

Comparison of the Toughening Mechanisms of Poly(vinyl chloride)/Chlorinated Polyethylene and Poly(vinyl chloride)/Acrylonitrile–Butadiene–Styrene Copolymer Blends

Liling Zhou, Xin Wang, Yusheng Lin, Jingyi Yang, Qiye Wu

Qingdao University of Science and Technology, Qingdao, 266042, People's Republic of China

Received 31 July 2002; accepted 8 January 2003

Published online 25 August 2003 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/app.12651

ABSTRACT: In this study, the influence of chlorinated polyethylene (CPE) and acrylonitrile–butadiene–styrene copolymer (ABS) on the mechanical properties of poly(vinyl chloride) (PVC)/CPE and PVC/ABS hybrids were examined. The experimental results show that the toughness of the hybrids could be modified greatly by the introduction of CPE or ABS. The microstructure and impact surfaces of the blends were investigated by scanning electron microscopy and transmission electron microscopy. ABS dispersed in the form of particles or agglomerates in the PVC matrix, and

CPE tended to disperse as a net structure. In the tensile test, ABS initiated crazes as stress concentrators to toughen the PVC matrix, whereas CPE, with the PVC matrix together, caused a yield deformation by shear stress to form a shear band. The formation of crazes and shear bands benefited the toughening of PVC, but to the different extent. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 916–924, 2003

Key words: poly(vinyl chloride) (PVC); morphology; toughness; yielding

INTRODUCTION

The toughening of brittle polymer material with elastomers has long been a focus of extensive studies.^{1–9} Until now, crazes and shear bands have been widely accepted the mechanisms of elastomer toughening. Both crazes and shear bands are induced by a small local deformation inside the material in the tensile test, and there exists a competition between the deformations in the form of crazes and shear bands. Polymer materials have shown various tendencies in competition. However, the cause of these different tendencies was still a question with no standard answer, as well as the factors influencing the tendencies. A damage competition group criterion of brittle–ductile transition has been proposed on the basis of linear elastic fracture mechanics.¹⁰ This criterion was correlated with some intrinsic and extrinsic parameters of the polymer material, such as mechanical properties and temperature, respectively. However, the competition of various ductile deformation modes was still out of theoretical consideration.

The toughening of rigid poly(vinyl chloride) (PVC) has been extensively investigated.^{11–14} To reveal the toughening mechanism, two kinds simple hybrids

based on PVC were prepared in this study. Chlorinated polyethylene (CPE) and acrylonitrile–butadiene–styrene copolymer (ABS), common modifiers of PVC, were introduced into the PVC matrix by melt mixing, and the PVC matrix was toughened. Shear bands and crazes were the toughening mechanisms of PVC/CPE and PVC/ABS hybrids, respectively. A detailed morphological investigation was carried out to reveal the dispersions and microstructures of the toughening additives. The influence of comprehensive factors on the competition between the propagation of crazes and shear bands, such as compatibility and microscopic stress conditions, are discussed.

EXPERIMENTAL

Materials

PVC, with an average polymerization degree of 1000, was supplied by Qilu Petrochemical Corp. (Zibo, China). CPE, with 35 wt % chloride, was supplied by Weifang Chemical Factory (Weifang, China). ABS (type 103), was supplied by Gaoqiao Petrochemical Corp. (Shanghai, China). Other additives were industrial products.

Preparation and characterization

The components of the hybrids were kneaded for 10 min in a high-speed kneader and plasticized at 170°C. The samples for tensile and Charpy impact tests were molded at 170°C with a flat-plate tablet machine and

Correspondence to: Q. Wu (wangxih@qingdaonews.com).

Contract grant sponsor: National Natural Science Foundation.

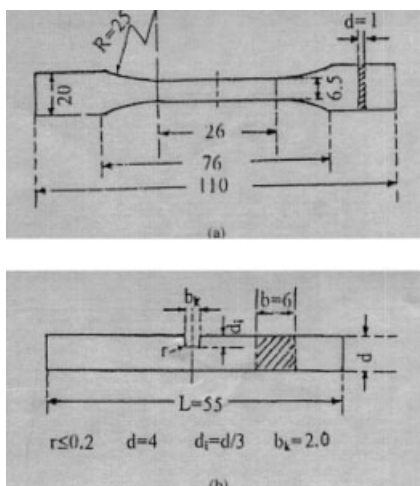


Figure 1 Geometric figures and sizes (mm) of the samples, (a) for tensile test; (b) for Charpy impact test (R = radius of the joint; d = thickness; L = length of the sample; b = thickness of the sample; d_1 = width of the notch; r = radius of the edge).

shaped with a universal clipper. The geometric figures and sizes (mm) of the samples are shown in Figure 1.

Tensile properties were determined in an electronic tensile tester (T-10 type, Monsanto Co., St. Louis, MO). Notched impact strength was determined in a Charpy-type tester (Chengdu Machinery Factory, Chengdu, China) Morphological structures were observed with an electron microscope (JEM-2000EX type, Japan Electron Co. Tokyo, Japan).

Before the morphological observation, the samples were stained to increase the contrast between the PVC and the additives. PVC/ABS samples were stained with osmium tetroxide (O_5O_4) directly because its polybutadiene (PB) component contained unsaturated bonds. PVC/CPE samples were treated with a method described in the literature.¹⁵ The samples were first immersed in chlorosulfonic acid at -5°C for 2 days, where CPE was sulfonated, and the following elimination reaction of part of the sulfonic groups led to the formation of unsaturated bonds in CPE. Then, the PVC/CPE samples were stained with O_5O_4 . The details of the microtoming are shown in Figure 2.

RESULTS AND DISCUSSION

Influence of ABS and CPE on impact properties

As shown in Figures 3 and 4, the impact strengths of the PVC/CPE and PVC/ABS hybrids were considerably improved by the introduction of CPE and ABS. The curves showing the dependence of impact strength on the content of CPE or ABS were s-shaped. According the position of inflexions, the curves could be divided into three regions corresponding to the toughness and the mode of impact fracture of the hybrids. The first was the low additive content region,

where the impact strength followed a gradual rise with the content of CPE or ABS. The hybrids exhibited a low ductility in this region, so it was named the *brittle region*. The second was the *brittle-ductile transition region* edged by the additive content from 10 to 20 phr, where impact strength was greatly influenced by the content of the additive. When the content exceeded 20 phr, the hybrids exhibited superhigh toughness, and the influence of additive to the impact strength became less. This was the *ductile region*.

PVC/CPE hybrids showed a higher ductility than PVC/ABS hybrids in impact fracture. For example, when the additive contents were both 20 phr, the impact strengths of PVC/CPE and PVC/ABS hybrids were 78 and 22 KJ/m^2 , respectively.

Morphology of impact fracture surface

Influence of CPE on fracture morphology

The morphology of the PVC/CPE hybrids is shown in Figure 5. Easy to recognize, pure PVC had a topically smooth fracture surface, implying brittle fracture under impact load. For PVC/CPE hybrid with an 11-phr CPE dosage, the fracture surface was rather coarse. The asperity indicated ductile fracture behavior under impact load. The hybrid with a 15-phr CPE dosage showed the most coarse ductile fracture surface. PVC fibers were extensively dispersed in the fracture surface, and the fibers were linked with each other to form an approximate network. When more CPE (>15 phr) was introduced into PVC matrix, the amount of fibers and the length of single fibers both increased, and the fiber network became whole and perfect.

The formation of PVC fibers induced by the introduction of CPE was no doubt an energy-dissipated process. Accompanied by the ductile morphology, PVC/CPE hybrids exhibited high ductility in impact.

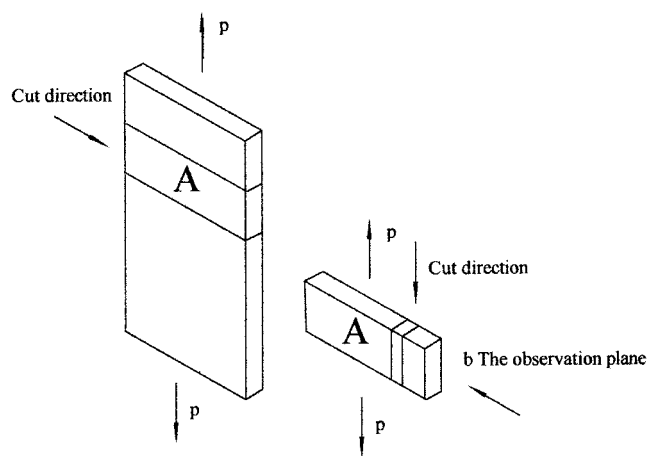


Figure 2 Sample preparation for TEM observation (p = tensile direction; A = the segment for microtoming; b = the observation plane in TEM).

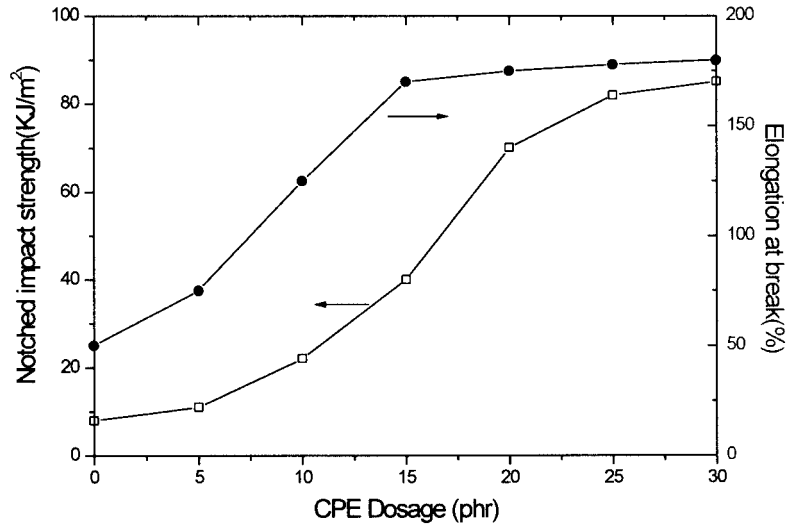


Figure 3 Influence of CPE on the toughness of PVC/CPE blends.

Influence of ABS on fracture morphology

The fracture surfaces of the PVC/ABS hybrids are shown in Figure 6. The surfaces were mainly composed of separate tiny platelets and were cloud-shaped in appearance. When more ABS was introduced into PVC, the asperity of the surface increased, and the platelets began to overlap each other. The morphology mentioned previously was also one of the characteristics of ductile fracture. Increasing ABS content resulted in an increase in the asperity and cloud-shaped platelet surface, so more energy dissipated in the fracture.

These results show that the fracture morphologies of PVC/CPE and PVC/ABS were quite different. PVC/CPE was characterized by dense polymer fibers on the fracture surface, whereas PVC/ABS had a rel-

atively smooth fracture surface composed of cloud-shaped platelets. Moreover, the introduction of CPE and ABS benefited the formation of a ductile morphology during impact process.

Corresponding to the different morphologies, the hybrids also exhibited differential impact ductilities, as illustrated in the Influence of ABS and CPE on Impact Properties section.

Dispersion of CPE and ABS in the PVC matrix

The transmission electron microscopy (TEM) images of PVC/CPE hybrids after tensile testing are shown in Figure 7. The gray areas in the images are CPE, and the white areas are PVC. It was obvious that CPE and PVC had an obscure edge, which indicated a good

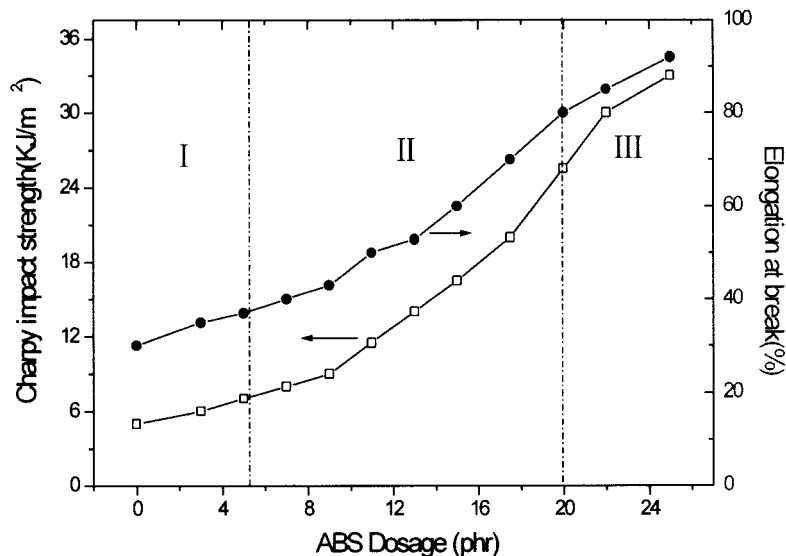


Figure 4 Influence of ABS on the toughness of PVC/ABS blends.

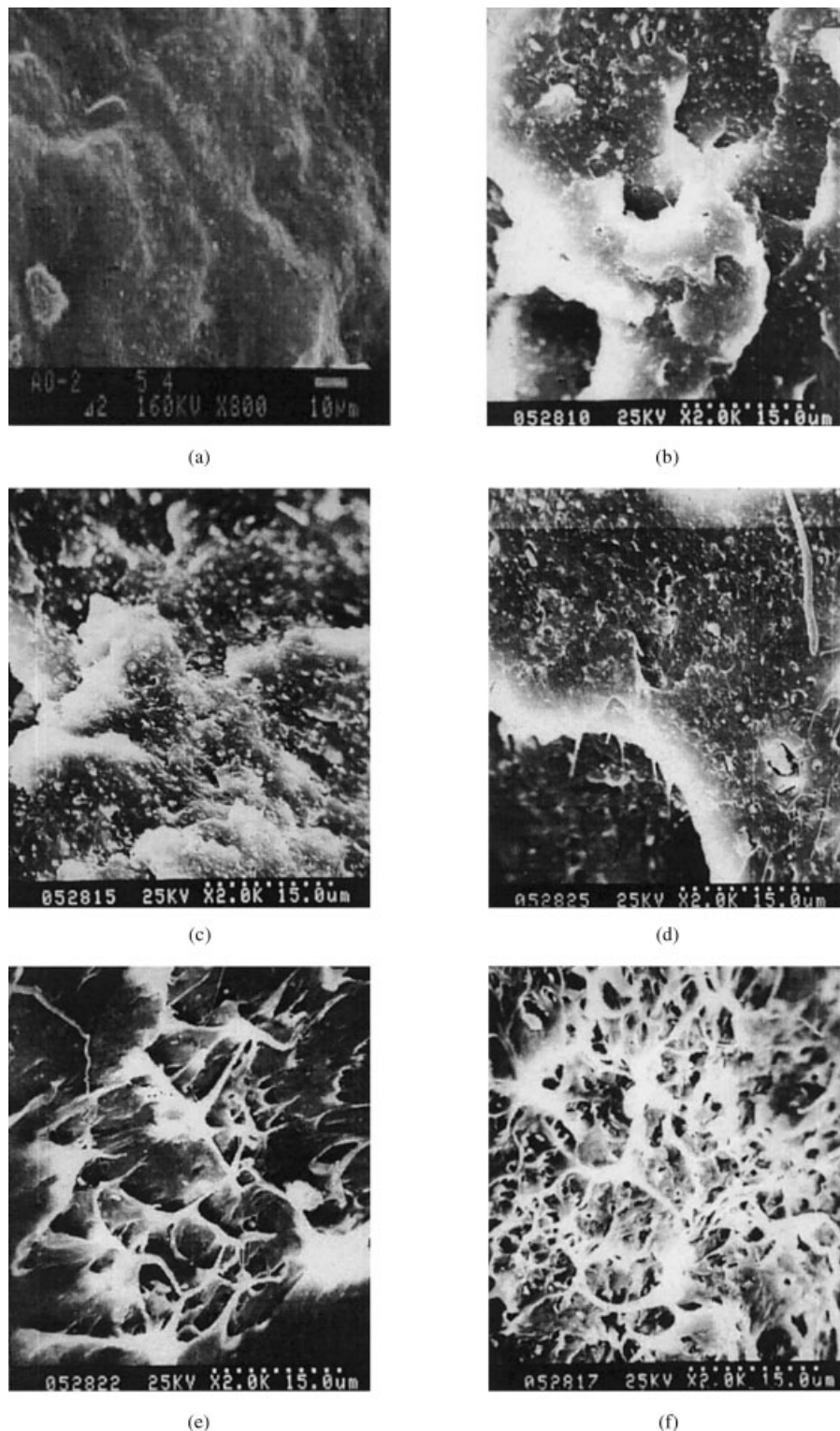


Figure 5 Scanning electron micrographs of the impact fracture surfaces of PVC/CPE blends: CPE = (a) 0, (b) 5, (c) 11, (d) 13, (e) 15, (f) 18, (g) 22, and (h) 25 phr.

compatibility between PVC and CPE. CPE was uniformly dispersed in the PVC matrix and formed an approximate network. From a comparison Figure 7(a) and Figure 7(b), we proved that when more CPE was introduced into the PVC matrix, the CPE network appeared denser.

Figure 8 shows the TEM images of PVC/ABS hybrids after tensile testing. PB, the rubber-like component of ABS, could be stained by O_5O_4 , whereas the rest of the components, polyacrylonitrile and polystyrene, could not. So the dark areas in Figure 8 are PB, and the white areas surrounded by dark areas are

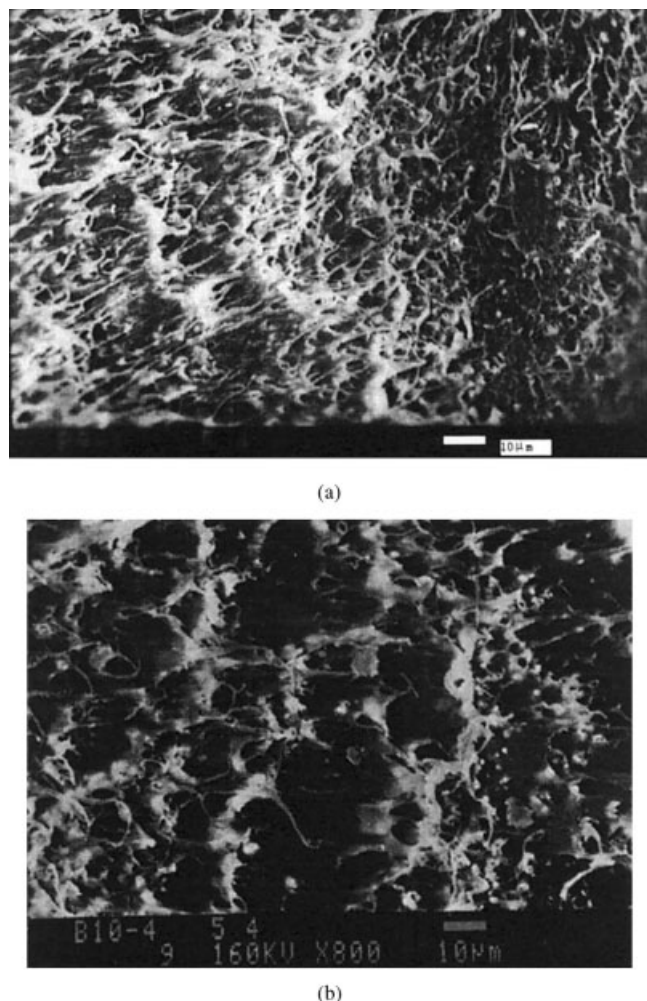


Figure 5. (Continued from the previous page.)

polyacrylonitrile and polystyrene. The continuous white area outside of the dark area is PVC.

As shown in Figure 8, ABS dispersed in the form of particles in the PVC matrix, and the size of particles was influenced by the ABS dosage. Figure 8(a) show that the ABS particles were 0.2–0.7 μm in length when the ABS dosage was 3 phr. When more ABS was introduced into the PVC matrix, some of the ABS particles gathered to form particle agglomerates. Figure 8(b) shows the dispersion of ABS in the PVC matrix when the ABS dosage was 25 phr. The ABS dispersed in the form of particles and agglomerates together, and the nominal diameter of agglomerates was more than 1 μm . Because the samples had undergone an elongation of 120% in the tensile testing before morphological observation, the ABS particles and the particle agglomerates were shaped as elliptical spheres. The microscopic deformation in the elongation direction was distinct, as noted.

The polyacrylonitrile and polystyrene components of ABS and the PVC were polar polymers. However, the polarity of the PB of ABS was quite different from that of PVC. So, ABS had a moderate compatibility

with PVC. In the morphology, ABS dispersed in the form of separate particles. Moreover, the edge between ABS and PVC was somewhere explicit and was obscure elsewhere. In comparison with ABS, CPE had a much better compatibility with PVC and dispersed in the network.

As is a well known principle, good compatibility improved the cohesive adhesion of the different phases of the hybrids and reduced the interfacial defects. Consequently, the ductility of the hybrids was improved. The different ductilities of PVC/CPE and PVC/ABS hybrids could have been partially caused by their diverse compatibility.

Ductile deformations of hybrids

The introduction of an elastomer into plastic is a commonly used toughening method. According to the classical theory on elastomer toughening,^{16–21} the improvement in the ductility of hybrids prepared this way is mainly caused by the brittle–ductile transition of the plastic matrix induced by the elastomer. In hybrids, the elastomer acts as a stress concentrator in the matrix, and two kinds of plastic deformation are induced. One is craze, and the other is shear bands. These two kinds of deformation were found in PVC/CPE and PVC/ABS hybrids, respectively, in our research.

Shear bands in the PVC/CPE hybrids

For a material under tensile stress, the direction of the maximum stress inside the material is at an angle of 45° with the normal tensile stress. When the maximum stress exceeds the inherent strength of the material, yielding deformation takes place to form shear bands. As shown in Figure 9, a large number of shear bands were observed in the tensile fracture surface of the PVC/CPE hybrid. All of the shear bands were at angles with the tensile stress ranging from 30 to 45°.

Crazes in PVC/ABS hybrids

As opposed to the PVC/CPE hybrids, PVC/ABS hybrids performed another ductile deformation, that is, craze, during the deformation process. As shown in Figure 8(b), beside the particle agglomerates, there were lots of small, awl-shaped flaws, and the developing direction of the flaws was perpendicular to the tensile direction, namely, in the elongation direction of ABS particles. The local image of the flaws (Fig. 10) showed that the width of the flaws ranged from dozens to hundreds of nanometers. All of the flaws were easily distinguished from the white PVC matrix. Moreover, the microstructure of the flaws is also shown clearly in Figure 10, with the smaller parallel lines inside of the flaws. The flaws were crazes formed in tensile testing, and the dark parallel lines are the solid parts of the crazes. Our results were similar to those reported in the literature.^{22,23}

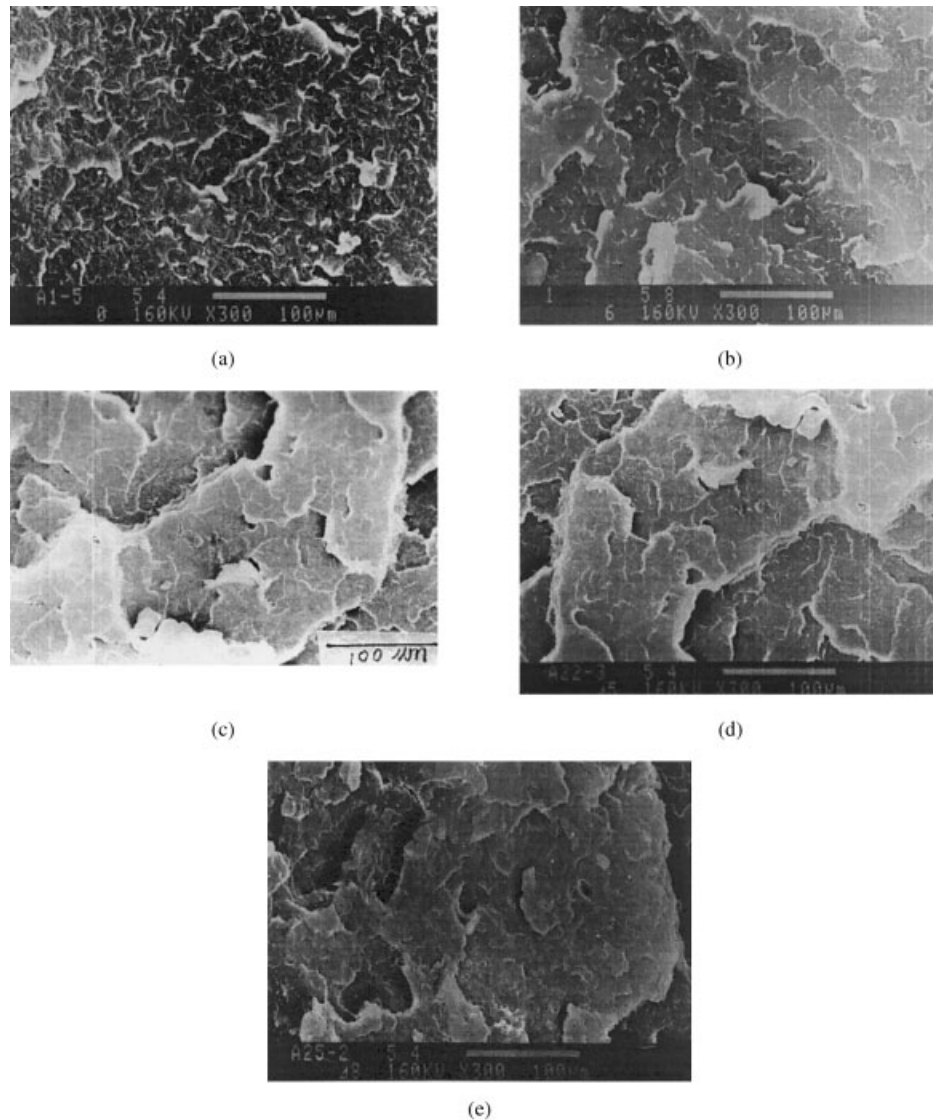


Figure 6 Scanning electron micrographs of the impact fracture surfaces of PVC/ABS blends: ABS = (a) 3, (b) 5, (c) 8, (d) 22, and (e) 25 phr.

As is well known, craze is the yielding deformation induced by local stress concentration. The propagation of crazes in the PVC/ABS hybrids was certainly influenced by microscopic heterogeneity. So besides initiation, ABS particles had an important effect on the propagation and the termination of the crazes. Figure 11(a) shows the initiation of crazes from the edge of one ABS particle and its termination at the edge of another ABS particle. Figure 11(b) shows the diffraction in the propagation of crazes. As shown, a craze passed around one ABS particle and developed ahead. This diffraction process has rarely been reported in literature. There is no question that large energy will be dissipated in the diffraction. Figure 11(c) shows the uniform and integral network inside of the crazes formed in its propagation. Figure 11(d) shows a combination structure of a whole craze and a fractured craze. The remainder of the fractured craze was like a branch stick to the mainland of the craze, inside of

which the solid lines were still almost parallel to each other.

In summary, ABS acted as a stress concentrator in the PVC/ABS hybrids and induced a large number of crazes during the deformation process. Moreover, ABS played an important role in the termination of the crazes; the further development of crazes was prevented. The formation of cracks was stopped to prevent the macroscopic fracture of the material.

Toughening mechanism analysis

As is well known, stress can be divided into two kinds, normal stress (σ_n) and shear stress (σ_s).^{24,25} When a material is subjected to a uniaxial tensile load, the maximum σ_n lies on the plane perpendicular to the tensile direction, and the stress itself lies parallel to the tensile direction. In the meantime, the maximum σ_s is at an angle of 45° with tensile direction. If a material

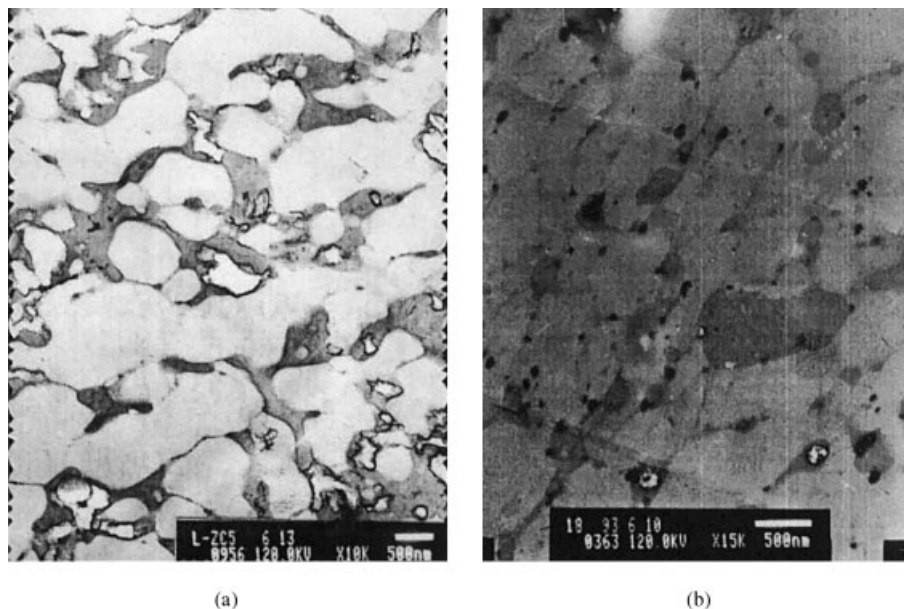


Figure 7 Transmission electron micrographs of PVC/CPE samples to show the dispersion of CPE in the form of networks: CPE = (a) 10 and (b) 15 phr.

has a high inherent shear strength to resist σ_s and a relatively low inherent normal strength, the material prefers to yield in the direction of σ_n . This yielding can be characterized by the crazes formed inside of the material and the corresponding energy dissipation, as shown in Figure 12. However, if a material has a high inherent normal strength rather than an inherent shear strength, the material tends to yield in the direction of σ_s , namely, the direction at an angle of 45° with tensile direction. This kind of yielding is illustrated in Figure 13, and it is characterized by shear bands and a huge energy dissipation.

In the heterogeneous polymer system, the stress conditions were rather complex. However, the yielding induced by stress concentration was still mainly of the two kinds illustrated previously. In the PVC/ABS hybrids, ABS dispersed in the PVC matrix in the form of particles or their agglomerates, and the stress was locally concentrated under a uniaxial tensile load. Then, the PVC matrix around the ABS particles yielded under σ_n . Figure 8(b) illustrates the crazes formed in this kind of yielding.

For comparison, CPE dispersed in the form of a network in PVC matrix, and the areas of stress con-

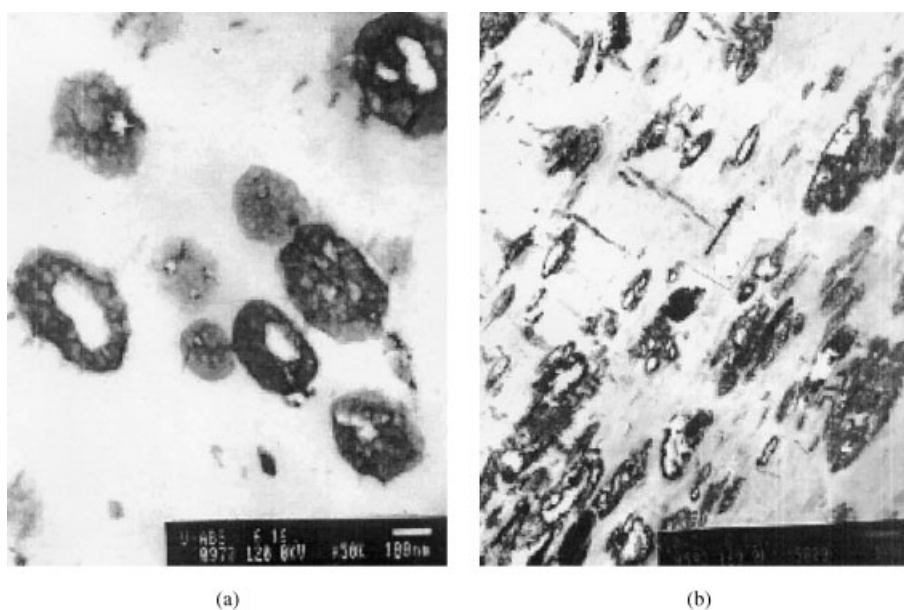


Figure 8 Transmission electron micrographs of PVC/ABS samples (the arrow indicates the flow direction): (a) ABS particles (ABS = 3 phr) and (b) agglomerates crazes (ABS = 25 phr).

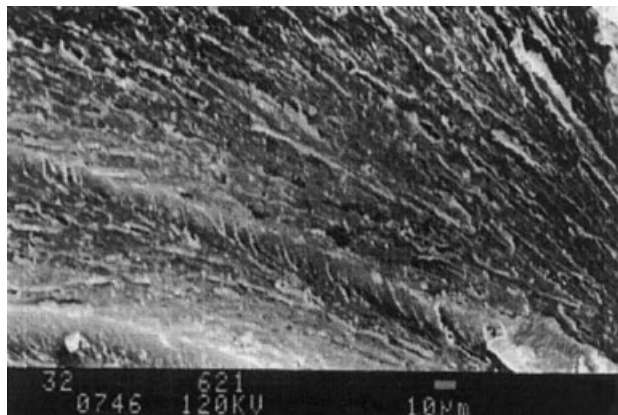


Figure 9 Scanning electron micrograph of the tensile fracture surface of a PVC/CPE blend.

centration induced by different parts of CPE network could overlap each other. This stress percolation was accepted as one of the criterion of a brittle–ductile transition. The overlap or the percolation of local plastic deformations was accepted as the way of a bulk-flow shear band. Figure 9 illustrates the shear band at an angle of 30–45° with elongation direction.

As mentioned in the section on the Influence of ABS and CPE on Impact Properties, PVC/CPE hybrids showed a higher energy dissipation than the PVC/ABS blends from the view of impact strength. The topical stress–strain curves of PVC/CPE and PVC/ABS hybrids are shown in Figure 14.²³ As shown in Figure 3 and 4, the elongations at break of PVC/CPE and PVC/ABS with a 20-phr additive dosage were 178 and 81%, respectively. The elongation at break of PVC/CPE was much larger than that of PVC/ABS, indicating that shear bands were relatively large plas-



Figure 10 Local image of crazes in a PVC/ABS blend.

tic deformations and more energy could be dissipated in the deformation in the form of shear bands than of crazes.

In the further study, the area under the stress–strain curves was divided into four parts according to the mode of energy dissipation in tensile testing. The first part (a_M and b_M) stood for the energy dissipated in the elongation deformation of the PVC matrix in tensile testing, characterized by high stress and low strain. The second part (a_K and b_K) was the energy dissipated by the deformation of the modification additive (CPE and ABS themselves). The features of this area were low stress and high strain. The third part (a_B and b_B) was the energy dissipated in just the moment of ma-

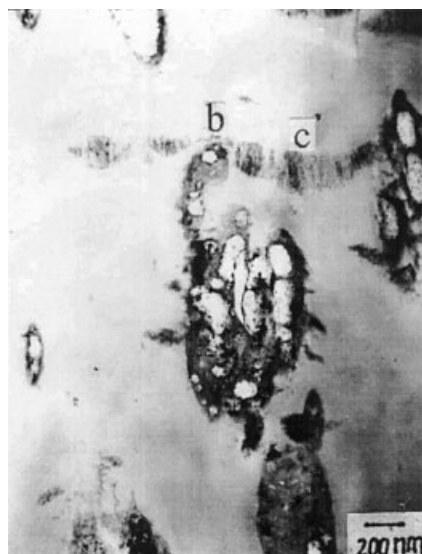


Figure 11 Photographs of the initiation, propagation, and termination of crazes in PVC/ABS blends: (a) initiation of crazes from the edge of one ABS particle and its termination at the edge of another ABS particle, (b) diffraction in the propagation of the crazes, (c) the uniform and integral network inside of the crazes formed in propagation, and (d) a combination structure of a whole craze and a fractured craze.

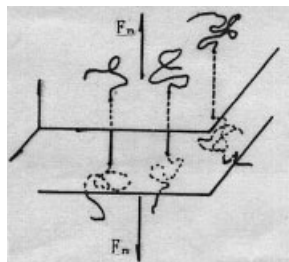


Figure 12 Schematic illustration of yielding under σ_n (F_n) to show the formation of crazes (the dotted line indicates crazes or the fracture of molecular chains).

terial breakage. These three parts were almost the same in the PVC/CPE and PVC/ABS hybrids.

The last part (a_C and b_S) was the energy dissipated by the matrix in the way of ductile deformation. In detail, a_C was the energy dissipated by the crazes induced by ABS, and b_S was the energy dissipated by the shear bands induced by CPE. The elongation at break, mentioned previously, indicated that b_S was much larger than a_C and proved that shear bands were better at energy dissipation than crazes.

CONCLUSIONS

1. PVC was successfully be toughened by the introduction of CPE and ABS. The impact strength of PVC/CPE and PVC/ABS hybrids increased with the content of the second phase, showing s-shaped curves. CPE exhibited a better toughening effect than ABS.
2. PVC/CPE and PVC/ABS hybrids showed different impact fracture behaviors, which were characterized by polymer fibers and platelets, respectively.
3. CPE dispersed in the PVC matrix in the form of a network for good compatibility with PVC, and ABS had a medium compatibility with PVC and dispersed in the form of particles and particle agglomerates.
4. In the fracture of the hybrids, CPE induced shear bands, and ABS induced crazes. The different

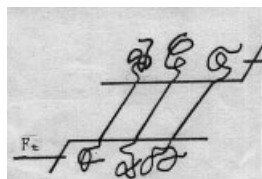


Figure 13 Schematic illustration of yielding under σ_s (F_s) to show the formation of shear bands.

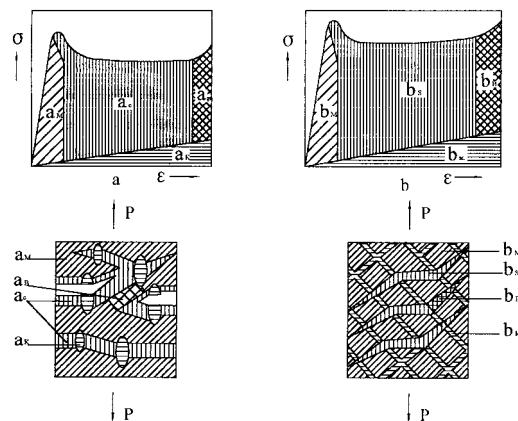


Figure 14 Schematic illustration of energy dissipation in the tensile course:²³ (a) PVC/ABS and (b) PVC/CPE (P indicates the tensile direction).

ductile deformations were caused by the individual stress conditions induced by CPE and ABS. In the combination of morphology and tensile behavior, shear bands exhibited a better ability to dissipate energy than crazes.

References

1. Kurauchi, T.; Ohta, T. *J Mater Sci* 1984, 19, 1699.
2. Koo, K. K.; Inoue, T.; Miyasaka, K. *Polym Eng Sci* 1985, 25, 741.
3. Fujita, Y.; Koo, K. K.; Angola, J. C. *Kobun-shi Tobunshil (Jpn)* 1986, 43, 119.
4. Angola, J. C.; Fujita, Y.; Sakai, T.; Inoue, T. *Polym Sci Pikym Phys* 1988, 26, 807.
5. Matsushige, K.; Radcliffe, S. V.; Baer, E. *J Appl Polym Sci* 1976, 20, 1853.
6. Takahashi, K. *Jpn Soc Compos Mater* 1982, 8, 46.
7. Eshelby, J. D. *Proc R Soc London Ser A* 1957, 241, 376.
8. Nalyzawa, Y. *Polymer Mechanics*; Aomu: Toyota, Japan, 1982.
9. Wang, K.; Wu, J. S.; Zeng, H. M. *China Mater Sci Eng* 2001, 19(3), 15.
10. Li, S. P.; Zhu, X. G.; Qi, Z. N. *J Polym Res* 1995, 2, 217.
11. Wu, Q. Y.; Yang, W. J.; Qiu, Y. M. *Chem J Chin Univ* 1993, 14, 440.
12. Zhou, L. L.; Wu, Q. Y.; Yang, W. J. *Acta Polym Sinica* 1996, 1, 87.
13. Yang, W. Y.; Wu, Q. Y.; Du, H. *Acta Polym Sinica* 1994, 2, 234.
14. Yang, W. J.; Wu, Q. Y. *J Appl Polym Sci* 1997, 66, 1455.
15. Liu, X. M.; Zhao, H. *China Polym Commun* 1985, 1, 66.
16. Siegmans, A. H. *Polym Eng Sci* 1984, 24, 11.
17. Mertz, E. H.; Claver, G. C.; Baer, M. J. *J Polym Sci* 1956, 22, 325.
18. Nenman, S.; Strella, S. *J Appl Polym Sci* 1965, 9, 2297.
19. Schmitt, J.; Keskula, H. *J Appl Polym Sci* 1960, 3, 132.
20. Buchnall, C. B. *J Mater Sci* 1972, 7, 203.
21. Kambour, R. P. *Polymer* 1964, 5, 143.
22. Kambour, R. P. *J Polym Sci Part A: Gen Pap* 1964, 2, 4159.
23. Michler, G. H. *Kunststoff-Mikromechanik*; Hanser: Munich, 1992; p 250.
24. Liu, F. Q.; Tang X. Y. *Polymer Physics*; Higher Education Press: Beijing, China, 1995.
25. Li, B. C. *Structure and Physical Properties of High Polymer*; Science Press: Beijing, China 1989.