Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 329–332

MATHEMATICAL DESCRIPTION OF THE SOFTENING TEMPERATURE OF POLY(VINYL CHLORIDE) BLENDS WITH SOLID-STATE CHLORINATED POLYETHYLENE

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A mathematical description of the dependence of softening temperature of poly(vinyl chloride) blends with solid-state chlorinated polyethylene on the degree of chlorination of polyethylene and the amount of chlorinated polyethylene were studied. A method for calculation the coefficients in the corresponding empiric equation was suggested. The latter can successfully be used for practical purposes in preparation of various composition with selected softening temperature.

Keywords: *empirical equation, mathematical description, PVC/CPE blends, softening temperature*

Introduction

Chlorinated polyethylene (CPE) is added to various polymers and copolymers in order to improve some of their properties like impact resistance, fire resistance, the brittle point, electrical properties, chemical and atmospheric stability, etc. One of the most perspective applications of CPE is, however, as additive to rigid poly(vinyl chloride) (PVC) to increase its impact resistance and facilitate its processability [1–6].

CPE obtained by different methods (chlorination of PE in solution, suspension and solid-state) has specific behavior in blends with PVC due to the different character of the distribution of chlorine atoms along PE chains. Usually, the chlorine atoms are distributed randomly along PE macromolecules when the chlorination is performed in solution [1, 2, 7, 8]. By chlorination in suspension and solid-state, the distribution can be either randomly (when the process is carried out at temperature close the PE melting temperature) or block-like (when the process is carried out at temperatures below 100°C) [7–13].

The blends of PVC with PE chlorinated in solution or suspension are thoroughly studied [2, 5] and much attention has been recently paid to the use of PE blocky chlorinated in aqueous suspension [11–13]. The use of solid-state chlorinated PE in binary and multicomponent blends based on PVC is comparatively less studied and CPE containing 30–38% Cl is the preferred initial material [14–16]. According to Bonotto and Wagner [14], PE non-uniformly chlorinated in solid-state and containing 30% Cl improves PVC impact resistance, as well as its mechanical strength, heat resistance and atmospheric stability. Since the structure of the chlorinated blocks changes depending on the chlorine content in the solid-state chlorinated PE [10], this should exert influence on the properties of its blends with PVC.

The aim of the present work is to describe mathematically the effect of the degree of chlorination and the amount of solid-state chlorinated PE on the softening temperature of its blends with rigid PVC.

Experimental

Materials

A suspension PVC with Fikentcher constant of 68.1, $\overline{M}_n$=86000, bulk mass of 540 kg m^{-3} and moisture content of 0.03% was used in all experiments. The experimentally determined chlorine content in PVC was 56.48%.

The chlorinated polyethylene (CPE) was prepared by chlorination of high-density polyethylene (HDPE) with $\overline{M}_\eta$=96500 g mol^{-1} and particle size of 0.125–0.250 mm. The chlorination of HDPE was conducted in a fluidized-bed reactor in the presence of a gaseous mixture, consisting of chlorine and nitrogen in volume ratio of 3:7, respectively. The experiments were carried out within the temperature interval from 20 to 80°C. The combined chlorine content was determined by burning out a 15 to 25 mg sample, according to the Schöeniger method, followed by potentiometric titration with 0.1N $AgNO_3$ solution [17].

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1388–6150/$20.00

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Blends preparation

A series of PVC-CPE blends were prepared. CPE used contained 10.2% Cl, 21.8% Cl, 27.3% Cl, 37.0% Cl, 45.2% Cl and 54.8% Cl. The content of CPE was calculated with respect to PVC and was varied from 10 to 75 mass%. A combination of stabilizers such as calcium stearate (1.0 mass%), modified dibutyltin maleate BT-22 (4.0 mass%), pentaerythrito-tetrakis[3-(3,5-ditert-butyl-4-hydroxyphenyl)] propionate, i.e., Irganox 1010 (0.25 mass%) was added to each polymer blend. The ingredients were first dry-mixed and then homogenized on rolls at 172–178°C for 8–10 min. The sheets obtained were subsequently pressed on a laboratory press type PHI (England) at 180°C under pressure of 3.0 MPa and average cooling rate of 25 K min^{-1}. They were conditioned at room temperature for 24 h.

Measurement

The Vicat softening temperature was determined on an apparatus of Frits Heckert company (Germany), according to the BSS EN ISO 306 [18] at a force of 50 N and a rate of temperature rising 50±5°C h^{-1}. The single value of softening temperature was determined as an average from six 3±0.1 mm thick samples.

Results and discussion

The following sequence was used to describe mathematically the softening temperature of blends of suspension PVC with solid-state chlorinated polyethylene as a function of the degree of chlorination and the amount of CPE in them. First, the dependence of the blends softening temperature on the degree of PE chlorination and PE amounts in them, which were 10, 20, 30, 50 and 70% *vs*. the mass of PVC, was drawn (Fig. 1, curves 1–5).

It can be seen in Fig. 1 that the softening temperature of all the blends studied was observed to decrease until 22–25% chlorine content in CPE was reached. It was most obvious for the blends containing 75% CPE. This is probably related to the effect exerted by non-chlorinated methylene groups in CPE, resulting in weakening of the polar interactions between the two polymers. At higher chlorine content in CPE (above 25%), the softening temperatures of the blends were found to increase due to the stronger polar interactions between the chlorine containing groups of the two polymers.

The shapes of these curves can be described mathematically by polynoms of various orders with coefficients determined empirically on the basis of experimental data. For this purpose, second order polynoms of the following type were used:

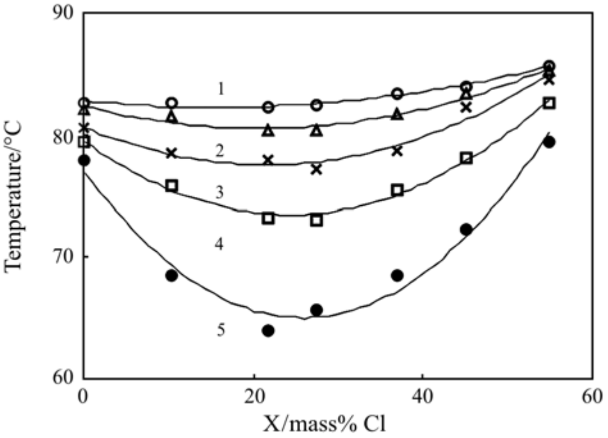

Fig. 1 Dependence of softening temperature of PVC/CPE blends on the PE degree of chlorination at: 1 – 10; 2 – 20; 3 – 30; 4 – 50 and 5 – 75 mass% CPE in them

$$t=\alpha+\beta X+\gamma X^2 \qquad (1)$$

where X is the degree of PE chlorination. To find the values of the empiric coefficients α, β and γ, it is necessary to draw graphically their dependence on the second parameter Y (Y is the amount of CPE in the blends, mass%). These dependencies are shown in Fig. 2a–c.

As can be seen from Fig. 2a, the dependence of coefficient α on the amount of CPE in the blends can be described by a linear equation with the following empiric coefficients:

$$\alpha=84.146-0.0961Y \quad R^2=0.9858 \qquad (2)$$

The dependence of coefficient β on the amount of CPE can be described by a second order polynom with the following empiric coefficients:

$$\beta=-0.0975+0.0031Y-0.0002Y^2 \quad R^2=0.9918 \qquad (3)$$

The dependence of coefficient γ on the amount of CPE can be described by a second order polynom with the following empiric coefficients:

$$\gamma=0.0016+1.0\cdot10^{-5}Y+3.0\cdot10^{-6}Y^2 \quad R^2=0.9893 \qquad (4)$$

The dependence of t on both X and Y can be derived by a method similar to that reported in [19, 20] by replacing the coefficients α, β and γ in Eq. (1) with their values obtained using the expressions (2), (3) and (4). The empiric equation obtained by this method had the following coefficients:

$$\begin{gathered} t=84.146-0.0961Y- \\ -(0.0975-0.0031Y+0.0002Y^2)X+ \\ +(0.0016+1.0\cdot10^{-5}Y+3.0\cdot10^{-6}Y^2)X^2 \end{gathered} \qquad (5)$$

The graphical representation of Eq. (5) within the range of experimental values of X and Y studied is shown in Fig. 3.

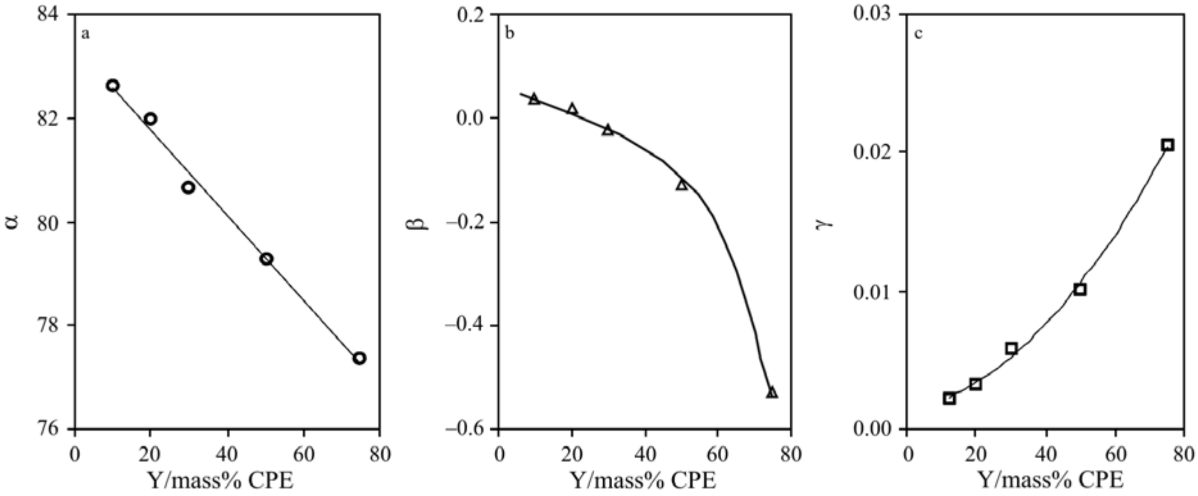

Fig. 2 Dependence of coefficients α, β and γ on the amount of CPE in PVC/CPE blends

Table 1 Comparison of experimental and calculated * values of the softening temperature of PVC/CPE blends at various values of the parameters *X* and *Y*

Composition, mass% CPE (*Y*)	Chlorine content, mass% Cl (*X*)						
	0	10.2	21.8	27.3	37.0	45.2	54.8
10	83.6 (83.2)	83.1 (82.5)	83.4 (82.2)	83.2 (82.3)	83.5 (82.7)	84.0 (83.3)	85.0 (84.4)
20	82.1 (82.2)	81.6 (81.3)	80.8 (81.8)	82.2 (81.2)	83.1 (82.0)	83.2 (83.0)	84.6 (84.8)
30	80.4 (81.3)	78.4 (79.8)	80.4 (79.4)	80.7 (79.6)	81.1 (80.6)	82.5 (82.2)	84.6 (84.8)
50	79.4 (79.3)	75.8 (75.8)	75.3 (74.1)	75.7 (74.3)	76.1 (75.9)	79.8 (78.7)	82.6 (83.6)
75	77.6 (76.9)	71.0 (70.7)	65.2 (64.3)	64.8 (64.0)	67.4 (66.3)	72.1 (71.1)	80.5 (80.0)

*The values of *t* in brackets were calculated using Eq. (5)

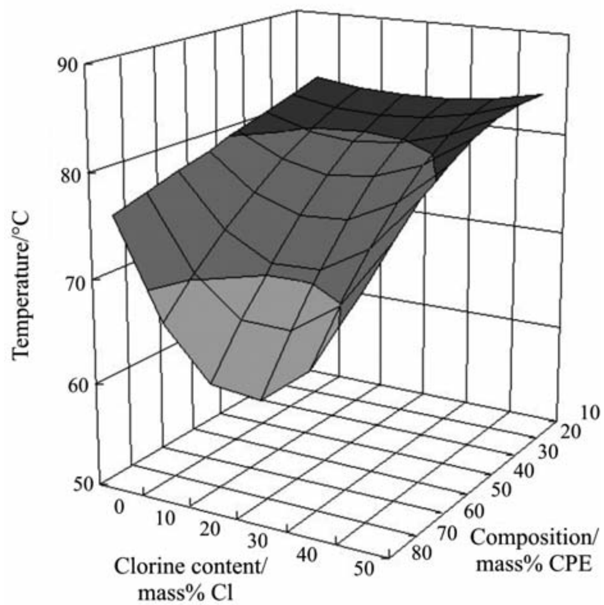

Fig. 3 Dependence of softening temperature of PVC/CPE blends on the degree of PE chlorination and the amount of CPE in the blends

Figure 3 shows the dependence as curved surface with complex configuration. Calculations were made to find *t* at different values of the parameters *X* and *Y* in order to check the possibility and reliability of the suggested empiric equation to describe the experimental data. The results obtained are presented for comparison in Table 1.

Using the data shown in Table 1, the percent deviation of softening temperature of PVC/CPE blends calculated with the empiric equation from the experimentally observed values can be found. Obviously, the relative error was not higher than ±1.5%. Following that, the empiric equation suggested describes precisely enough the experimental data and that these data had been correctly obtained during the experiment.

Conclusions

An empiric equation describing quite well the dependence of the softening temperature of PVC/CPE blends on the degree of CPE chlorination and its amount in the blends was derived. It can be successfully used for preparation of blends with preliminarily selected softening temperature and with mechanical properties and flowability consistent with practical requirements.

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Received: September 12, 2004
In revised form: March 17, 2005

DOI: 10.1007/s10973-005-6640-9