The Experimental Results and Simulation of Temperature Dependence of Brittle-Ductile Transition in PVC/CPE Blends and PVC/CPE/Nano-$CaCO_3$ Composites

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Received 6 December 2010; accepted 7 April 2011
DOI 10.1002/app.34662

ABSTRACT: The effect of chlorinated polyethylene (CPE) content and test temperature on the notched Izod impact strength and brittle-ductile transition behaviors for polyvinylchloride (PVC)/CPE blends and PVC/CPE/nano-$CaCO_3$ ternary composites is studied. The CPE content and the test temperature regions are from 0–50 phr and 243–363 K, respectively. It is found that the optimum nano-$CaCO_3$ content is 15 phr for PVC/CPE/nano-$CaCO_3$ ternary composites. For both PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ ternary composites, the impact strength is improved remarkably when the CPE content or test temperature is higher than the critical value, that is, brittle-ductile transition content (C_{BD}) or brittle-ductile transition temperature (T_{BD}). The T_{BD} is closely related to the CPE content, the higher the CPE content, the lower the T_{BD}. The temperature dependence of impact strength for PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ ternary composites can be well simulated with a logistic fitting model, and the simulation results can be illustrated with the percolation model proposed by Wu and Jiang. DMA results reveal that both PVC and CPE can affect the T_{BD} of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. When the CPE content is enough (20 phr), the CPE is more important than PVC for determining the T_{BD} of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. Scanning electron microscopy (SEM) observations reveal that the impact fractured mechanism can change from brittle to ductile with increasing test temperature for these PVC systems. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1833–1842, 2012

Key words: polyvinylchloride; chlorinated polyethylene; nanometer-sized calcium carbonate; impact toughness; brittle-ductile transition; SEM

INTRODUCTION

As a kind of typical brittle materials, polyvinylchloride (PVC) has been modified to extend its applications, and many impact modifiers have been commercialized and used for many years, such as chlorinated polyethylene (CPE), acrylonitrile butadiene styrene (ABS), poly (methyl-methacrylate-*co*-methacrylate) (ACR).[1–4] Inorganic or organic rigid particles also have been used to modify the mechanical properties of PVC.[5–10]

CPE and calcium carbonate ($CaCO_3$) are the most commonly used modifiers and the effects of them on the properties of PVC blends/composites have been studied widely.[11–29] Maksimov et al.[11–13] studied the elastic and thermophysical properties, creep behavior, and thermal deformation of PVC/CPE blends. Chen et al.[14–17] studied the fusion characteristics and morphological aspects of PVC/CPE blends. Breen[18] studied the crack growth of PVC and PVC/CPE blend in vapor and liquid environments. Natasa Stipanelov Vrandecic et al.[19–21] studied the thermooxidative degradation behavior and kinetics of poly(vinyl chloride)/chlorinated polyethylene (CPE) blends. Many researchers investigated the toughening and its mechanism of PVC or/and PVC blends through the addition of nanoparticulate calcium carbonate.[22–25] Zeng et al.[26] studied the influence of the diameter of $CaCO_3$ particles on the mechanical and rheological properties of PVC composites. Some researchers studied the effect of $CaCO_3$ on the degradation of PVC, it was found that, in the presence of $CaCO_3$, the peak temperature of dehydrochlorination was shifted to a higher temperature, the rate of mass loss was decreased, and the generation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans was greatly reduced and the possible mechanism for the suppressing effect of $CaCO_3$ is discussed.[27,28] Some investigations revealed that there was a synergistic effect between CPE and $CaCO_3$ on the improvement of toughness for PVC.[6,29]

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Contract grant sponsor: National Key Technology R and D Program; contract grant number: 2007BAE10B02.

Journal of Applied Polymer Science, Vol. 123, 1833–1842 (2012)

Many researchers have paid attention to the correlation between the mechanical properties and morphological structure of PVC systems.[10,30] Among them, some researchers studied the brittle-ductile transition behaviors in PVC systems.[31–34] Zhao[31] studied the effect of the particle size on the brittle-ductile transition of impact-modified poly (vinyl chloride) (PVC), and it was found that the brittle-ductile transition of the PVC/acrylic impact modifiers (AIMs) blends was independent of the particle size in the range of 55.2–341.1 nm. When the particle size was greater than 341.1 nm, however, the brittle-ductile transition shifted to a higher AIM concentration with an increase in the particle size. Liu[32–34] studied the effect of morphology on the brittle-ductile transition of poly (vinyl chloride)/nitrile rubber (NBR) blends. They found that the NBR rubber particle size distribution is one of the morphological parameters dominating the toughness and the toughening mechanisms of PVC/NBR blends; the NBR rubber particles act as stress concentrators to promote shear yielding of PVC respectively, in the pseudonetwork bands and in the blends with the morphology of well-dispersed particles; the pseudonetwork morphology is much more effective in toughening PVC than the morphology of well-dispersed rubber particles.

Besides the morphological structure, the test temperature is also an important factor to affect the properties of polymeric materials. In fact, as a kind of commonly used chemical building materials, the applying environmental temperature of PVC may change from 233 K to 323 K. It is well known that with the increasing temperature the motion ability of polymer molecular will increase with a glass transition behavior, which may lead to the brittle-ductile transition behavior. But many modification studies for PVC are carried out at about 296 K. It is very important for the PVC systems to know about the effect of temperature on the toughness. In this paper, the dependence of the notched Izod impact strength on the temperature is studied for PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. Meanwhile, an equation is used to simulate the correlation between the notched Izod impact strength and the temperature. The morphology of the impact fractured surfaces for these PVC systems is also investigated.

EXPERIMENTAL

Material and sample preparation

The PVC resin used in this work was a commercial suspension grade with Degree of Polymerization of 1100–1000 (SG5, from Guizhou Jinhong Chemical Co., China), and a commercial CPE was supplied by Zibo Aoqi Additive Co., (China) with chlorinity of 35 wt %. Nanometer-sized calcium carbonate (nano-$CaCO_3$) is manufactured by Shanghai Haichao Nanometer-sized Materials Technology (China). The PVC was mixed with 5 phr (parts per hundred parts of resin) combined lead salt stabilizer, 2 phr lubricant, and 2 phr processing aid before use.

The PVC/CPE blend, PVC/nano-$CaCO_3$ composites, and PVC/CPE/nano-$CaCO_3$ ternary composites samples were prepared by blending PVC with a certain amount of CPE (0–50 phr) and nano-$CaCO_3$ (0–30 phr) for a period of 8 min in a twin roll mixer at 453 K, and followed by compression molding at 458 K and 15 MPa pressure for 5 min, then naturally cooled to room temperature under pressure. The test specimens for mechanical properties were cut from the molded sheets.

Measurements and characterization

The Izod notched impact strength was performed on a XJ-40A Impact tester (Chengde, China) and the sample dimensions are $65 \times 10 \times 4$ mm^3. A notch of 2.0 mm depth with an angle of 45° was made on the specimens. The V-notched impact samples were put into a high and low temperature alternating humid chamber (GDJS-408, Suzhou Yiwei test Equipment Co., Suzhou, China) at a set temperature for 2 h, the fluctuation was ± 0.5 K, then the impact strength test was carried out within 10 s on the impact tester. All tests above were carried out with six specimens for each sample.

The dynamic mechanical analysis (DMA) was conducted on a DMA-Q800 (TA instruments, Newcastle, DE) in a tensile mode with a frequency of 1 Hz and a heating rate of 3 K/min within the range of 213–403 K. The temperature accuracy was 0.1 K, and the resolution of force was 0.00001N. The specimen dimensions were $40 \times 6 \times 1$ mm^3.

The Izod impact fractured surfaces were observed by a XL30FZG scanning electron microscopy (SEM) instrument (Philips, Amsterdam, Netherland) with an accelerating voltage of 20 kV.

The Vicat softening point was determined according to standard ISO 306 : 2004 on the computerized deflection temperature under load (DTUL)/VICAT tester (HDV-2, ATLAS, MA). The load is 5 kg, and the heating rate is 50 K/h.

The simulation of the notched Izod impact strength is finished with computer software (First Optimization, 7D-Soft High Technology, Beijing, China). The used algorithm optimization is Differential Evolution and convergence errors are $\leq 1.0 \times 10^{-10}$.

RESULTS AND DISCUSSION

The effect of CPE or/and nano-$CaCO_3$ on the notched Izod impact strength of PVC

The effect of CPE content on the notched Izod impact strength of PVC/CPE blends is shown in

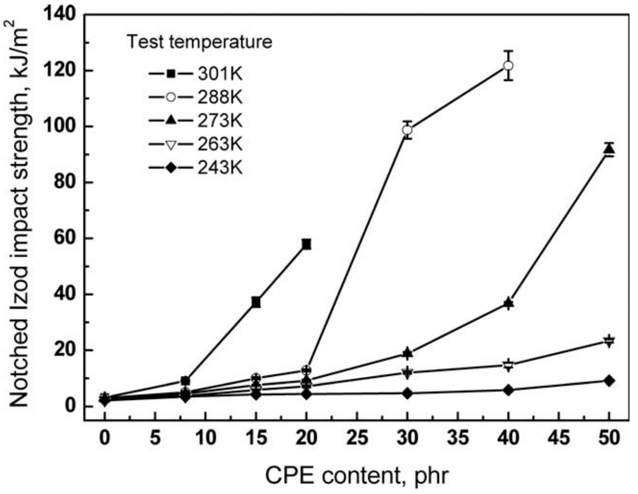


Figure 1 The effect of CPE content on the notched Izod impact strength of PVC/CPE blends at various test temperatures.

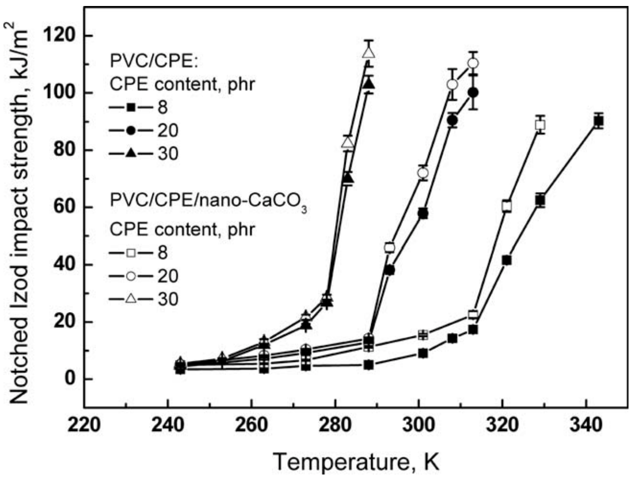


Figure 3 The comparison of notched Izod impact strength between PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites (nano-$CaCO_3$ content: 15 phr).

Figure 1. It can be observed that the notched Izod impact strength of PVC/CPE blends increases with CPE content at various test temperature. At or above 273 K, there are transition behaviors for the notched Izod impact strength of PVC/CPE blends with the increasing CPE content. The CPE transition content is different at various test temperatures, and the lower the test temperature, the higher the CPE transition content. At 243 K and 263 K, the notched Izod impact strength of PVC/CPE blends is comparatively lower, and there are no transition behaviors at the experimental CPE range. In Figure 2, the effect of nano-$CaCO_3$ content on the notched Izod impact strength of PVC/nano-$CaCO_3$ composites is studied. It can be observed that 15 phr is the optimum nano-$CaCO_3$ content at various test temperatures. So in the following PVC/CPE/nano-$CaCO_3$ ternary composites, the nano-$CaCO_3$ content is kept as 15 phr and all these composites with different CPE content are completely expressed in brief as PVC/CPE/nano-$CaCO_3$. From Figure 3, it can be observed that the notched Izod impact strength of PVC/CPE/nano-$CaCO_3$ composites is bigger than that of PVC/CPE blends, indicating that there is a synergetic effect between CPE and nano-$CaCO_3$ on the improvement of toughness for PVC/CPE/nano-$CaCO_3$ composites.

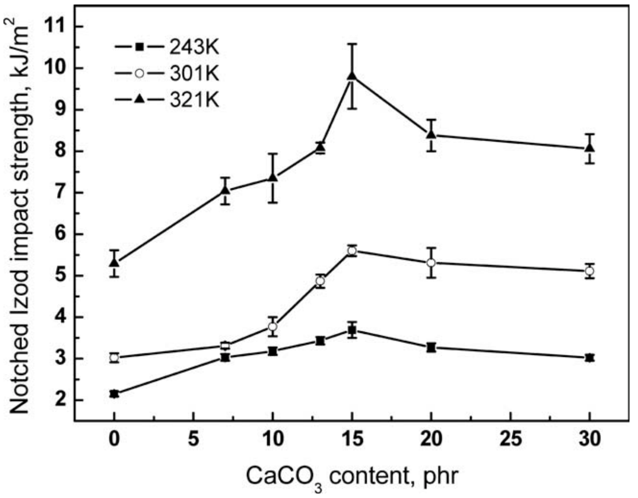


Figure 2 The effect of nano-$CaCO_3$ content on the notched Izod impact strength of PVC/$CaCO_3$ composites at various test temperatures.

The temperature dependence of notched Izod impact strength and its simulation for PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites

The temperature dependence of notched Izod impact strength was studied for PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites with different CPE contents, and the results are shown in Figures 4 and 5. With the increasing test temperature, the notched Izod impact strength increases, and there are transition behaviors for all PVC systems studied here, in other word, there is a brittle-ductile transition temperature (T_{BD}) for all these PVC systems. When the test temperature is lower than the T_{BD}, the notched Izod impact strength just increases slowly with the increasing test temperature and CPE content. Especially at 243 K, the notched Izod impact strength just changes from 2.15 kJ/m^2 for PVC to 5.28 kJ/m^2 and 9.19 kJ/m^2 for PVC/CPE (100/40) and PVC/CPE (100/50) blends, respectively. The fractured behavior is brittle at this situation. But if the test temperature is higher than the T_{BD}, the notched Izod impact strength increases greatly with the increasing test temperature, and the fracture behavior turns to ductile. Meanwhile, the T_{BD} is

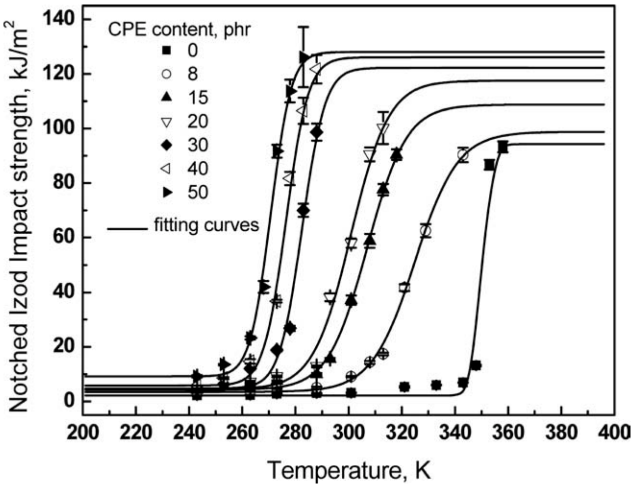


Figure 4 The temperature dependence of the notched Izod impact strength for PVC/CPE blends with different CPE contents.

dependent of the CPE content, the higher the CPE content, the lower the T_{BD}. At a comparatively high test temperature, the specimens cannot be broken completely during the impact test; accurate notched impact strengths can not be obtained. For PVC/CPE/nano-$CaCO_3$ ternary composites, there are the same behaviors as those of PVC/CPE blends with the increasing test temperature (Fig. 5).

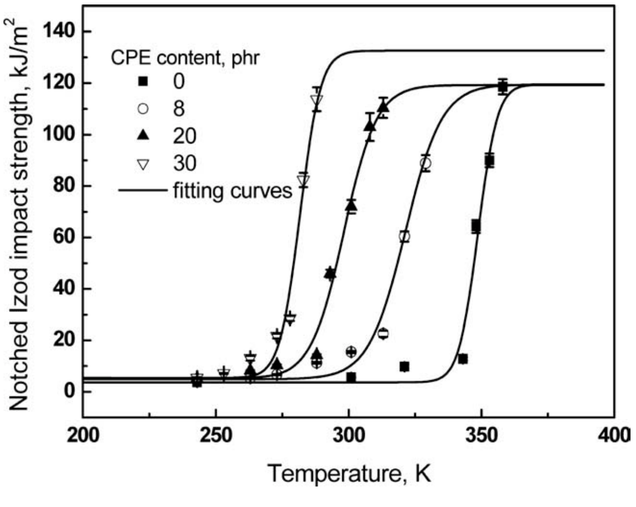


Figure 5 The temperature dependence of the notched Izod impact strength for PVC/CPE/nano-$CaCO_3$ ternary composites with different CPE contents (nano-$CaCO_3$ content: 15 phr).

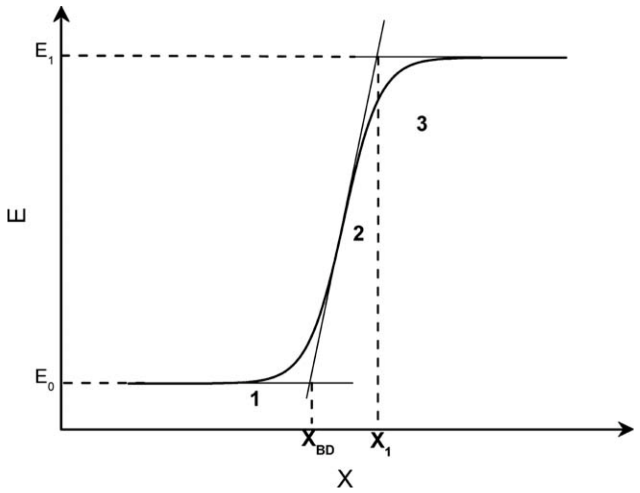


Figure 6 Schematic diagram of the brittle-ductile transition in polymer

In fact, the brittle-ductile transition is a common behavior for many materials. In general, the brittle-ductile transition of a polymer is like the schematic diagram in Figure 6,[35] where E is a physical quantity about toughness or energy of materials, E_0 and E_1 are the lower and upper shelf E, respectively. X is a physical quantity which can lead to the brittle-ductile transition in polymer, such as the mechanical properties of dispersed phase,[36,37] temperature,[38,39] the matrix molecular weight,[40,41] the strain rate,[42,43] the notch radius[44] and so on. X_{BD} and X_1 are the physical quantities where the brittle-ductile transition and the upper shelf E appear respectively. Although this schematic diagram looks simply, the impact data are collected only at discrete condition. So the obtainment of a fitting curve for these limited data is very important for not only theoretical reason but also applying value. John L. Helm[45] proposed a logistic function [eq. (1)] to fitting the Charpy impact test data of materials:

$$E(T) = \mathrm{LSE} + \frac{\mathrm{USE} - \mathrm{LSE}}{1 + e^{-\beta(T - T_m)}}, \tag{1}$$

where $E(T)$ is the temperature dependent Charpy impact energy, LSE and USE are the lower and upper shelf energies, respectively, T_m locates the curve center point. In this article, to describe the brittle-ductile transition of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites, we slightly rewrite the eq. (1) as following form:

$$I = I_0 + \frac{I_1 - I_0}{1 + ke^{-mT}}, \tag{2}$$

where, I is the notched Izod impact strength of blends or composites for a given temperature T, the unit of T is K (the unit of absolute temperature), I_0 is the minimum impact strength, and I_1 is the maximum impact strength. k and m is a constant. The correlation between the notched Izod impact strength of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites is fitted with eq. (2) and computer software (First Optimization). The simulation results of the parameters in eq. (2) are listed in Table I. The fitting correlation coefficient (R) is also

TABLE I
The Simulation Parameters for PVC/CPE Blends and PVC/CPE/nano-$CaCO_3$ Ternary Composites (nano-$CaCO_3$ Content: 15phr)

CPE content, phr		I_0	I_1	m	k	R
PVC/CPE	0	2.15	93.47	0.90	1.67E136	0.9990
	8	3.46	98.81	0.13	9.45E17	0.9988
	15	4.26	108.73	0.14	7.06E18	0.9992
	20	4.44	117.45	0.15	1.52E19	0.9945
	30	4.72	123.32	0.26	3.67E31	0.9943
	40	5.82	126.09	0.27	2.41E32	0.9982
	50	9.19	128.07	0.30	2.16E35	0.9983
PVC/CPE/$CaCO_3$	0	3.69	119.46	0.33	4.65E49	0.9916
	8	4.93	119.49	0.15	1.63E21	0.9963
	20	5.14	119.25	0.17	1.40E22	0.9943
	30	5.40	132.63	0.30	5.10E36	0.9933

listed in this table. The fitting curves are shown in Figures 4 and 5.

From Figures 4, 5, and Table I, it can be observed that the curves are well fitted to the experimental notched Izod impact strengths; the correlation coefficients (R) are bigger than 0.99, indicating that eq. (2) is appropriate for the description of the brittle-ductile transition in PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. It can also be obtained that I_0 and I_1 increase with the increasing CPE content. This is due to the toughness contribution of CPE. In addition, except the PVC and PVC/nano-$CaCO_3$ systems (CPE is 0 phr for PVC/CPE blend and PVC/CPE/nano-$CaCO_3$ composite), m and k increase with the increasing CPE content, indicating that the higher the CPE content, the more sensitive of the notched Izod impact strength to the test temperature.

From the fitting curves, the transition parameters can be obtained like the method shown in Figure 6, the results are listed in Table II. It can be obtained that the T_{BD} and T_1 (upper shelf temperature) decrease with the increasing CPE content for PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. This is due to the lower glass transition temperature of CPE. Meanwhile it can be observed that the difference of the T_{BD} and T_1 induced by nano-$CaCO_3$ is very small, indicating that 15 phr nano-$CaCO_3$ content does not induce apparent morphological change. In addition, the difference between T_{BD} and T_1 is no more than 32 K (shown in Table II), indicating that the two transitions finished within a comparatively narrow temperature range for PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites, in other word, the applying temperature range of these materials is very limited. There is an interesting fact that the value of T_1/T_{BD} is kept about 0.9, which is almost independent of CPE content. When the test temperature is high enough, the notched Izod impact strength of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites cannot be accurately obtained, so the maximum impact strength is almost not obtained in experimental test. With eq. (2) and the computer simulation, the maximum impact strength can be obtained. Although it has not been verified by experimental data, it is still important for us to understand the second transition behavior of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites.

For polymer blends, it is well known that the critical interparticle distance (ID_c) is very important to

TABLE II
The Transition Parameters of the Fitting Curves of PVC/CPE Blends and PVC/CPE/Nano-$CaCO_3$ Composites (nano-$CaCO_3$ Content: 15phr)

CPE content, phr		T_{BD}	T_1	$T_1 - T_{BD}$	T_{BD}/T_1
PVC/CPE	0	347.68	352.45	4.77	0.99
	8	309.93	341.88	31.95	0.91
	15	293.50	322.72	29.22	0.91
	20	284.89	315.48	30.59	0.90
	30	274.44	291.14	16.70	0.94
	40	268.30	284.02	15.72	0.95
	50	262.39	279.32	16.93	0.94
PVC/CPE/$CaCO_3$	0	342.10	355.22	13.12	0.96
	8	304.82	336.45	31.63	0.91
	20	286.13	310.26	24.13	0.92
	30	274.67	288.80	14.13	0.95

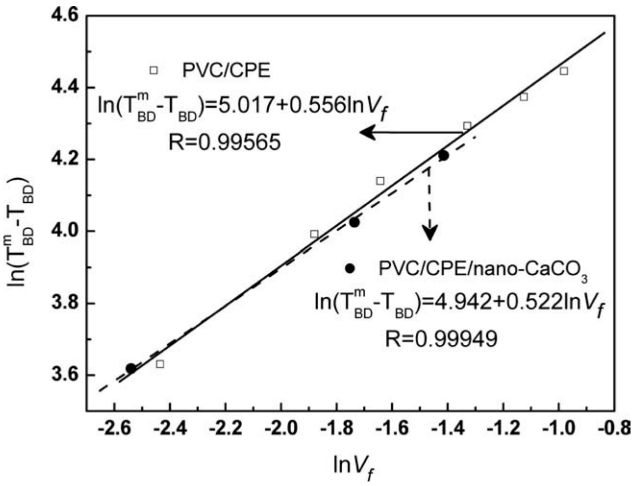


Figure 7 The correlation between ln $(T^m_{BD} - T_{BD})$ and ln V_f for PVC/CPE blends and PVC/CPE/nano-CaCO$_3$ composites (nano-CaCO$_3$ content: 15 phr).

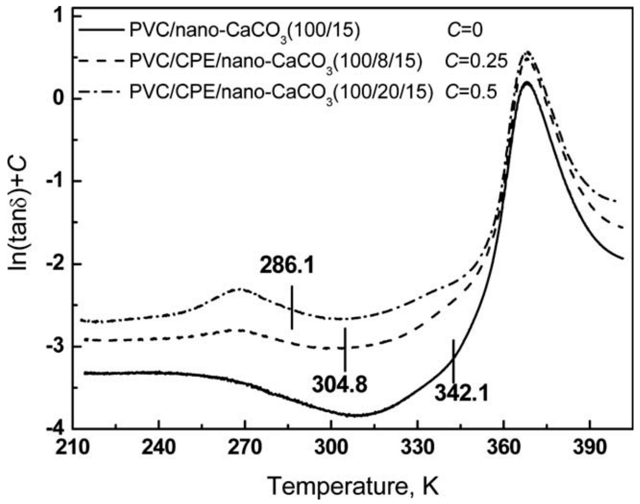


Figure 9 The tan δ versus temperature curves of PVC/CPE/nano-CaCO$_3$ composites with various CPE content (C is a vertical shift factor).

the brittle-ductile transition, and Wu[46] has proposed a model to describe this phenomenon:

$$\mathrm{ID}_c = d\left[\left(\frac{\pi}{6V_f}\right)^{1/3} - 1\right], \tag{3}$$

In other study, Jiang[47] proposed another equation for the critical interparticle distance:

$$\mathrm{ID}_c = \left[\frac{QE}{(T^m_{\mathrm{BD}} - T_{\mathrm{BD}})^2} + d^3\right]^{1/3} - d, \tag{4}$$

where the definitions of d, ID_c, T^m_{BD}, T_{BD}, V_f, E are the critical particle diameter of dispersed phase, the critical interparticle distance between the surfaces of two nearest neighboring particles, the brittle-ductile transition temperature of the matrix polymer, the brittle-ductile transition temperature of the polymer blend, the volume fraction of dispersed particles, the total strain energy in the matrix in the stressed volume respectively, and

$$Q = \frac{12M_1V^2}{\pi R_G^2[\ln(B/\dot{\gamma})]^2}, \tag{5}$$

where M_1 is the modulus of the matrix, V is the activation volume, R_G is the gas constant, B is a constant, $\dot{\gamma}$ is the strain rate. Eqs. (3) and (4) can be rearranged to the following form:

$$(T^m_{\mathrm{BD}} - T_{\mathrm{BD}})^2 = \frac{6QE}{d^3(\pi - 6V_f)}V_f, \tag{6}$$

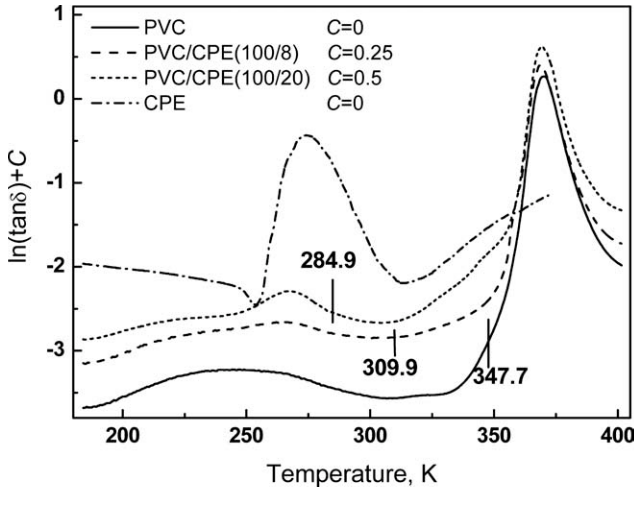


Figure 8 The tan δ versus temperature curves of PVC/CPE blends with various CPE content (C is a vertical shift factor).

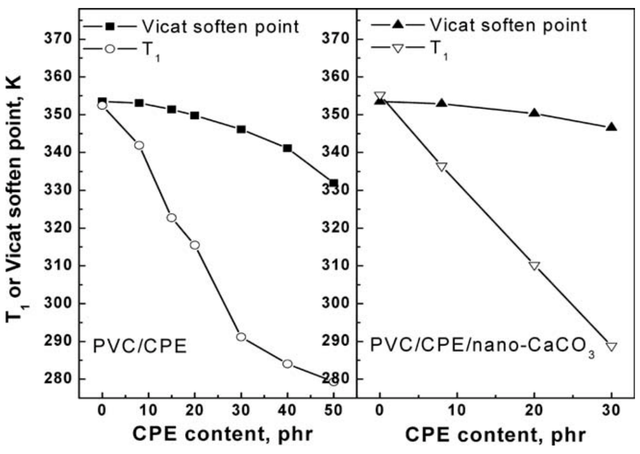
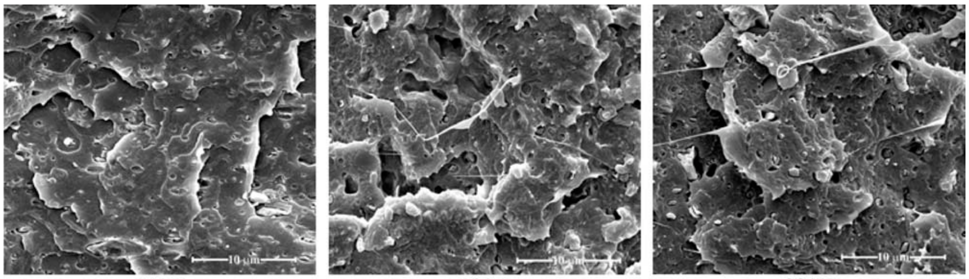


Figure 10 The comparison of T_1 and Vicat soften point of PVC/CPE blends and PVC/CPE/nano-CaCO$_3$ composites (nano-CaCO$_3$ content: 15 phr).



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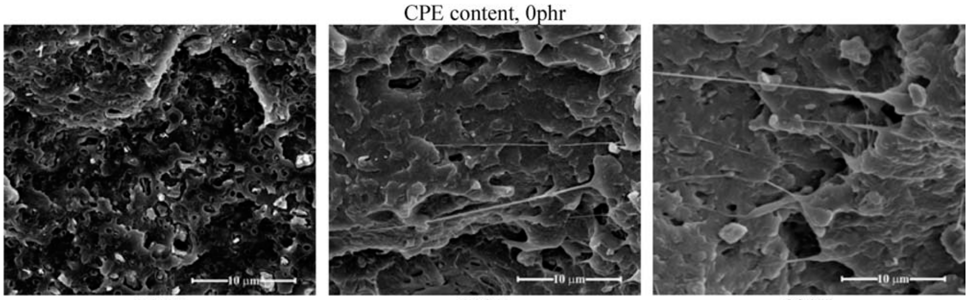
CPE content, 0phr



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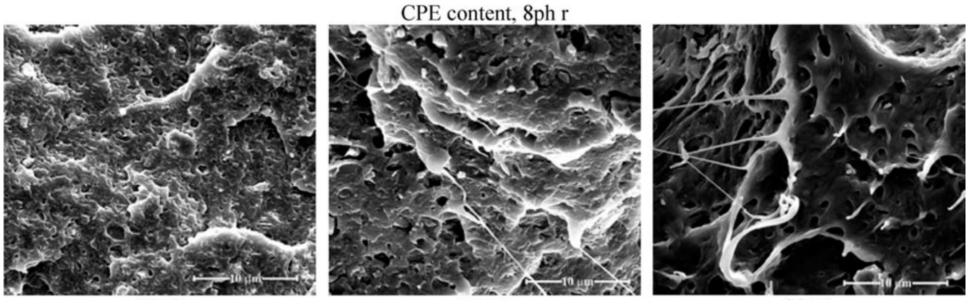
CPE content, 8ph r



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CPE content, 20phr

Figure 11 The impact fractured surfaces of PVC/CPE blends at different test temperatures.

if we define

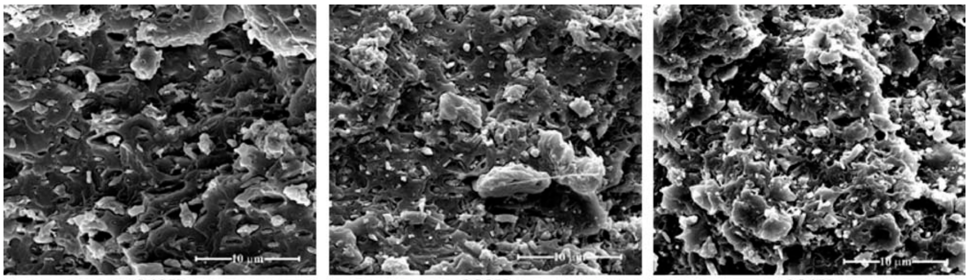
$$A = \frac{6QE}{d^3(\pi - 6V_f)}, \tag{7}$$

Equation (6) can be rewritten as the following form:

$$(T_{\mathrm{BD}}^{m} - T_{\mathrm{BD}})^2 = AV_f \tag{8}$$

So the correlation of $(T_{\mathrm{BD}}^{m} - T_{\mathrm{BD}})^2 \sim V_f$ or $\ln(T_{\mathrm{BD}}^{m} - T_{\mathrm{BD}}) \sim 0.5 \ln V_f$ can be roughly obtained. The density of PVC, CPE, and nano-$\mathrm{CaCO_3}$ is 1.38 g/$\mathrm{cm^3}$, 1.15 g/$\mathrm{cm^3}$, and 2.60g/$\mathrm{cm^3}$, respectively, and the volume of PVC/CPE blends and the volume of PVC/CPE/nano-$\mathrm{CaCO_3}$ composites are assumed as the linear addition of the volume of PVC, CPE, and nano-$\mathrm{CaCO_3}$. $\ln(T_{\mathrm{BD}}^{m} - T_{\mathrm{BD}})$ and $\ln V_f$ are calculated out and the correlation between them is given in Figure 7. It can be observed that there is a linear correlation between $\ln(T_{\mathrm{BD}}^{m} - T_{\mathrm{BD}})$ and $\ln V_f$, the linear regression correlation coefficient (R) is more than 0.99, and the slope is about 0.556 for PVC/CPE blends and 0.522 for PVC/CPE/nano-$\mathrm{CaCO_3}$ composites, which are both close to 0.5. On one level, although the dispersed particle diameter is not easy to determine in our studies, the experimental results still verify the correctness of the equations proposed by Wu[46] and Jiang.[47] Obviously, A is related to V_f, that is the reason why there is the difference between the obtained slope and the rough theoretical slope (0.5).

About the mechanism of these transitions, we assume that the T_{BD} and T_1 are corresponding to the glass transition temperature and Vicat soften point of polymer blends or/and composites. So the DMA and Vicat soften point test are carried out. The DMA results are shown in Figures 8 and 9. To make a distinction between the different systems, a vertical shift factor C is added to the value of ln(tanδ), and the value of C for different systems is listed in these figures. The T_{BD} values are listed at the curves for the corresponding systems. It can be observed that the β transition of PVC overlaps the CPE glass transition; the higher the CPE content, the bigger the loss tangent peak of CPE. The loss tangent peak of PVC is almost not affected by CPE and nano-$\mathrm{CaCO_3}$.



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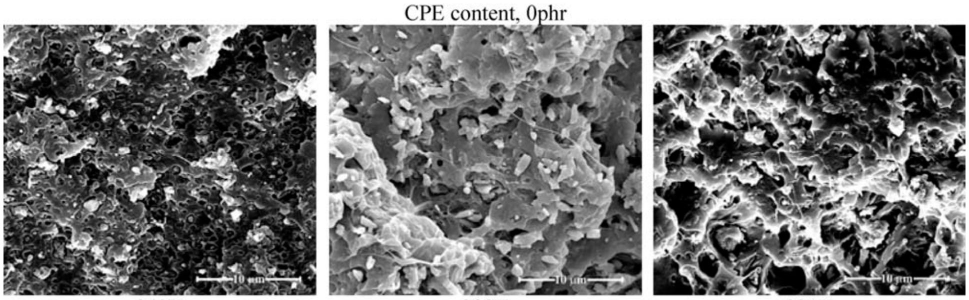
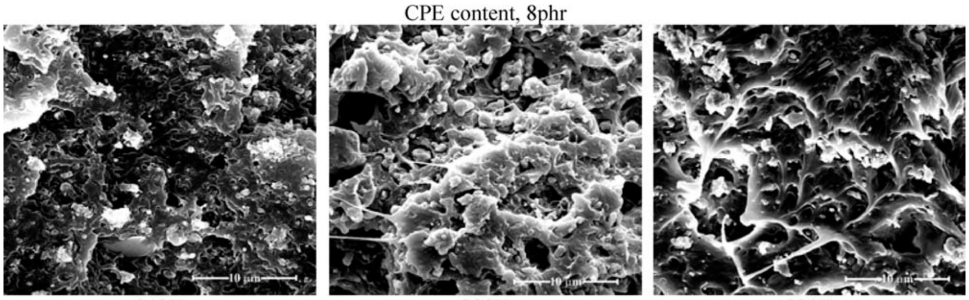
CPE content, 0phr



243K 288K 321K

CPE content, 8phr



243K 288K 321K

CPE content, 20phr

Figure 12 The impact fractured surfaces of PVC/CPE/nano-$CaCO_3$ composites at different test temperatures (nano-$CaCO_3$ content: 15 phr).

The T_{BD} of PVC and PVC/nano-$CaCO_3$ (100/15) composites are corresponding to the beginning temperature of PVC's glass transition; when the CPE content is 8 phr, the T_{BD} of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites are located between the PVC and CPE glass transitions; when the CPE content is 20 phr, the T_{BD} of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites are located at the higher temperature range of CPE glass transition. With the increasing CPE content, the T_{BD} changes to the lower temperature range of CPE glass transition; and the higher the CPE content, the lower the T_{BD}. When the CPE content is 50 phr, the T_{BD} of PVC/CPE blend is almost located at the lowest temperature range of the CPE glass transition. The T_{BD} is independent of nano-$CaCO_3$. All these indicate that the glass transitions both of the matrix and the dispersed phase have effect on the T_{BD} of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. When there is no CPE, the glass transition of PVC determines the T_{BD} of PVC and PVC/nano-$CaCO_3$ composites. When the CPE content is 8 phr, both PVC and CPE have effects on the T_{BD} of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. When there is enough CPE, such as 20 phr CPE, the glass transition of CPE play a more important role than that of PVC in determining the T_{BD} of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. But from Figure 10, it can be observed that except the PVC and PVC/nano-$CaCO_3$ systems (CPE is 0 phr for PVC/CPE blend and PVC/CPE/$CaCO_3$ composite), there are apparent difference between the T_1 and Vicat soften point; the T_1 is much lower than the Vicat soften point. The higher the CPE content, the bigger the difference between the T_1 and Vicat soften point. The reason may be the different strain rates used in the tests of the notched Izod impact strength and Vicat soften point, and the not enough or accurate experimental data result in inaccurate fitting curves and T_1. In addition, the Vicat soften point is corresponding to the PVC glass transition, but the T_1 is more dependent on the CPE glass transition. The mechanism of T_1 needs further study.

SEM observation of the impact fractured surfaces

Figure 11 and 12 shows the impact fractured surfaces of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites at three different test temperatures. When the test temperature is 243 K, on the whole, the PVC matrix shows a brittle fractured surface no matter whether there is CPE or/and nano-$CaCO_3$ in the PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. On the contrary, when the test temperature is 321 K, the ductile fractured surfaces appear. At 288 K, both brittle and ductile fractured surfaces appear if there is no or not enough CPE in PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites; if the CPE content is 20 phr in PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites, the ductile fractured surfaces appear. Apparently there is transition behavior in the impact fractured mechanism with the increasing test temperature for the PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. When the CPE content and the test temperature are the same, the impact fractured surfaces of PVC/CPE/nano-$CaCO_3$ composites are coarser than those of PVC/CPE blends. In addition, when the test temperature is the same, the higher the CPE content, the coarser the impact fractured surfaces for the PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites.

CONCLUSIONS

The effects of CPE, nano-$CaCO_3$, and test temperature on the notched Izod impact strength of PVC are studied. The CPE and nano-$CaCO_3$ can improve the mechanical properties of PVC with a synergetic effect on the toughness of PVC/CPE/nano-$CaCO_3$ composites. The optimum nano-$CaCO_3$ content is 15 phr. With the increasing test temperature, brittle-ductile transitions appear for all studied PVC systems; and the brittle-ductile transition temperatures (T_{BD}) are closely related to the CPE content, the higher the CPE content, the lower the T_{BD}. A logistic fitting model is used to simulate the correlation curves between the notched Izod impact strength and test temperature for both PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. By making use of the percolation model and the equation proposed by Wu[46] and Jiang,[47] respectively, the T_{BD} is found to be linear correlation to the volume fraction of CPE with a slope near to 0.5, indicating that the used models and equation are suitable to describe the temperature dependence of Brittle-Ductile Transition in PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites on one level. DMA results reveal that both PVC and CPE have effects on the T_{BD} of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. When the CPE content is enough, such as 20 phr CPE, the CPE is more important than PVC for determining the T_{BD} of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites. Nano-$CaCO_3$ has no effect on the T_{BD}. The upper shelf temperature (T_1) is not directly corresponding to the Vicat soften points of PVC/CPE blends and PVC/CPE/nano-$CaCO_3$ composites, and mechanism needs further study. SEM observations reveal that the impact fractured behaviors can change from brittle to ductile with increasing test temperature for these PVC systems.

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