

Blend Toughening of Poly(vinyl chloride) by Chlorinated Polyethylene/Hydroxy Ethyl Acrylate Graft Copolymer

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ABSTRACT: Blends of poly(vinyl chloride) (PVC) and chlorinated polyethylene-chlorinating graft-hydroxy ethyl acrylate copolymer (CPE-*cg*-HEA) were prepared. CPE-*cg*-HEA, as toughening modifier, is a graft copolymer with a backbone of chlorinated polyethylene (CPE) and branched chains of poly(2-hydroxy ethyl acrylate) (PHEA). Compared with PVC/CPE, CPE-*cg*-HEA demonstrated better toughening effects on the blends in the tensile strength, elongation at break, and impact strength. Particularly, compared to PVC/CPE blends PVC/CPE-*cg*-HEA blends with 5 phr CPE-*cg*-HEA showed an increase in the tensile and notched impact strength by 17.9 and 30% respectively, compared to the PVC/CPE blends. Differential

scanning calorimetry analysis indicated that the miscibility of PVC/CPE-*cg*-HEA was better than that of PVC/CPE. An analysis of morphological structure showed that the grafting component of PHEA onto CPE promoted amalgamation between the primary particles of PVC and CPE-*cg*-HEA. Further research suggested that the toughening mechanism of the PVC/CPE-*cg*-HEA blends was different from that of the PVC/CPE blends. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 86–96, 2011

Key words: blends; graft copolymers; miscibility; poly(vinyl chloride) (PVC); toughness

INTRODUCTION

Blending is one of the most important methods for improving the mechanical properties and processability of polymer materials.^{1–3} Poly(vinyl chloride) (PVC), as a major class of common plastics, possesses many unique mechanical properties, and it is suitable for a wide variety of applications. To get the best results, the overall material characteristics, including the mechanical properties, processability, and thermal stability, must be considered when a polymeric material is selected. Because of its brittleness and poor processing capabilities, PVC is usually blended with an elastomer toughening modifier to expand its applications.⁴ The direct incorporation of rubbery polymers can improve the ductile and processing behavior of PVC but will inevitably lower the tensile strength of its blends.⁵ Additionally, the miscibility of PVC and rubbery polymers also influences the mechanical properties by affecting the microcosmic morphology.⁶ So it is important, in both theory and application, to develop new tougheners and better toughening methods.

Toughening theory has been studied since 1950s.^{7,8} A two-phase physical model, which includes a brittle matrix and dispersed rubber, was suggested to explain the toughening mechanism. Generally, there are two kinds of cases with rubber toughening systems in the polymer morphology, those composed of a disperse phase and a continuous phase and a network system. The two-phase structure may be vividly described by a sea island or core-shell model; the latter refers to an inclusion or network structure in a macromolecular arrangement. On the basis of the two systems, we can distinguish three main toughening mechanisms: multiple crazing, multiple shear yielding, and network yielding.⁹

In recent decades, a great amount of progress has been made in the development of PVC toughening technology. Arayapranee et al.¹⁰ blended PVC with (natural rubber)-*g*-(styrene-*co*-methyl methacrylate) to improve the impact of the PVC matrix. Among them, natural rubber served as the soft component, and the branch chains of styrene-*co*-methyl methacrylate served as the compatibilizer. The impact strength of the blends increased 17% when 10 phr graft copolymer was added. When incorporated into the PVC matrix, grafted styrene-*co*-methyl methacrylate existed at the interface between the rubber and plastic particles to lower the interface energy. Hence,

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grafted chains were necessary for sufficient adhesion between the two incompatible phases. Yang et al.⁵ added rigid particles of styrene-*co*-acrylonitrile resin (AS) into PVC/chlorinated polyethylene (CPE) blends to keep a higher tensile strength, whereas the ductility and processability of the PVC matrix were improved. When 4 phr AS was added to PVC/CPE blends (10 phr CPE), the tensile strength did not decrease, and the impact strength increased by 30% compared with that of PVC/CPE blends. The addition of the AS component promoted the formation of a CPE network that embedded the primary particles of PVC; this further supported the mechanical properties.

In this study, a new graft copolymer was prepared by the grafting of 2-hydroxy ethyl acrylate (HEA) onto CPE. The graft copolymer was blended with PVC to achieve impact modification of the PVC matrix and prevent the loss of much strength. Because of the better miscibility with PVC and the lower cost versus an acrylic copolymer, CPE and HEA were chosen as the backbone and graft chain, respectively. HEA had solution parameters close to PVC, about 9.0×10^{-3} (cal/m³)^{1/2}. The introduction of the poly(2-hydroxy ethyl acrylate) (PHEA) graft chain was expected to enhance the miscibility between PVC and the toughening modifier and to improve microstructure and mechanical strength of the blends.

The former research showed that a suitable amount of CPE added to the PVC matrix promoted the formation of a network, which embedded the primary particles of PVC;^{4,11-14} this corresponded to the toughening mechanism of network yielding. To further confirm the toughening mechanism of the PVC/chlorinated polyethylene-chlorinating graft-hydroxy ethyl acrylate copolymer (CPE-*cg*-HEA) blends, a volume change (ΔV) experiment¹⁵ and morphological investigation were introduced.

EXPERIMENTAL

Materials

High-density polyethylene (melt index = 0.5), as the matrix polymer, was made by LG Chemical (Seoul, Korea). HEA (chemical grade), as the grafted monomer, was made by Luxing Chemical Co., Ltd. (Zibo city, Shandong province, China). Chlorine was supplied by Haijing Chemical Industrial Co. (Qingdao city, Shandong province, China). Silicon dioxide was a commercial-grade material as the dispersant of in situ chlorinating graft copolymerization (ISCGC). PVC (HS1300) was obtained from Haijing Chemical Industrial Co. CPE (135A, chlorine content: 36%, Haijing Chemical Industrial Co.) was used as the reference modifier to determine the modification effect of CPE-*cg*-HEA. Tribasic lead sulfate and dibasic lead sulfate were industrial grade and were used as thermal stabilizers.

Synthesis of CPE-*cg*-HEA

ISCGC was placed in a 500-mL, round-bottom, three-necked flask equipped with a vane stirrer, a thermometer, and gas delivery. The gas delivery was connected with an absorbent bottle, which absorbed hydrogen chloride (HCl) produced by ISCGC. A certain amount of PE powder and HEA were put into the glass flask and mixed thoroughly by stirring for about 1 h. Then, a little SiO₂ powder was added to prevent the agglomeration of PE. The reaction mixture was deaerated by N₂ at about 40°C for 15 min to eliminate oxygen. As the chlorine (Cl₂) was introduced instead of N₂, the reaction was initiated. The reaction temperature ascended gradually as the reaction heat was released. The temperature was controlled within an appropriate range, lower than 80°C before a chlorine content of 17% and about 134°C when the chlorine content was from 17% to the goal value. The reaction process was indirectly indicated by the release quantity of HCl. When the required chlorine content was reached, chlorine gas was stopped, and the reaction system was cooled to terminate the reaction. The chlorine in the reactor was drawn out by a vacuum until 100°C, and then, air was let into the reactor. The vacuum and air influx operations were performed alternately sometimes to ensure the residual chlorine was cleaned out completely.¹⁶

Preparation of the blends

The blends of PVC/CPE-*cg*-HEA and PVC/CPE were prepared according to a series of PVC/elastomer ratios (weight percentages). Tribasic lead sulfate (6 phr) and dibasic lead sulfate (4 phr) were added, respectively, to every blend in proportion to 100 phr PVC matrix. These batches were kneaded in a high-speed kneader for 10 min, plasticized for 15 min at 165°C, and then, thin-passed 10 times on a double-roll plasticator (SK-160B, Shanghai Rubber Mechanical Co., Shanghai, China). We molded the prepared blends at 175°C with a flat-plate tablet machine (XLB tablet machine, Qingdao Yadong Rubber Mechanical Co., Qingdao city, Shandong province, China), holding 15 MPa of compressive stress for 5 min at hot press and 5 min at cold press. The molded sheets were shaped as test specimens according to GB/T 16421 for tensile testing and GB/T 1043 for impact testing.

Mechanical properties

Tensile strength measurements were performed on a universal testing machine (GOTECH AI-7000M, Taichung city, Taiwan) according to GB/T 16421-1996 with a crosshead speed of 10 mm/min at room

TABLE I
Mechanical Properties of Different PVC/CPE-*cg*-HEA and PVC/CPE Systems

Toughening modifier content (phr)	Tensile strength (MPa)		Notch impact strength (kJ/m ²)		Elongation at break (%)		Hardness (Shore D)	
	PVC/CPE	PVC/CPE- <i>cg</i> -HEA	PVC/CPE	PVC/CPE- <i>cg</i> -HEA	PVC/CPE	PVC/CPE- <i>cg</i> -HEA	PVC/CPE	PVC/CPE- <i>cg</i> -HEA
0	53		8		79		84	
5	43.5	51.3	10	13	121	185	83	83
10	41	44.5	28	33	166	170	82	83
15	34.6	39	31	36	122	138	80	83
20	32	33.5	43	56	81	111	78	80
30	24.1	28.5	81	88	60	95	77	78

PVC was considered to be a matrix polymer with 100 phr, and CPE was purchased from Haijing Chemical Industrial Co.

temperature and 55% relative humidity. The notch impact strength was determined according to the Chinese standard 1043-93 (XCJ-40 type tester, Chengde Machinery Factory, Chengde city, Hebei province, China). All of the reported data of mechanical properties are the average values of five experiments. The shapes and dimensions of the samples for the mechanical property determination were from literature.⁵

Dynamic mechanical analysis (DMA)

Dynamic mechanical analyses was carried out with a dynamic mechanical analyzer (Netzsch DMA242, Selb, Bavaria state, Germany). The test temperature ranged from -50 to 150°C at a heating rate of $3^{\circ}\text{C}/\text{min}$ and a 1-Hz constant frequency.

Scanning electron microscopy (SEM)

The morphologies of the fracture surfaces from the tensile testing specimen were studied by SEM (JEOL JSM-6700F, Tokyo, Japan) and were obtained at room temperature without solvent disposal. The fracture surfaces were coated with gold by a JFC-1600 (JEOL, Tokyo, Japan) auto fine coater.

Differential scanning calorimetry (DSC)

A Perkin Elmer DSC-7 calorimeter (Altham, Massachusetts state, America) was used to investigate the thermal properties of the blends. The temperature was increased from -50 to 150°C at a heating speed of $10^{\circ}\text{C}/\text{min}$ in a nitrogen atmosphere.

ΔV experiment

There was about a 50% void volume in crazing, so the volumes of the blends toughened by multiple crazing yielding evidently increased, and the increase in the volume varied directly with the amount of crazing.¹⁵ Bucknall and Clayton¹⁷ applied

this fundamental to investigate the crazing yielding of rubber-toughened plastics in the pioneering stage.

We simulated ΔV experiments, which were designed initially by Darlington and Saunders,¹⁸ to investigate the crazing yielding of the PVC/CPE-*cg*-HEA blends. In this experiment, a GOTECH AI-7000S testing machine and other instruments were needed to carry out the creep deformation experiment of the PVC/CPE-*cg*-HEA and PVC/CPE blends. First, two groups of dumbbell-shaped test samples of PVC with 5 phr CPE and CPE-*cg*-HEA were, respectively, prepared according to the requirements in the literature.¹⁵ Their width and thickness had to be accurately measured. Second, the tensile testing machine was set on the mode of constant stress. Then, we adjusted the tensile force to an accurate value equal to 36 MN for 1 m^2 in the work section of the samples. This parameter was established according to the literature.¹⁵ The creep deformation was started, and we recorded the strain in the thickness direction (e_1) and the strain in the tensile direction (e_3). The values of the strains had to be measured accurately by a strain gauge along with testing time. ΔV at any time was calculated by eq. (1).¹⁵ At last, the curves of ΔV correlated to e_3 were drawn, and their slopes, which were related to crazing, were measured. Because the contribution of crazing to creep deformation can be determined by e_3 , the slopes between ΔV and e_3 reveal the degree of multiple crazing yielding:

$$\Delta V = e_3 + 2e_1 \quad (1)$$

RESULTS AND DISCUSSION

Mechanical properties of the PVC/CPE and PVC/CPE-*cg*-HEA blends

To study the toughening effects of the PVC/CPE-*cg*-HEA and PVC/CPE blends, the mechanical properties of various blends with different toughening

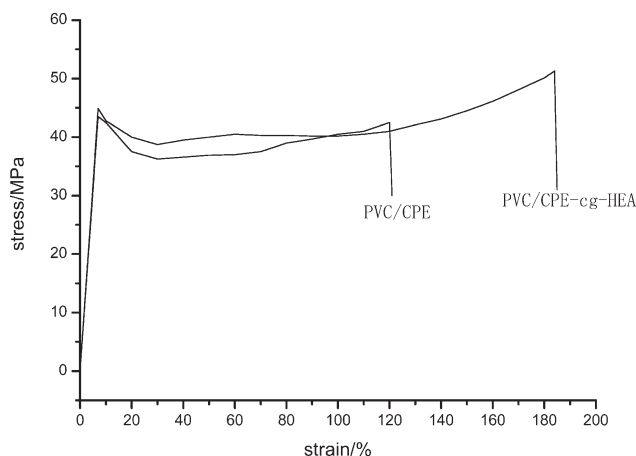


Figure 1 Stress–strain curves of the PVC/CPE-*cg*-HEA and PVC/CPE blends with a 5-phr toughening modifier content.

modifier contents were studied. The results are shown in Table I.

As shown in Table I, the mechanical properties of the PVC/CPE-*cg*-HEA blends were superior to those of the PVC/CPE blends, especially at the 5 phr modifier content, the tensile strength and the notched impact strength, respectively, increased to 51.3 MPa and 13 kJ/m², respectively; these were 17.9 and 30% higher, respectively, than those of the PVC/CPE blends. Compared with pure PVC, the tensile strength lost only 3.2%, and the notch impact strength improved up to 62.5%. The PVC/CPE-*cg*-HEA toughening blends with 5 phr CPE-*cg*-HEA were similar to pure PVC in tensile strength but improved much in notched impact strength.

The toughness of the PVC/CPE blends only increased slightly when a small amount of CPE was added to PVC (100 phr), although a brittle–ductile mutation region of the blend was formed when 10–20 phr CPE was added.² In contrast with CPE, CPE-*cg*-HEA was more efficient to modify the toughness of PVC and maintained the strength of blends synchronously. The tensile strength of PVC/CPE-*cg*-HEA preserved nearly 90% of the pure PVC matrix when the CPE-*cg*-HEA amount added to the PVC matrix was 5–10 phr. At the same time, the notched impact strength and elongation at break, which represented the toughness of the PVC/CPE-*cg*-HEA blends, increased greatly to form a brittle–ductile mutation region.

The stress–strain curves of the PVC/CPE-*cg*-HEA and PVC/CPE blends with 5 phr toughening modifier are shown in Figure 1. The two curves were a typical description of rubber-modified brittle polymer. As shown in the curves, the PVC/CPE-*cg*-HEA blends were much better than the PVC/CPE blends in terms of the tensile strength and elongation at break, and they were similar in tensile modulus.

Furthermore, the stress of the PVC/CPE-*cg*-HEA blends showed a constant increase after the forced high-elastic deformation occurred, and it was larger than that of the PVC/CPE blends in the strain-hardening stage.

As discussed previously, the virtue of the PVC/CPE-*cg*-HEA blends was that a small amount of elastomer added showed sufficient toughness, and the tensile strength of the blends preserved enough. In contrast with the PVC/CPE-*cg*-HEA blends, the PVC/CPE blends lost too much tensile strength, whereas the blends obtained sufficient toughness.

As a good toughening modifier, it is important to have a small dosage and a little influence on the tensile strengths of blends. As discussed previously, the PVC/CPE-*cg*-HEA blends with 5 phr modifier exhibited the desired result; this indicated that the tensile strength lost only 3.2%, and the notch impact strength improved up to 62.5%.

Dynamic mechanical analysis of the PVC/CPE and PVC/CPE-*cg*-HEA blends

To investigate the mechanical properties of the PVC/CPE-*cg*-HEA blends at different temperatures, dynamic mechanical analysis was performed. The storage modulus (E') and loss tangent ($\tan \delta$) of the blends with 5 phr toughening modifier are shown in Figure 2.

Some microcosmic characteristics were illuminated through the two parameters, E' and $\tan \delta$, of the blends with 5 phr toughening modifier. As shown in Figure 2, when the temperature was much lower than the glass-transition temperature ($T_g < -10^\circ\text{C}$), $\tan \delta$ of the PVC/CPE-*cg*-HEA blends was smaller than that of the PVC/CPE blends, although both of them were small. Under these conditions, the slight deformation of the blends was caused by the change in the bond length and bond angle, and the deformation of the blends was small enough to make the diversification of bond length and bond angle keep up with the variation of stresses. Above 20°C, $\tan \delta$ of the PVC/CPE-*cg*-HEA blends became higher than that of PVC/CPE blends. As the temperature rose, the two blends reached the high-elastic state, and the maximum tangent value of the two blends was observed at about 100°C. The $\tan \delta$ maximum (loss maximum) of the PVC/CPE-*cg*-HEA blends was higher than that of the PVC/CPE blends at T_g . The phenomena was explained by the frictional resistance, which obstructed the movement of the branched chain and lateral group of polymers above 20°C. In addition, the graft chains in the PVC/CPE-*cg*-HEA blends made the intermolecular distance large and the molecular arrangement disordered, so the movement unit of the PVC/CPE-*cg*-HEA blends had greater activity than that of PVC/CPE blends. Also, because of the internal friction of the chain segments of the polymer molecules, loss maximum

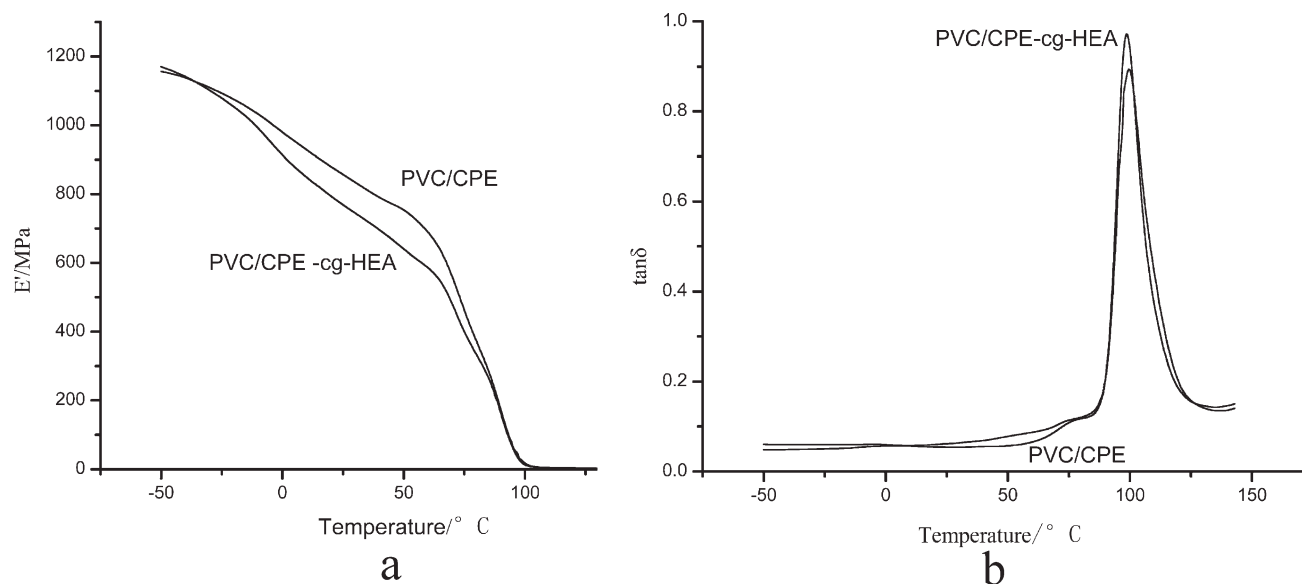


Figure 2 Temperature dependence on (a) E' and (b) $\tan \delta$ of the PVC/CPE-cg-HEA and PVC/CPE blends with 5 phr toughening modifier.

(δ_{\max}) of the PVC/CPE-cg-HEA blends at T_g was higher than that of the PVC/CPE blends. As the temperature rose further, the free volume of the two toughening systems increased continually, the chain segment movement became free, and $\tan \delta$ decreased.

As shown in Figure 2, E' of the PVC/CPE-cg-HEA blends was lower than that of the PVC/CPE blends at -40 to 0°C . As the temperature rose, the PHEA branch chain in CPE-cg-HEA became more active, which made E' of PVC/CPE-cg-HEA blends decrease more rapidly than that of the PVC/CPE blends. Above 90°C , the movement of chain segments became comparatively easy in the two blends. The branch chains of CPE-cg-HEA might be ignored, and there was no substantive difference between the two blends, so their E' curves became close gradually.

Miscibility of the toughening blends

The toughening process of the PVC/CPE-cg-HEA blends was quite different from that of the PVC/CPE blends. The reasons can be described by two aspects. On the one hand, the miscibility of CPE-cg-HEA with PVC was better than that of CPE. The branched chain of PHEA, having a greater miscibility with PVC,^{19–22} enhanced the affinity between the modifier and PVC and contributed to a higher toughness for the toughening blends. On the other hand, CPE-cg-HEA and CPE might have had different toughening mechanisms. In the PVC/CPE toughening blends, a network that embedded the primary particles of PVC could form, as long as a definite amount of CPE was blended,^{5,11–13} which corresponded to the toughening mechanism of network yielding. However, CPE-cg-HEA contained an

amount of acrylate groups because of the branch chain of PHEA. This kind of polymer usually forms a mass of crazing in the toughening process of PVC, and the toughening mechanism should be reasonably explained by multiple crazing mechanisms.^{23,24} The molecular structure of CPE-cg-HEA had as its structural characteristics more branch chains and relatively short branch chains.²⁵ The abundant branched chains of CPE-cg-HEA increased the contact area between the continuous phase and the disperse phase and were beneficial to the formation of a good interface. The existence of branched chains and homopolymers of PHEA may have changed the CPE network in the PVC blends and formed some crazing in addition to the network. This may have been the reason that the toughening effect of the PVC/CPE-cg-HEA blends was superior to that of the PVC/CPE-cg-HEA blends.

On the basis of this discussion, one can rationally explain the toughening effect of the PVC/CPE-cg-HEA system by focusing on the differences in the miscibility and toughening mechanism between the PVC/CPE-cg-HEA and PVC/CPE blends.

The miscibility of the disperse phase and continuous phase influenced the mechanical properties of the blends through the phase interface of the blended system. The miscibility of the PVC/CPE-cg-HEA system was investigated by the morphological structure and T_g .

Morphological structure of the PVC/CPE-cg-HEA and PVC/CPE systems

The best toughening blends of PVC/CPE-cg-HEA were obtained when the content of CPE-cg-HEA was

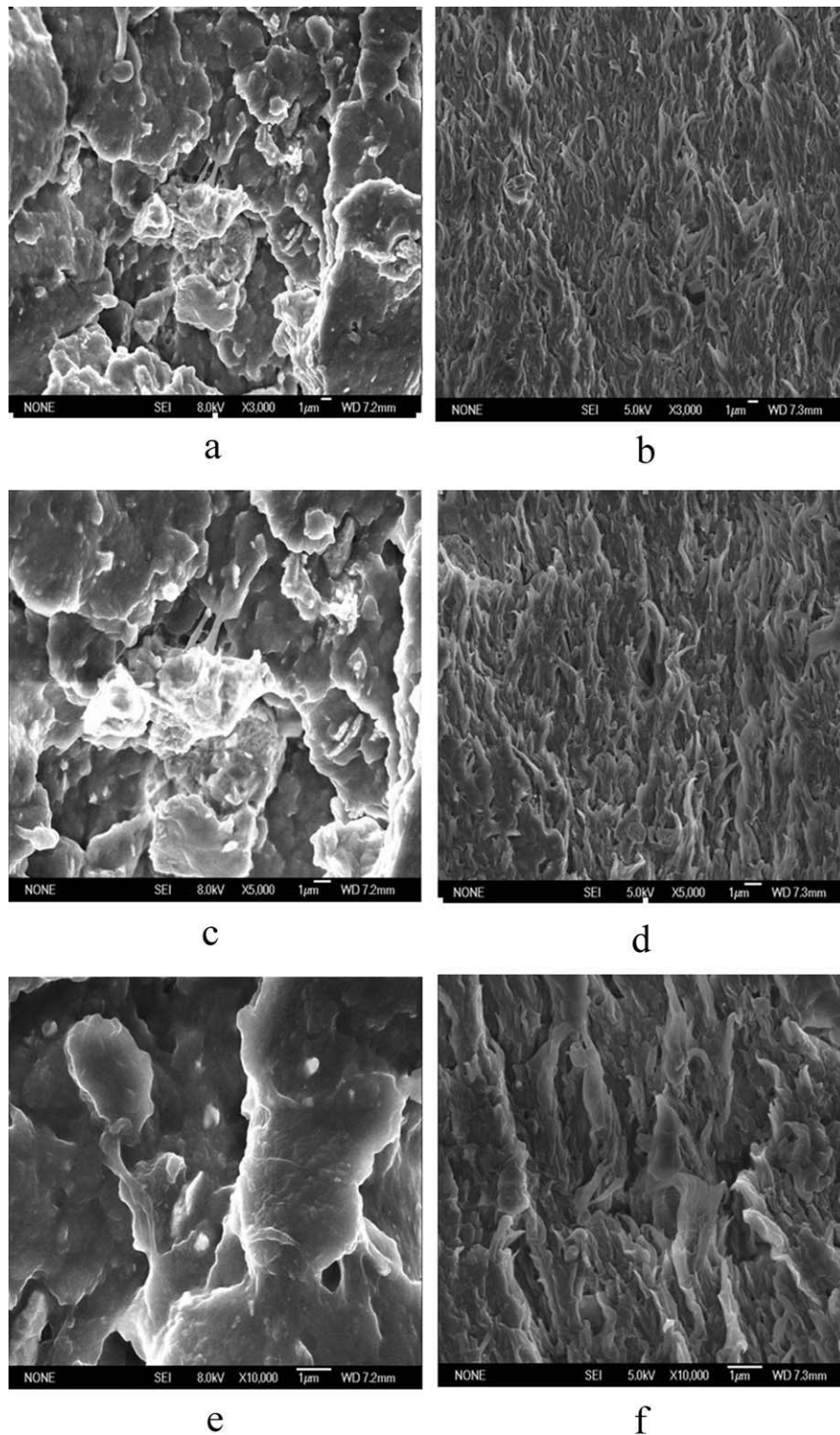


Figure 3 SEM images of the tensile fracture surface of the (a,c,e) PVC/CPE-*cg*-HEA and (b,d,f) PVC/CPE blends at a 5-phr toughening modifier content.

5 phr. SEM micrographs were taken to investigate the miscibility of the PVC/CPE-*cg*-HEA and PVC/CPE blends with 5 phr toughening modifier.

Figure 3 shows the fracture appearances of the PVC/CPE-*cg*-HEA and PVC/CPE blends. The jagged and coarse appearance of the two toughening blends

clearly showed a typical characteristic of ductile yielding. However, differences between the two blends were observed in the shape and arrangement of the phase states. The fracture microstructure of the PVC/CPE blends was netlike, multiply overlapped, and composed of a mass of tiny domains. In contrast

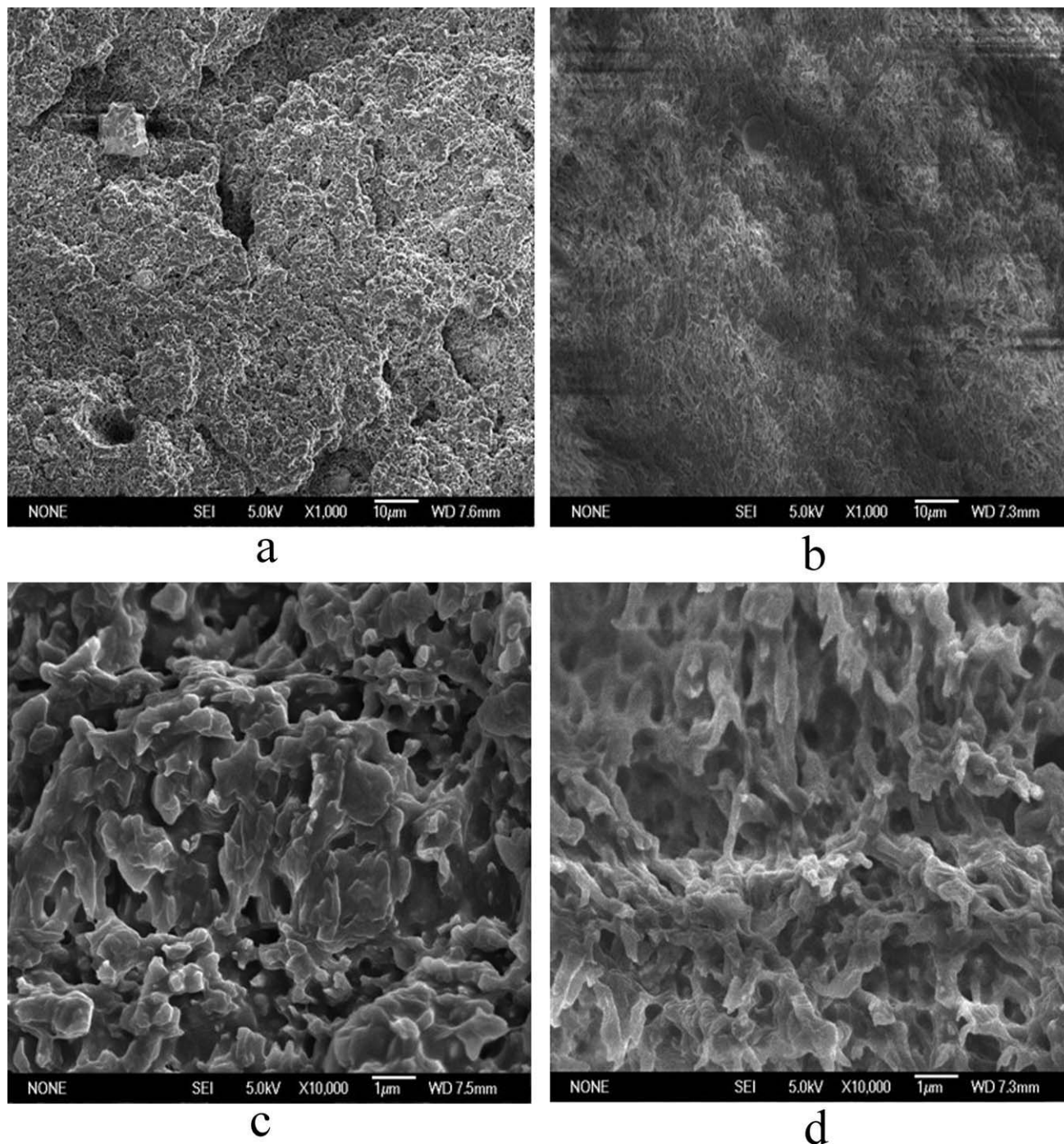


Figure 4 SEM images of the tensile fracture surface of the (a,c) PVC/CPE-cg-HEA and (b,d) PVC/CPE blends at a 30-phr toughening modifier content.

to the PVC/CPE blends, the fracture surface of the PVC/CPE-cg-HEA blends formed a more successive domain with a larger region. Moreover, as shown in Figure 3 (d,f), the fracture of the PVC/CPE system was too jagged to form the perfect interface between the PVC and CPE particles, and it obstructed the amalgamation between the PVC and CPE particles. The fuzzy phase interface between PVC and CPE-cg-HEA reflected the amalgamation between PVC and

the toughening modifier. In the image of the PVC/CPE-cg-HEA blends, the domain of the microstructure was wide and continuous with relatively less phase interface. Furthermore, the particles in the domain were well merged, and the phase interfaces were blurry; this indicated a homogeneous amalgamation between the PVC and CPE-cg-HEA particles.

Figure 4 shows the SEM microstructure of two toughening blends with 30 phr modifier. The

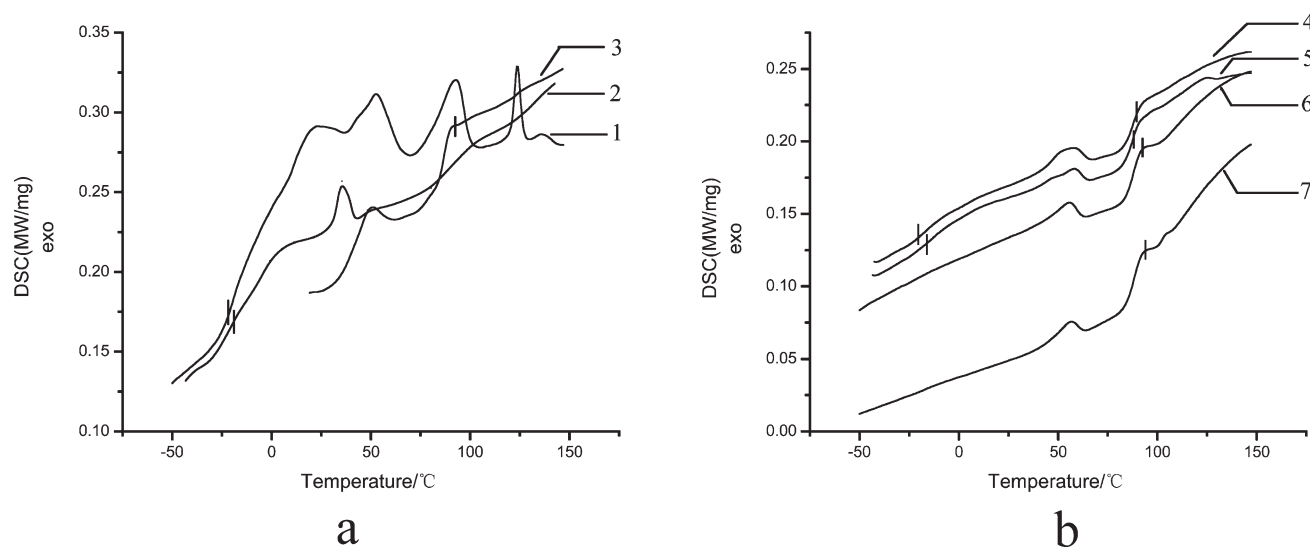


Figure 5 DSC tracings of PVC, CPE, CPE-cg-HEA, PVC/CPE-cg-HEA, and PVC/CPE 1 CPE; 2 CPE-cg-HEA; 3 PVC; 4 PVC/CPE blends with 30 phr CPE; 5 PVC/CPE-cg-HEA blends with 30 phr CPE-cg-HEA; 6 PVC/CPE-cg-HEA blends with 5 phr CPE-cg-HEA; 7 PVC/CPE blends with 5 phr CPE.

fracture surface of the PVC/CPE blends formed a perfect network, as shown in Figure 4(b,d). The perfect network showed a character of ductile fracture more distinct than that with 5 phr modifier. Compared with the PVC/CPE blends, there was the network of the PVC/CPE-cg-HEA blends, but it was not plain, and amalgamation with bigger domains existed in the microstructure of the blends.

DSC analysis of the PVC/CPE-cg-HEA and PVC/CPE blends

The miscibility of the PVC/CPE-cg-HEA and PVC/CPE blends was investigated through the change of T_g , which was determined by DSC, as shown in Figure 5.

As shown in Figure 5, the DSC curves of PVC, CPE, and CPE-cg-HEA had only one T_g , respectively. The toughening blends with 5 phr modifier showed one T_g , too, caused by less modifier content. As the content of toughening modifier rose to 30 phr, two T_g values appeared in the curves of DSC. The miscibility of the different toughening blends was evaluated by the T_g values.

As shown in curves 3 (pure PVC), 6 (PVC/CPE blends with 5 phr toughening modifier), and 7 (PVC/CPE-cg-HEA blends with 5 phr toughening modifier) in Figure 5, only one T_g for every blend was observed. They were 88.9°C for pure PVC, 88°C for PVC/CPE (5 phr), and 86.7°C for PVC/CPE-cg-HEA (5 phr), respectively. The lower T_g of PVC/CPE-cg-HEA exhibited that CPE-cg-HEA had a better miscibility with PVC than CPE had with PVC and would form miscible interfaces.

When the dosages of the toughening modifiers was increased to 30 phr, two T_g for one blend appeared in its DSC curves, respectively, for the PVC and elastomer phases. The two T_g 's of PVC/CPE were -16.3 and 87.4°C, respectively, shifted 1.7 and 1.5°C compared to pure CPE (-18°C) and pure PVC (88.9°C). For the PVC/CPE-cg-HEA blends, the two T_g values were -14.4 and 85.9°C, respectively, shifted 2.1°C (pure CPE-cg-HEA = -16.5°C) and 3.0°C (pure PVC = 88.9°C). The shifts of T_g could have indirectly indicated the interpenetration and miscibility between the PVC phase and the elastomer phase. The two T_g 's in PVC/CPE-cg-HEA with 30 phr toughening modifier tended to be closer and narrower, in contrast to that of the PVC/CPE blends. The larger T_g shifts of the PVC/CPE-cg-HEA blends showed better miscibility of PVC/CPE-cg-HEA compared to PVC/CPE.

Mechanism of the toughening blends

The toughening mechanisms of the PVC/CPE-cg-HEA and PVC/CPE blends were further investigated by morphological analysis and ΔV experiments.

Morphological structure of the PVC/CPE-cg-HEA and PVC/CPE blends

The stress endured by a specimen under a uniaxial tension can be decomposed into normal stress (σ_n) and shear stress (σ_s).^{26,27} The maximal σ_n is perpendicular to the uniaxial stress, and the maximal σ_s is a 45° angle. If the inherent σ_n of a polymer material

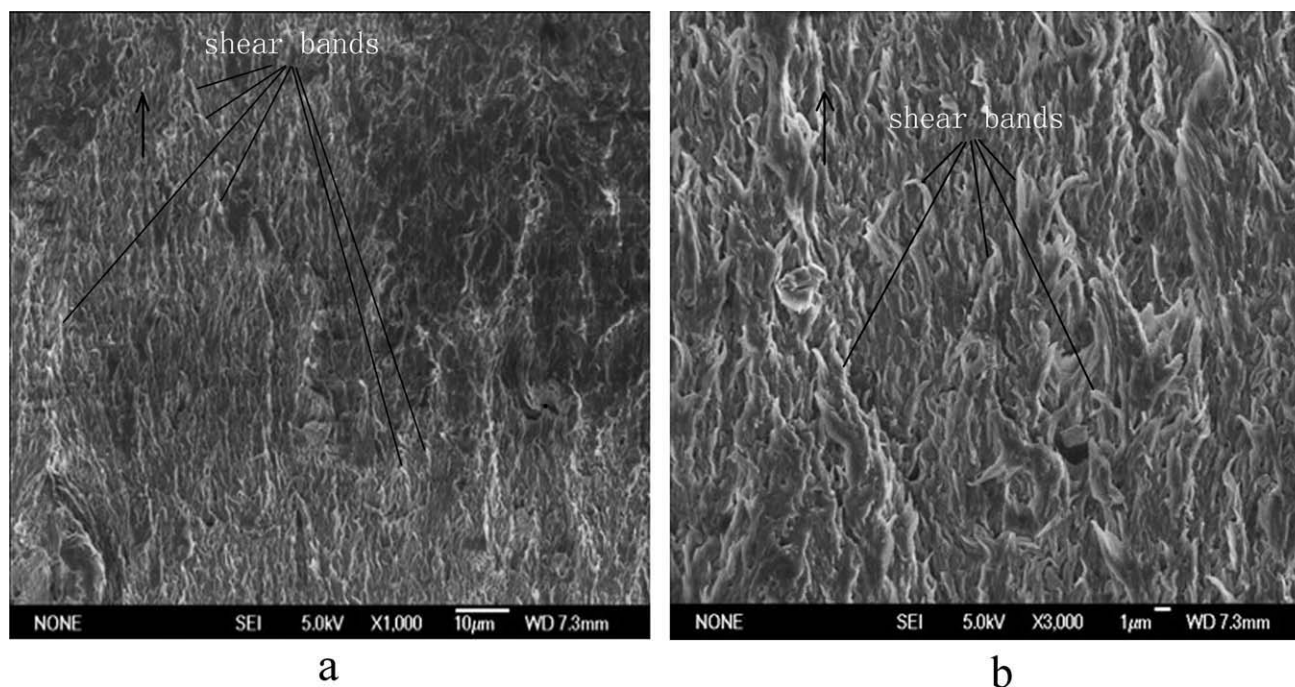


Figure 6 SEM images of the tensile fracture surface of the PVC/CPE blends at a 5-phr toughening modifier content at different magnifications. The forced direction of the samples is shown as the direction of the arrowhead.

is higher than its inherent σ_s , the stress of the material tends to yield σ_s , and the ductile deformation is preferentially induced by shear yielding. On the contrary, the ductile deformation is induced by crazing yielding.¹⁴

There was a mass of shear bands in the PVC/CPE blends with 5 phr toughening modifier, shown in Figure 6, which showed a similar result to a former investigation.¹⁴ The angles of the shear bands were located from 30 to 45° to the uniaxial stress. This suggested that the ductile deformation of the PVC/CPE blends with 5 phr modifier were induced by multiple shear yielding. Moreover, as shown in Figure 4(b,d), a perfect network formed in the PVC/CPE blends with 30 phr modifier, where CPE particles dispersed in the PVC matrix in the form of a network structure. Stressed by an outside force, a local stress concentration could induce moving and overlapping of the other adjacent network, which further increased the toughening of the blends. In this case, the toughening mechanism of the PVC/CPE blends with 30 phr modifier content was basically network yielding.

As shown in Figure 3, the tensile fracture surface of the PVC/CPE-*cg*-HEA blends with 5 phr toughening modifier was quite different from that of PVC/CPE blends. The blends of PVC/CPE-*cg*-HEA tended to amalgamate on the plane vertical to uniaxial tensile stress, which was different from the PVC/CPE blends. The phenomenon indicated the exist-

tence of crazing in the PVC/CPE-*cg*-HEA blends with 5 phr toughening modifier.^{14,28} The introduction of the grafted chains of PHEA onto CPE changed the toughening mechanism of the blends with 5 phr toughening modifier. In addition, the structure of PVC/CPE-*cg*-HEA with 30 phr toughening modifier did not form a perfect network as the PVC/CPE blends. Carefully observing Figure 4, we noted the appearance of a cratered structure with a cavity in the PVC/CPE-*cg*-HEA blends; this suggested that PHEA grafted onto CPE made the toughening mechanism of the PVC/CPE-*cg*-HEA blends more complex. A synergistic effect of the multimorphological structures was the reason for the better mechanical properties of the PVC/CPE-*cg*-HEA blends compared to those of PVC/CPE. We concluded that the toughening of the PVC/CPE-*cg*-HEA blends with 5 phr toughening modifier accorded with the crazing yielding mechanism, and the toughening mechanism was a compounding mechanism with an abundant toughening modifier, such as 30 phr toughening modifier, including crazing yielding and network yielding. The PVC/CPE-*cg*-HEA blends and PVC/CPE blends were different in toughening mechanisms.

Bucknall ΔV experiment

The relationship of ΔV and axial strain (e_3) is illustrated in Figure 7, from which the enormous difference from the two toughening blends was found.

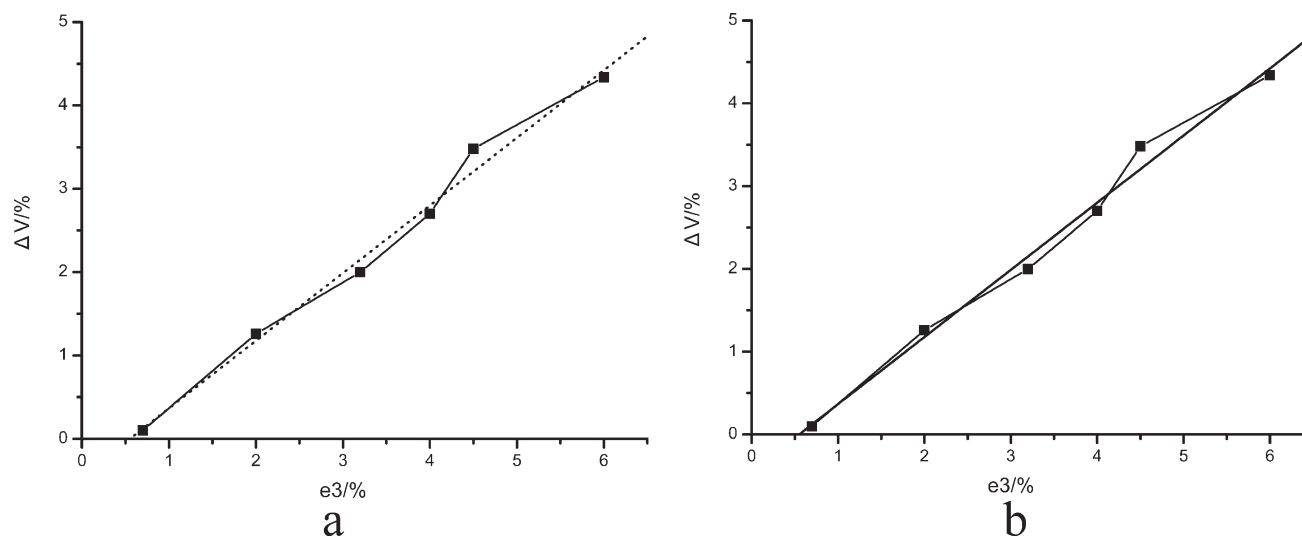


Figure 7 Relationship of ΔV and the axial strain (e_3) resulting from the ΔV experiments of (a) PVC/CPE-*cg*-HEA and (b) PVC/CPE blends, both with 5 phr toughening modifier.

The slope between ΔV and e_3 reflected the extent of multiple crazing yielding. By calculation, the slope of PVC/CPE-*cg*-HEA system with 5 phr modifier was 0.81; this indicated that 81% of the time dependence of creep deformation was induced by multiple crazing yielding in creep deformation. Meanwhile, the slope of the PVC/CPE blends with 5 phr modifier was 0.186, which indicated that 18.6% of time dependence of creep deformation was induced by multiple crazing yielding in creep deformation. Other time dependence of creep deformation was induced by multiple shear yielding. The results were consistent with the discussion of the morphological structure.

CONCLUSIONS

1. The toughening effect of CPE-*cg*-HEA was better than that of CPE when we blended with PVC. The tensile strength and notched impact strength of the PVC/CPE-*cg*-HEA blends with 5 phr toughening modifier were 17.9 and 30% higher, respectively, than that of the PVC/CPE blends. A small amount of elastomer added caused only a 3.2% loss of tensile strength of PVC.

2. The addition of CPE-*cg*-HEA promoted the formation of interfaces between PVC and the toughening modifier. The miscibility of the PVC/CPE-*cg*-HEA blends was finer than that of the PVC/CPE blends.

3. The PVC/CPE-*cg*-HEA blends had a different toughening mechanism than the PVC/CPE blends. The toughening mechanism of the PVC/CPE-*cg*-HEA blends with 5 phr toughening modifier accorded with the crazing yielding mechanism. When 30 phr toughening modifier was used, the

morphological structure did not form a perfect network. The compounding mechanism, including network yielding and crazing yielding, was the reason for the better mechanical properties of the PVC/CPE-*cg*-HEA blends compared to those of the PVC/CPE blends.

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