated. The submicroscopic morphology of the blends was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results demonstrate that when the weight ratio of CPE to CPP is about 6 : 1, a sample with the best impact strength and without obvious decline in tensile strength can be obtained. The impact strength correlates well with SEM morphologies, and TEM micrographs in the necking of the tensile specimen indicate that a cold-drawing deformation of rigid particles happens as reported by T. Kurauchi and T. Ohta (J Mater Sci 1984, 19, 1699). Therefore, a conclusion can be drawn that CPP particles acting similar to elastic particles can toughen PVC, and the cold-drawing deformation is the primary reason for toughening the PVC blends. In addition, the addition of CPP can promote the processibility of PVC ternary blends. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2478–2483, 2003

Key words: elastomers; poly(vinyl chloride) (PVC); rigid organic particles; rheology; toughness

INTRODUCTION

The improvement of mechanical properties of polymer materials, especially impact strength, is a very important task in polymer science. Rubbers have been widely used to toughen polymeric materials, because of their action as stress concentrators and induction of energy dissipation by both crazing and shear yielding of the matrix.[1] However, blending with rubbers often result in the decline of properties of polymeric materials such as the tensile strength, modulus, and resistance to heat and processing.[2–6]

In 1984, Kurauchi and Ohta[7] first reported that rigid organic particles could improve the toughness of polymeric materials, whereas the tensile strength had no decrease. The toughening mechanism is thought to be that the disperse phase is deformed in a cold-drawing and the cold-drawing is caused by the difference between the elastic modulus of the dispersion and the matrix. Thereafter, by using the two-dimensional finite element method (FEM) simulations, Yee et al.[8] gave a theoretical explanation, that is, for the plane stress condition, if the rigid toughener possesses either (1) a 60% difference in the elastic modulus from that of the matrix at any given strain level prior to failure or (2) smaller yield or craze strain than the yield strain of the matrix, then a sufficient stress around the inclusion will arise and cause the matrix to undergo localized shear deformation. This indicates that if the rigid toughener satisfies the two conditions, it can be used to improve the toughness of polymer. Because of these results, our interest was aroused in studying the toughening of polymeric materials by using nonelastic particles in polymer blending.

To date, a great deal of work has been published on the topic. The rigid particles used include inorganic particles, such as glass beads,[9] calcium carbonate $(CaCO_3)$,[10] kaolin,[11] as well as organic particles. However, the addition of inorganic particles often leads to the increase of shear viscosity of polymers,[12,13] and processibility may also suffer. In other research, rigid polymers were also used to toughen polymeric materials,[14,15] and the results showed that suitable rigid polymers could not only improve the impact strength and yield strength, but also improve the processibility of polymers.[15] Thus, further investigation on the toughening mechanism of rigid organic particles in polymeric materials is worthy.

Poly(vinyl chloride) (PVC) as a common thermoplastic that has been widely used in many fields because of its low cost. However, poor impact resistance and weak heat stability are often observed in it. To improve both the yield strength and the toughness of PVC, a much work has been done in our group.[16–19] In

Correspondence to: Y. Zhang (YD-Zhang@brici.ac.cn).

* Current address: Beijing Research Institute of Chemical Industry, SINOPEC, Beijing, 100013, China.

this work, chlorinated polypropylene (CPP) was used as a rigid organic particle because of its compatibility with PVC and chlorinated polyethylene (CPE), in theory, according to the solubility parameter δ (δ_{PVC} = 9.4–10.8, δ_{CPP} = 8.2–9.2, δ_{CPE} = 8.92).[19] The purpose of the present research is to study the mechanical and rheological properties of the blend system of PVC/elastomers/rigid organic particles; the toughening mechanism is also discussed.

EXPERIMENTAL

Materials and specimen preparation

The materials used in this study were commercial grades of PVC with an average polymerization degree of 500 (TH-400, Tianjin Chemical Factory, Tianjin, China) as matrix, CPE with 35 wt % weight content of chloride (135A, Weifang Chemical Factory, China) as elastomer, and CPP (Xinzhou Chemical Factory, China) as rigid toughener.

The PVC/CPE, PVC/CPP, and PVC/CPE/CPP blends were first mixed for several minutes in a high-speed mixer and then were extruded on a SJ-20 × 25 single-screw extruder with L/D ratio of 25 at 170°C. The blends were injection molded on a mini-mixer[20] to give samples for impact testing and tensile tests.

Mechanical properties testing

Notched Charpy impact strength was measured according to GB1049-79 by a CHARPY XOJ-4 testing machine. Tensile tests (GB1040-79) were performed on an Instron-1185 universal testing machine.

Microscopy

The fracture surface of the impact specimen was coated with a gold layer and observed with a Cambridge S250 MK3 scanning electron microscope (SEM).

The ultrathin sections were cut in the necking of the tensile samples and sliced cryogenically along the parallel direction to the tensile orientation of the specimen and stained by RuO_4. Then, the morphology of the specimen was observed on a Hitachi H-800 transmission electron microscope (TEM).

Rheological property

Rheological tests were conducted by using a capillary rheometer (Instron-3211) in a temperature range of 170 to 200°C, and the shear rate varied from 10^1 to 10^3 s^{-1}.

RESULTS AND DISCUSSION

Mechanical properties of PVC blends

The mechanical properties of PVC/CPE blends are shown in Figure 1. With an increase in the CPE content, the notched Charpy impact strength of PVC/CPE blends increased. When the content of CPE is 10–20 wt %, the brittle–ductile transition occurs, whereas the addition of CPE obviously reduces the tensile strength of the blends. When the CPE content was 25 wt %, the notched Charpy impact strength was nine times higher than that of pure PVC, whereas the tensile strength decreased by 56%. This is typical behavior of polymers toughened with elastomeric particles.[15,19]

To obtain the balanced properties of PVC blends, CPP particles, as a rigid polymer with better compatibility with PVC than polypropylene (PP) with PVC,[19] were added into the PVC and PVC/CPE matrix, respectively. As shown in Figure 2, when only CPP particles were used to blend with PVC, the CPP content showed little effect on the notched impact strength of PVC/CPP blends. In contrast, compared with pure PVC, the notched impact strength of PVC/CPE/CPP blends with 25 wt % CPE content increased 11 times under the CPP content of 2–4 wt %. This indicates that the combination of CPP with CPE has a synergistic effect on the toughening of PVC, with impact strength two times higher than that of PVC/CPE blends. Moreover, with the increase of CPE content, the toughening effect is more noticeable; when the CPE/CPP is about 6 : 1 (w/w), the best impact resistance can be obtained under different CPE contents. Besides, Figure 2 shows that the excess CPP leads to the decrease of impact strength, which is similar to the experimental results of Yang et al.[14] and Zhou et al.[15] This may be attributed to the influence of excess CPP particles on the stress fields of the hydraulic pressure of PVC matrix; consequently, the cold-drawing of CPP particles is suppressed.
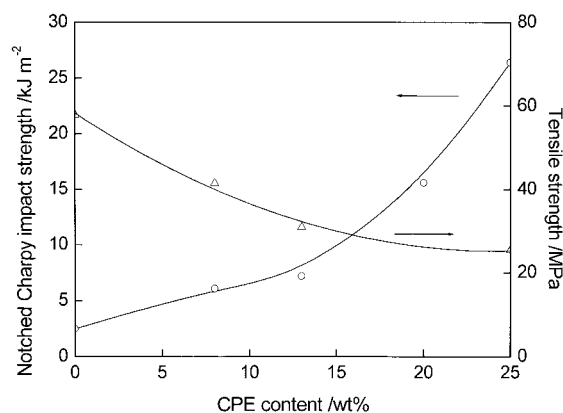

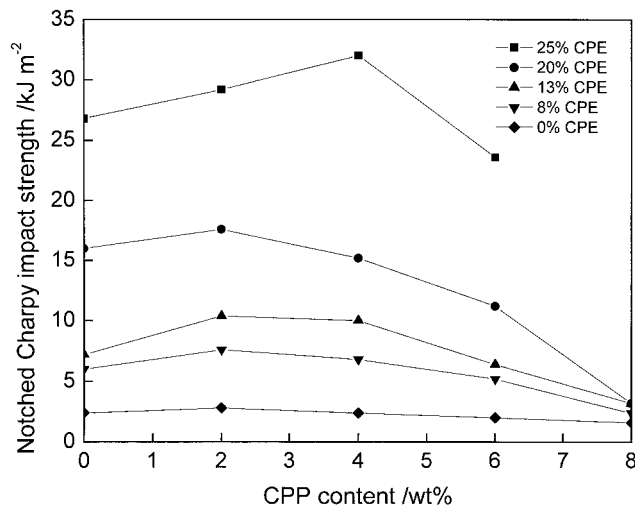**Figure 1** Dependence of mechanical strength of PVC/CPE blends on CPE content.

Figure 2 Effect of CPP content on the notched Charpy impact strength of PVC/CPE/CPP blends.

Figure 4 Influence of CPP content on the brittle–ductile transition of PVC ternary blends.

The tensile strength as a function of CPP content observed at different CPE contents is demonstrated in Figure 3. It is noted that the tensile strength of PVC ternary blends decreases slowly with an increase of CPP content in the brittle–ductile transition regions (PVC/CPE = 100/15) of PVC blends. However, the incorporation of rigid particles with high modulus can increase the modulus and yield strength of polymer blends[7]; the tensile strength of blends remains almost unchanged with the variation of CPP particles over the range of 2–8 wt %. Accordingly, the CPP particles can improve the impact strength of PVC/CPE matrix with a small effect on the tensile strength.

Figure 4 shows the effect of incorporation of CPP on the brittle–ductile transition of PVC/CPE/CPP blends. It can be seen that when the CPP content is below 6 wt %, the formation of brittle–ductile transition of blends at lower CPE content is observed; however, when the CPP content is above 8 wt %, the
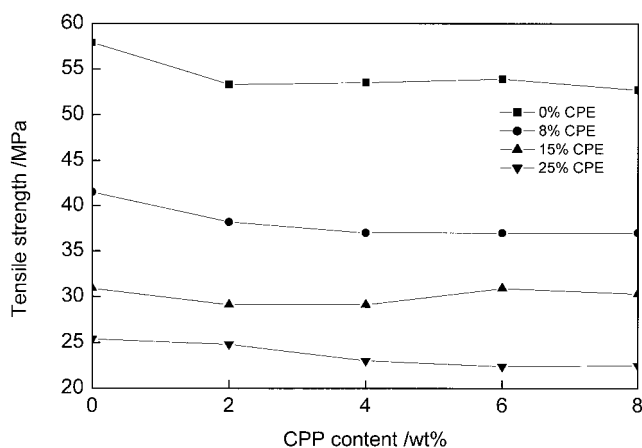
brittle–ductile transition cannot occur even at the 20 wt % CPE and the brittle–ductile transition is delayed. The reason may be that the excess rigid particles cannot undergo cold-drawing or plastic deformation and then result in a low toughness.

Morphology

The morphology of fracture surface of the impact specimen for PVC ternary blends is demonstrated in Figure 5. As can be seen that when the CPP content is about 2 wt %, the fracture surface is rough and has many rooty whiskers, suggesting that the impact specimen breaks yieldingly. However, when the content of CPP is 8 wt %, the fracture surface of the ternary blends shows brittle features and some debonding of the dispersed phase appears. This indicates that the interfacial adhesion between PVC and CPP is weak; as a result, excess CPP leads to the decline of mechanical properties of blends. The morphology is in good agreement with the previous mechanical results of PVC blends.

Figure 6 shows the morphology in the neck part of broken tensile specimen of PVC binary and ternary blends. In Figure 6, the dark phases are CPP particles and gray phases are the dispersed CPE particles. It can be seen that in the PVC/CPP blend, the dispersed CPP appears as almost elliptical particles, and few of them exist as elongated particles, although, for PVC/CPE matrix, the cold-drawing deformation of CPP particles occurs except for the formation of elongated CPE phase, and the largest ratio of length to-diameter of CPP particles is 15 or so. This is in good agreement with Kurauchi's result.[7] According to Kurauchi's explanation, when the hydraulic pressure formed by matrix is operating on the rigid dispersed particles, the particles will be forced to deform and absorb en-
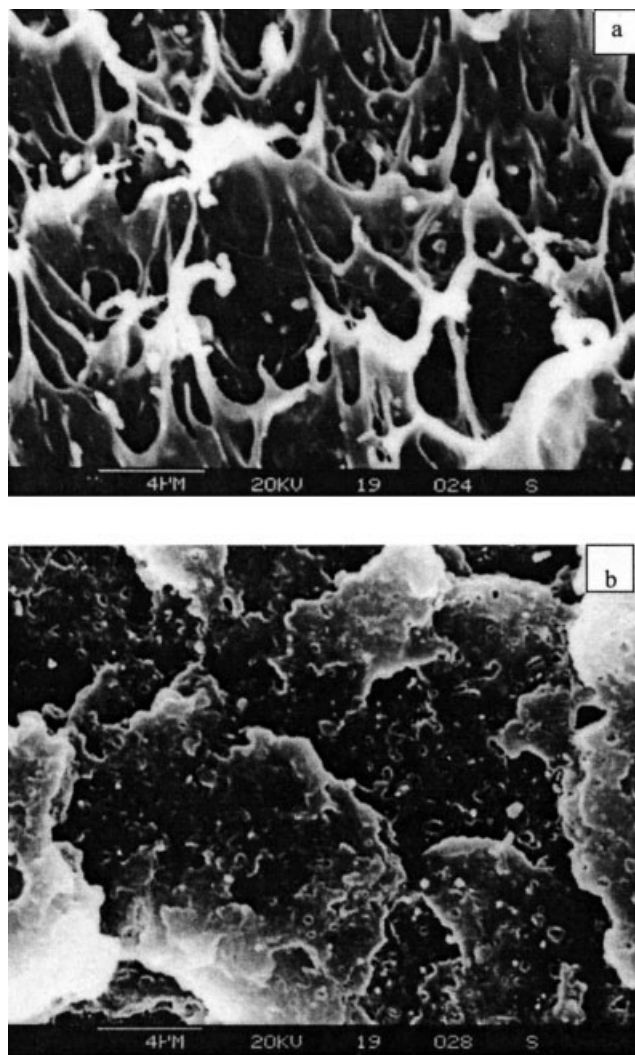

Figure 3 Effect of CPP content on the tensile strength of PVC/CPE/CPP blends.

total energy absorbed in the fracture process of polymer materials is the summation of energy absorbed by crazing, shear yielding band, and deformation of dispersed phase particles. In Kurauchi's article,[7] only the energy absorbed through cold-drawing deformation of rigid dispersed phase was noticed, and the energy absorbed by crazing and the shear yield band of matrix was neglected. When the matrix is brittle, it is difficult for the matrix to deform and produce the hydraulic pressure, which will constrain the rigid disperse phase to deform brittlely before polymer fracture; hence, the impact strength of polymer blends cannot be improved effectively by using rigid particles. However, when the matrix is toughened by both elastomers and rigid particles, hydraulic pressure can be formed effectively in the matrix; as a result, cold-drawing deformation of rigid particles can be produced easily, and the polymeric materials are toughened.

Figure 5 SEM photographs of the fracture surface of the impact specimen (a) PVC(100)/CPE(20)/CPP(2); (b) PVC(100)/CPE(20)/CPP(8).

ergy; therefore, the matrix is toughened. Figure 6 also suggests that the more easily the matrix deforms, the more energy the rigid particles absorb and therefore the effective toughening of PVC could be obtained by adding rigid particles.

According to the above-mentioned results, a conclusion can be drawn that there are always two factors to affect simultaneously the impact strength of polymer blends, that is, the matrix and the dispersed phase. When the dispersed phase is an elastomer with low modulus, low energy is needed in the plastic deformation of disperse phase, and the main energy is absorbed and dissipated through the formation of crazing and shear yielding band of matrix. As the modulus of the dispersed phase increases, more and more energy is needed to deform the dispersed particles. When the dispersed phase is rigid, a lot of energy is needed to deform rigid particles, which will become the main part in the total energy needed. Thus, the
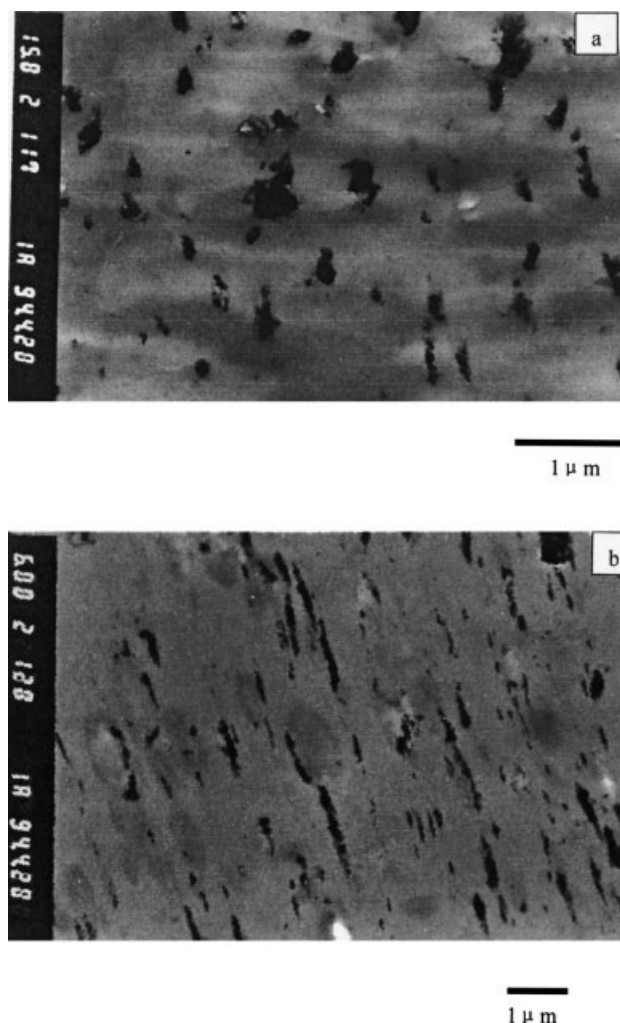

Figure 6 TEM photographs of the deformed tensile specimen. (a) PVC(100)/CPP(5); (b) PVC(100)/CPE(10)/CPP(5).
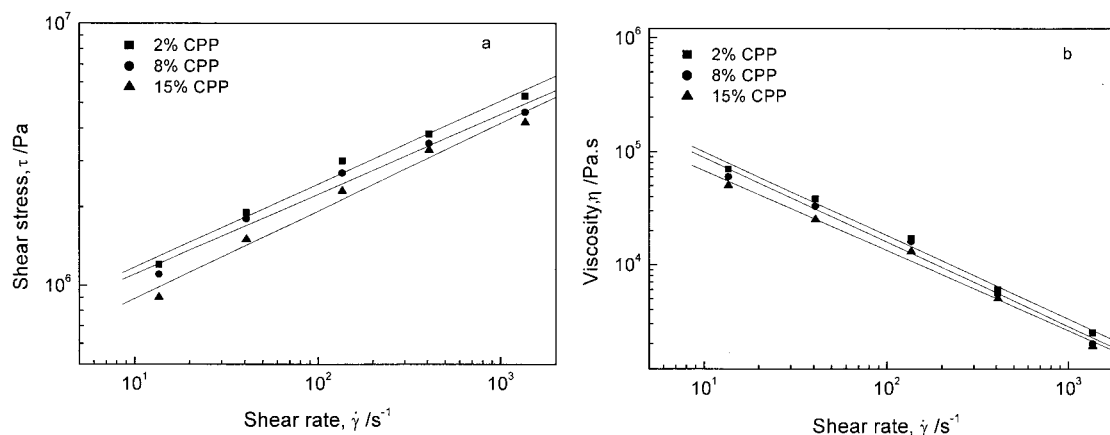
Figure 7 Effect of CPP content on the rheological property of PVC(100)/CPE(8)/CPP blends at 180°C. (a) Shear stress versus shear rate; (b) viscosity versus shear rate.

Rheological behavior

It is well known that the rheological property of polymer melts is very important for the processing and the equipment or mold design, and the capillary extrusion tests are very close to the practical conditions of processing of polymers. Therefore, the rheological behavior of PVC/CPE/CPP blends was studied by using a capillary rheometer. Figure 7 shows the melt flow curves [Fig. 7(a)] of the PVC ternary blends and the relationship between the apparent shear viscosity and the shear rate [Fig. 7(b)]. It can be seen that the shear stress increases and apparent shear viscosity decreases by increasing the shear rate. Moreover, with the increase of CPP content, both shear stress and apparent shear viscosity decreases. Consequently, the CPP particles can improve the processibility of PVC/CPE blends.

The relationship between shear stress and shear rate suggests that the melt shear flow basically obeys a power law relationship, that is,[13]

$$\tau = k\dot{\gamma}^n \tag{1}$$

where k is the constant and n is the flow behavior index, τ is the shear stress, and $\dot{\gamma}$ is shear rate. For the PVC blends studied, n is the non-Newtonian index. The n values under different shear rates and various compositions are listed in Table I. By increasing the shear rate, the non-Newtonian index decreases, and n changes slightly with the increase of CPP and CPE content. This illustrates that the non-Newtonian properties of the blend melts will be significantly enhanced at a higher shear rate.

Figure 8 shows the influence of temperature on apparent shear viscosity (η) of PVC ternary blends. It can be observed that ln η for melts increases linearly with $1/T$. Moreover, we know that the viscosity of polymer melts decreases with a rise of temperature and the relationship between them coincides with the Arrhenius equation, for instance,

$$\eta = Ae^{\Delta E_\eta/RT} \tag{2}$$

TABLE I
Non-Newtonian Index (n) of PVC Blends at 185°C

Blends	Shear rate /s^{-1}					
	4.10	13.6	40.8	136	408	1360
PVC(100)/CPE(0)/CPP(2)	0.45	0.44	0.40	0.37	0.33	0.29
PVC(100)/CPE(0)/CPP(8)	0.37	0.44	0.46	0.37	0.28	0.23
PVC(100)/CPE(0)/CPP(15)	0.47	0.47	0.46	0.38	0.29	0.28
PVC(100)/CPE(8)/CPP(2)	0.40	0.44	0.44	0.33	0.25	0.24
PVC(100)/CPE(8)/CPP(8)	0.43	0.45	0.42	0.34	0.25	0.17
PVC(100)/CPE(8)/CPP(15)	0.46	0.42	0.38	0.38	0.31	0.22
PVC(100)/CPE(13)/CPP(2)	0.39	0.41	0.41	0.32	0.25	0.24
PVC(100)/CPE(13)/CPP(8)	0.44	0.43	0.44	0.33	0.27	0.23
PVC(100)/CPE(13)/CPP(15)	0.46	0.43	0.42	0.35	0.27	0.27
PVC(100)/CPE(20)/CPP(2)	0.50	0.47	0.40	0.30	0.26	0.25
PVC(100)/CPE(20)/CPP(8)	0.47	0.47	0.41	0.30	0.26	0.25
PVC(100)/CPE(20)/CPP(15)	0.43	0.48	0.44	0.31	0.27	0.25
PVC(100)/CPE(25)/CPP(8)	0.42	0.43	0.40	0.30	0.27	0.26
PVC(100)/CPE(25)/CPP(15)	0.45	0.44	0.44	0.36	0.27	0.25

where η is apparent shear viscosity, A is the factor related to shear rate, shear stress, and molecular structure, $\Delta_E\eta$ is the activation energy of viscous flow, and R is the universal gas constant. Both A and $\Delta_E\eta$ can be calculated from the curves in Figure 8 by using a linear regression analysis method. Results are presented in Table II. With the increase of shear rate, A increases and $\Delta_E\eta$ decreases. This means that the sensitivity of the apparent shear viscosity of PVC blends can be weakened by increasing the shear rate. Therefore, increasing the shear rate and temperature can promote the processing behavior of PVC ternary blends.

CONCLUSION

(1) The incorporation of CPP can improve the notched impact strength of the PVC/CPE blend without an obvious decline in the tensile strength. The higher the ductility of the polymer matrix, the more remarkably the notched impact strength increases. The sample with the best toughness is obtained at about a 6 : 1 weight ratio of CPE/CPP. TEM morphology in the necking of deformed tensile specimen indicates that the CPP particles in the PVC/CPE matrix deform in a cold-drawing form.

(2) The polymers are toughened in two ways: one way is the cold-drawing deformation of rigid particles; the other way is crazing and shear-yielding band formed in the matrix. With respect to the PVC/CPE/
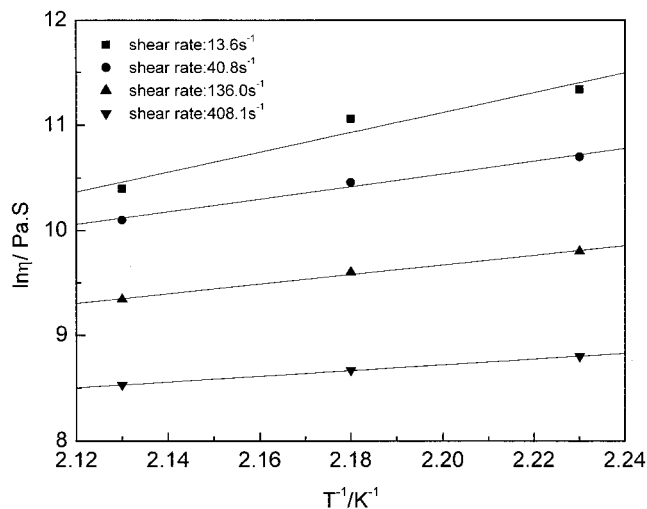
TABLE II
Relationship Between Shear Rate and ΔE_η, A

Shear rate /s^{-1}	A	ΔE_η/J mol^{-1}	Relative coefficient
13.6	7.05×10^{-5}	78.2	0.9738
40.8	6.99×10^{-2}	49.9	0.9934
136.0	6.39×10^{-1}	38.2	0.9972
408.1	1.61×10^{1}	22.4	0.9998

CPP blend system, the cold-drawing deformation is the main factor used to toughen the PVC blends.

(3) The incorporation of CPP can decrease the apparent shear viscosity and results in the promotion of the processibility of PVC blends. In addition, increasing the temperature and shear rate can reduce the apparent shear viscosity, consequently, to improve the processing of PVC blends.

References

1. Paul, D. R.; Bucknall, C. B. Polymer Blends; Wiley: New York, 2000.
2. Breen, J. (a) J Mater Sci 1993, 28, 3769; (b) J Mater Sci 1994, 29, 39; (c) J Mater Sci 1995, 30, 5833.
3. Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W. J Appl Polym Sci 1995, 58, 1087.
4. Klaric, I.; Vrandecic, N. S.; Roje, U. J Appl Polym Sci 2000, 78, 166.
5. Marossy, K. Polym Bull 1991, 25 (3), 385.
6. Hale, W.; Lee, J. H.; Keskkula, H.; Paul, D. R. Polymer 1999, 40, 3621.
7. Kurauchi, T.; Ohta, T. J Mater Sci 1984, 19, 1699.
8. Sue, H. J.; Pearson, R. A.; Yee, A. F. Polym Eng Sci 1991, 31, 793.
9. Yuan, Q.; Jiang, W.; Zhang, H. X.; Yin, J. H.; An, L. J.; Li, R. K. Y. J Polym Sci, Part B: Polym Phys 2001, 39, 1855.
10. Wilbrink, M. W. L.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 2001, 42, 10155.
11. Fellahi, S.; Chikhi, N.; Bakar, M. J Appl Polym Sci 2001, 82, 861.
12. White, J. L.; Crowder, J. W. J Appl Polym Sci 1974, 18, 1013.
13. Liang, J. Z.; Li, R. K. Y. J Appl Polym Sci 1999, 73, 1451.
14. Yang, W. J.; Wu, Q. Y.; Zhou, L. L.; Wang, S. Y. J Appl Polym Sci 1997, 66, 1455.
15. Zhou, Q.; Yang, W. J.; Wu, Q. Y.; Zhang, B.; Huang, J. M.; Shen, J. C. Eur Polym J 2000, 36, 1735.
16. Zhang, Y. D.; Jin, R. G. in Proceeding of 3rd National Symposium on Deformation, Damage and Fracture of Polymer; Chengdu, China, 1994; p 53.
17. Zhang, Y. D.; Jin, R. G. The National Symposium on Polymers Preprint, Guangzhou, China, 1995; p 716.
18. Zhang, Y. D.; Shi, N.; Xu, D. F. 36th IUPAC International Symposium on Macromolecules, Seoul, Korea, 1996; p 912.
19. Zhang, Y. D.; Jin, R. G. (a) Polym Mater Sci Eng 1998, 14, 64; (b) Polym Mater Sci Eng 1997, 13, 93; (c) Polym Mater Sci Eng 1998, 14, 92 (China).
20. Zhang, Y. D. ZL 97215879.0.

Figure 8 Influence of temperature on melt viscosity of PVC(100)/CPE(8)/CPP(2) blends under different shear rates.