

Effect of Poly(vinyl chloride)/Chlorinated Polyethylene Blend Composition on Thermal Stability

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ABSTRACT: Blends of poly(vinyl chloride) (PVC) with different ratios of chlorinated polyethylene (CPE) were degraded by the thermogravimetric method under dynamic conditions (50–600°C) in an inert atmosphere. The effect of the miscibility and composition of the PVC/CPE blends on the thermal stability were investigated. DSC curves of the blends show neither a shift of the PVC glass transition temperature nor a shift of the CPE melting temperature, which means that these blends are heterogeneous. The characteristics of the TG curves were determined, some of which ($T_{1\%}$, $T_{5\%}$, Δm_1) can be used as indicators of the thermal stability of the blend. The apparent activation energy of PVC dehydrochlorination in the blends was also calculated. Comparison of the experimental TG curves and TG curves predicted by the additivity rule indicates the existence of the components' interaction in the PVC/CPE blends. The addition of CPE improves the thermal stability of PVC for all the investigated blends in the temperature range where α_{calc} is greater than α_{exp} . © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 166–172, 2000

Key words: CPE modifier; DSC curves; dynamic TG analysis; kinetic parameters; PVC/CPE blends; TG curves; thermal stability

INTRODUCTION

Poly(vinyl chloride) (PVC) is often mixed with other polymers to improve its properties of processibility and toughness. Chlorinated polyethylene (CPE) is a commonly used impact modifier of PVC and its compatibility depends upon the chlorine content and the distribution of the chlorine atoms on the polyethylene (PE) backbone. CPE with 36% chlorine is the optimum composition for obtaining the necessary features of impact, processing, and strength.¹ The morphology of the polymer blend has a significant effect on the impact behavior of the material. At a concentration of less than 13 mass % CPE in the PVC/CPE

blend, PVC is the continuous phase while CPE is the noncontinuous phase. Increasing the CPE concentration above 13 mass % reversed the phase distribution.²

Homopolymer PVC has a rather poor thermal stability.^{3–7} It starts degrading above glass transition temperature (ca. 80°C) by initiation (random at normal repeat units and at structural defects) followed by fast zip elimination of HCl and, at the same time, formation of conjugated double bonds (polyenes) in the backbone of the polymer. The dehydrochlorinated chains take part in the secondary processes, which results in volatile aromatic and aliphatic compounds. On the other hand, the saturated backbone of CPE results in a temperature stability that allows CPE to perform well continuously at temperatures of 150°C before it will start evolving HCl.⁸ The result of chain scission followed by dehydro-

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chlorination of the chlorinated part of the polymer chain are the several aromatic hydrocarbons (benzene, toluene, styrene, naphthalene) and series of aliphatic hydrocarbons, which are also the major pyrolysis products of PVC. Dehydrochlorination is also the dominant reaction in the CPE degradation; however, while the dehydrochlorination of PVC is an autocatalytic reaction, dehydrochlorination of CPE is statistical.⁹

It is well established that blending may greatly influence the thermal stability of the individual polymers.^{10–12} Under degradation conditions, considerable interactions may occur between components in the blend and/or their degradation products. The type of interaction will depend on the degree of miscibility of the components, as well as on their ratio in the blend. Therefore, the purpose of our work was to investigate the miscibility of PVC and CPE and the influence of the PVC/CPE blend composition on the thermal stability of PVC.

EXPERIMENTAL

The materials used in this study were suspension-grade PVC (K value 70; $\overline{M}_v = 80,650$; $[\eta]_{25^\circ\text{C}} = 93.45 \text{ cm}^3 \text{ g}^{-1}$ in cyclohexanone, chlorine content 56.0%) supplied by Inavinil (K. Sudurac, Croatia) and CPE (chlorine content 38.5%, heat of fusion 9.17 J g^{-1} , $[\eta]_{80^\circ\text{C}} = 133.53 \text{ cm}^3 \text{ g}^{-1}$ in chlorobenzene) supplied by Dow (Stude, Germany).

The PVC/CPE blends of different mass fractions of polymers (100/0, 90/10, 80/20, 70/30, 50/50, 30/70, and 0/100) were prepared by dry mixing the components (100 g) in the mixer and then melt blending on a laboratory roller mill at 160°C for 60 s. The thickness of the drawn-out foils were $0.25 \pm 0.05 \text{ mm}$.

The miscibility of the polymers was investigated in a Perkin–Elmer DSC-4 differential scanning calorimeter connected to a thermal analysis data station 3600 (TADS). The samples of 4–12 mg pressed in aluminum pans were heated at a rate of $10^\circ\text{C min}^{-1}$ from 30 to 150°C in the a nitrogen atmosphere (30 mL min^{-1}), kept at 150°C for 10 min, and cooled to 30°C at $10^\circ\text{C min}^{-1}$. The second run was registered. Indium was used as the standard for calibrating the temperature axis and the enthalpy output.

The thermal degradation of the blends (sample mass $2.0 \pm 0.2 \text{ mg}$) was carried out thermogravimetrically in the temperature range $50\text{--}600^\circ\text{C}$ using a Perkin–Elmer TGS-2 system with TADS.

The nitrogen flow rate was 30 mL min^{-1} and the heating rates were 2.5, 5, 10, 20, and $40^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

The miscibility of PVC and CPE was investigated using differential scanning calorimetry (DSC). The results of the investigation are shown in Figure 1 as normalized DSC curves (heat flux versus temperature). On the DSC curve of PVC, the glass transition¹³ (midpoint about 83.7°C) can be noticed, while on the CPE curve, the endotherm can be noticed with a peak maximum at 115.4°C as the melting temperature of crystallites and the heat of fusion about 4.8 J g^{-1} . The DSC curves of the PVC/CPE blends show the glass transition of PVC at about 83°C and the endotherm of the melting of CPE with a peak temperature about 115°C . The change of the blend composition of 90/10, 80/20 . . . 30/70 does not cause a shift of the PVC glass transition temperature or a shift of the CPE melting temperature. The amorphous PVC and partly crystal CPE are immiscible for all the investigated compositions of the blends in the temperature range $30\text{--}150^\circ\text{C}$, that is, PVC/CPE blends are heterogeneous.

The results of dynamic heating of the PVC/CPE blends are the thermogravimetric (TG) curves (mass loss versus temperature). These curves, obtained in the temperature range $50\text{--}600^\circ\text{C}$ for the heating rate $2.5^\circ\text{C min}^{-1}$ and the corresponding derivative thermogravimetric (DTG) curves (mass loss rate versus temperature) are shown in Figure 2(a,b). The TG curves scanned at higher heating rates (5, 10, 20, and $40^\circ\text{C min}^{-1}$) are shifted to higher temperatures. Both pure polymers, PVC and CPE, undergo through two basic degradation steps [Fig. 2(a), curves 1 and 7]. In the first one, the dehydrochlorination of the polymers occurs, and in the second one, the degradation of dehydrochlorinated residues and the formation of compounds of low molecular masses take place. The maximal rate of PVC dehydrochlorination is about six times greater than is the maximal rate of CPE dehydrochlorination [Fig. 2(b), curves 1 and 7]. The TG curves of the PVC/CPE blends [Fig. 2(a), curves 2–6] show also two basic degradation steps, but from the corresponding DTG curves, it is evident that the first basic step consists of two steps: The one with the peak temperature between 250 and 290°C is attributed to dehydrochlorination of PVC, and the one with the peak temperature at

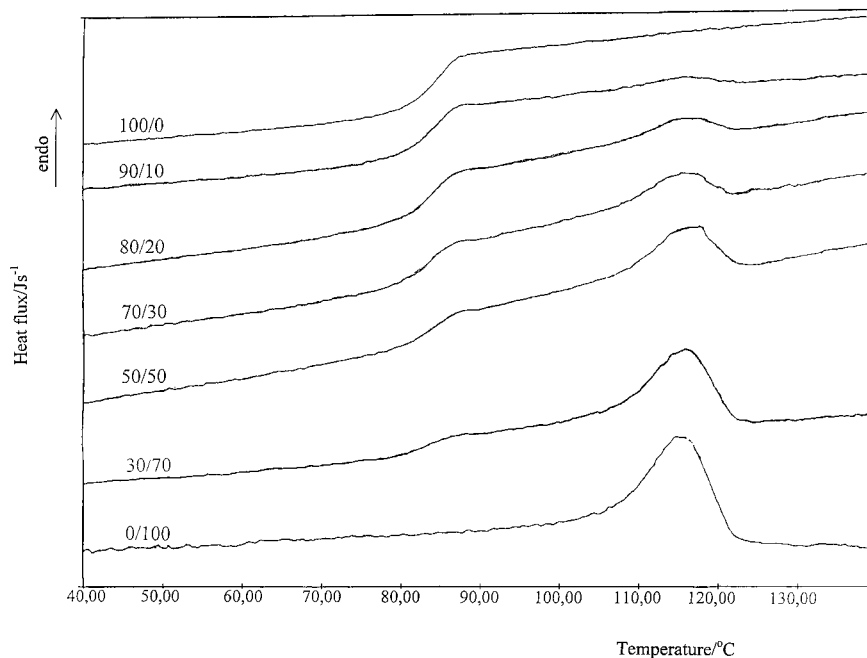


Figure 1 DSC curves (normalized) for PVC/CPE blends of different compositions; heating rate $10^{\circ}\text{C min}^{-1}$.

about 330°C is attributed to dehydrochlorination of CPE. The maximal rate of PVC dehydrochlorination in the blends decreases to half of the preceding value for each 20% addition of CPE and the corresponding peak temperature is shifted to higher values [Fig. 2(b), curves 2–6].

The characteristics of the TG curves^{13,14} for the first basic degradation step were obtained by applying the Perkin–Elmer Standard Program and they are the onset temperature (T_1^0), the temperature for a 1% degree of conversion ($T_{1\%}$), the temperature for a 5% degree of conversion ($T_{5\%}$), the temperature (T_1^m) and degree of conversion (α_1^m) at the maximal rate of PVC dehydrochlorination, and the mass loss at the end of the first basic degradation step (Δm_1). [The degree of conversion α is defined as the ratio $(m_0 - m)/m_0$, where m_0 is the initial and m the instantaneous mass of the sample during the degradation). These TG curve characteristics depend on the heating rate and on the composition of the PVC/CPE blends. In Figure 3, the dependence of the characteristics on the CPE ratio in the blend is shown for the heating rate $2.5^{\circ}\text{C min}^{-1}$. By increasing the CPE ratio from 0 to 70 mass %, the temperatures T_1^0 and $T_{5\%}$ are shifted to higher values for about 20°C , the T_1^m for about 30°C , while $T_{1\%}$ decreases for about 20°C . At the same time, Δm_1 decreases linearly from 61.3 to 49.7%

and the conversion α_1^m decreases from 19.5 to 9.3%. The characteristics of the TG curves scanned at other heating rates show an analogous behavior.

The peak temperatures T_1^m can be used for calculating of the kinetic parameters according the Kissinger equation¹⁵:

$$\frac{\beta E}{RT_m^2} = Zn(1 - \alpha_m)^{n-1} \exp\left(-\frac{E}{RT_m}\right)$$

where β is the heating rate; E , the apparent activation energy; Z , the preexponential factor; n , the “reaction order”; R , the gas constant; T_m , the thermodynamic temperature at the maximal mass loss rate (peak temperature); and α_m , the conversion at the corresponding peak temperature. The Kissinger method has shown that the product $n(1 - \alpha_m)^{n-1}$ equals 1 and is independent of the heating rate. The dependence of $\ln(\beta/T_m^2)$ versus $(1/T_m)$ represents a straight line with the slope $(-E/R)$ and the intercept $\ln(ZR/E)$ on the ordinate. In Figure 4, the Kissinger equation applied to the dehydrochlorination of PVC (curve 1), CPE (curve 7), and PVC in the PVC/CPE blends (curves 2–6) is shown. The calculated value of the apparent activation energy for PVC dehydrochlorination is 124.5 and $139.8 \text{ kJ mol}^{-1}$ for the de-

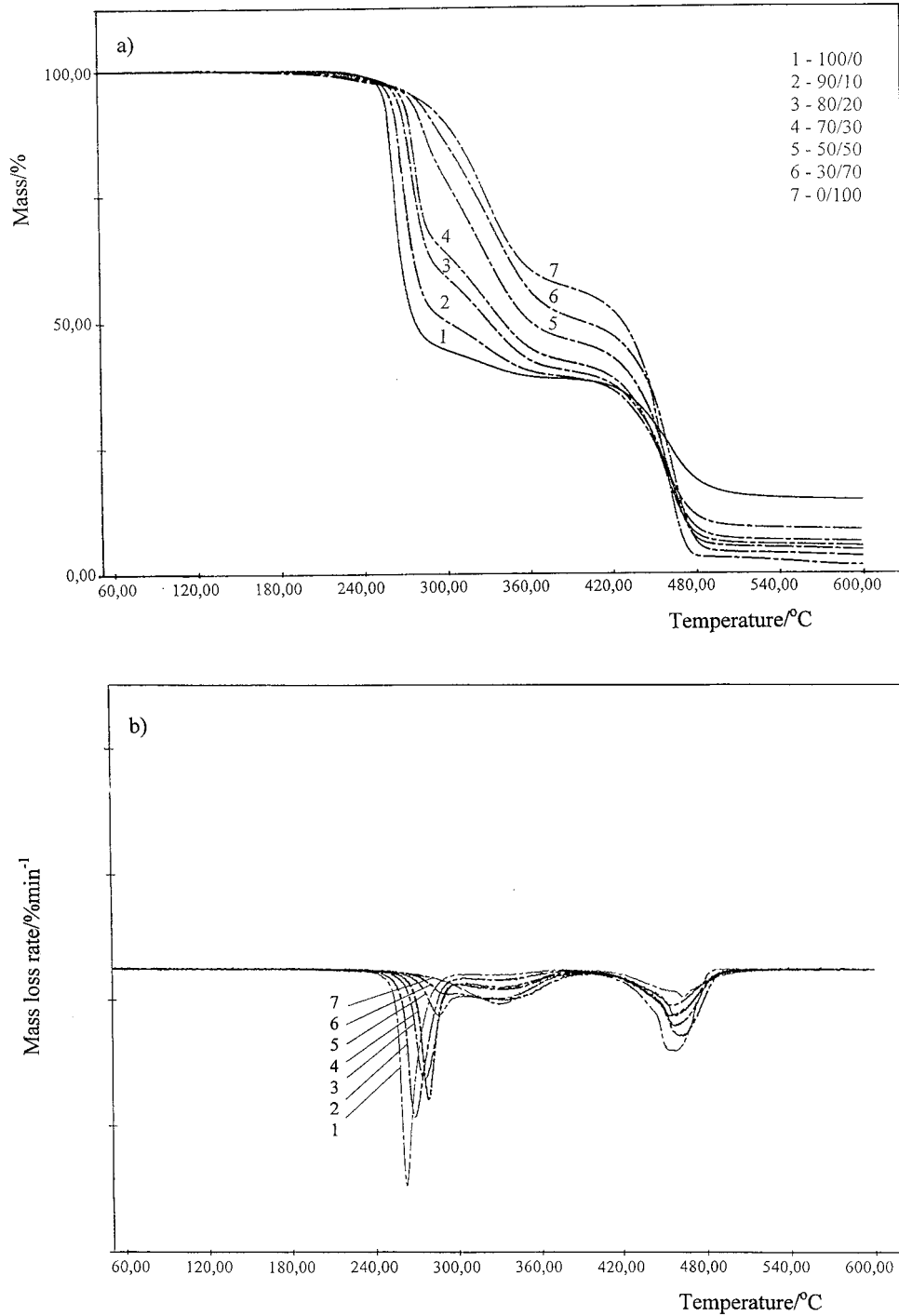


Figure 2 (a) TG and (b) DTG curves for PVC/CPE blends of different compositions; heating rate $2.5^{\circ}\text{C min}^{-1}$.

hydrochlorination of CPE. The values of the pre-exponential factor are $3.30 \times 10^9 \text{ s}^{-1}$ and $2.40 \times 10^9 \text{ s}^{-1}$, respectively. By changing the composition of the PVC/CPE blend, the activation energy for PVC dehydrochlorination changes

slightly ($111.3\text{--}130.0 \text{ kJ mol}^{-1}$) with a considerable change of the preexponential factor ($8.08 \times 10^7\text{--}1.96 \times 10^9 \text{ s}^{-1}$). However, the values of the activation energies and the logarithm of the pre-exponential factors for PVC dehydrochlorination

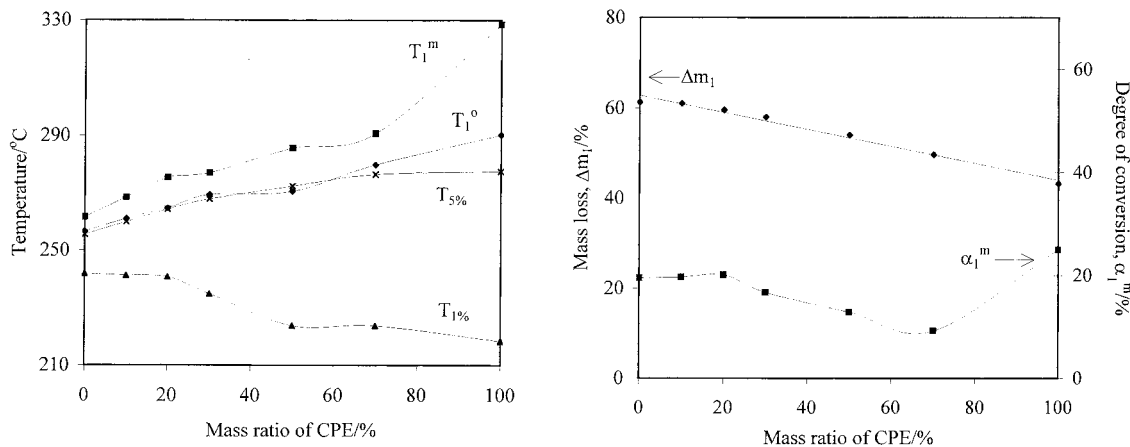


Figure 3 Effect of PVC/CPE blend composition on the first degradation step characteristics.

in the PVC/CPE blends are related to the linear relationship (Fig. 5), the so-called kinetic compensation effect (C.E.).^{16,17} It follows that not only the kinetic constants but also the slope of the C.E. plot can be related to the change of measuring parameters.^{18,19} The activation energy can be used only together with the values of the suitable preexponential factor and the reaction order as the criterion of the blend's thermal stability.²⁰

Comparing the experimental TG curves of the blend with the curves predicted on the basis of the TG curves of the unblended components (additivity rule) indicates the existence interactions in

the blends.^{12,21} In Figure 6, an example of the thermal degradation of the PVC/CPE 50/50 blend is shown. The behavior of this blend (curve 3) differs from that predicted (curve 4) on the basis of the individual polymers (curves 1 and 2). In this heterogeneous blend, the interaction does exist between the polymers. In the temperature range about 240–370°C (the first degradation step), the blend is more stable than was calculated according to the additivity rule. For example, at 300°C, the blend has lost approximately 10% mass less than predicted. At temperatures over 370°C, the blend shows less stability. The

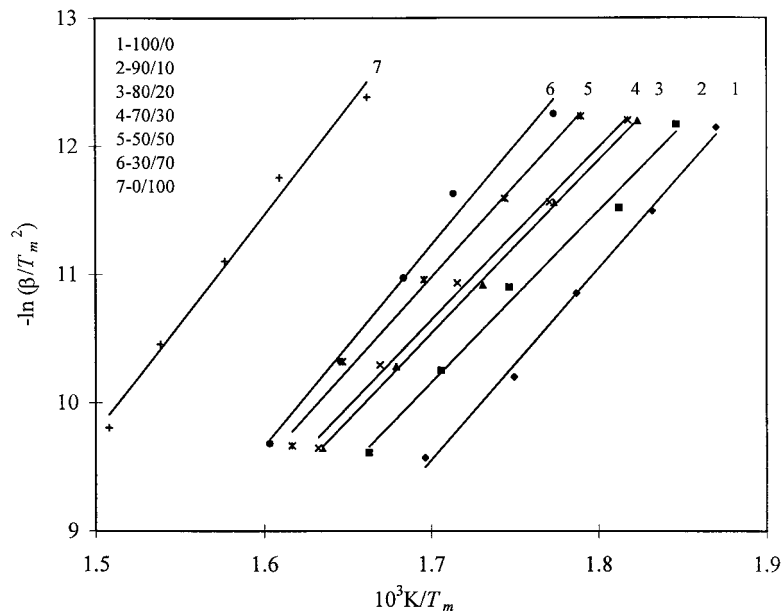


Figure 4 TG data plotted according to Kissinger's method.

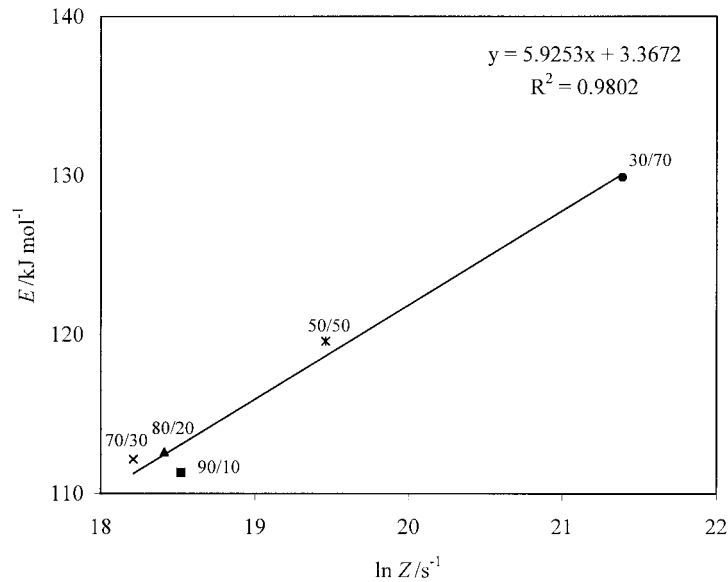


Figure 5 Kinetic compensation effect in thermal degradation of PVC/CPE blends of different compositions.

values $\Delta\alpha = (\alpha_{\text{exp}} - \alpha_{\text{calc}})/\alpha_{\text{calc}}$ were also calculated²² for all investigated blend compositions at a heating rate $2.5^\circ\text{C min}^{-1}$ and they are shown in Figure 7. The PVC/CPE blends are thermally more stable in the temperature range for which $\alpha_{\text{calc}} > \alpha_{\text{exp}}$, that is, $\Delta\alpha < 0$. If $\Delta\alpha > 0$, the PVC/CPE blends are less stable than would be predicted from the behavior of the pure polymers.

CONCLUSIONS

The PVC/CPE blends of all the investigated compositions are heterogeneous since their DSC

curves indicate two transition temperatures (about 80°C and about 115°C), which correspond to the PVC glass transition temperature and the CPE melting temperature. The homopolymers PVC and CPE are degraded in the temperature range $50\text{--}600^\circ\text{C}$ inertly through two basic steps: In the first degradation step, the dehydrochlorination of the polymers is quantitative. The maximal rate of PVC dehydrochlorination is achieved at the degradation conversion 19.5% and is six times greater than the maximal rate of CPE dehydrochlorination, which is achieved at the conversion of 25.0%.

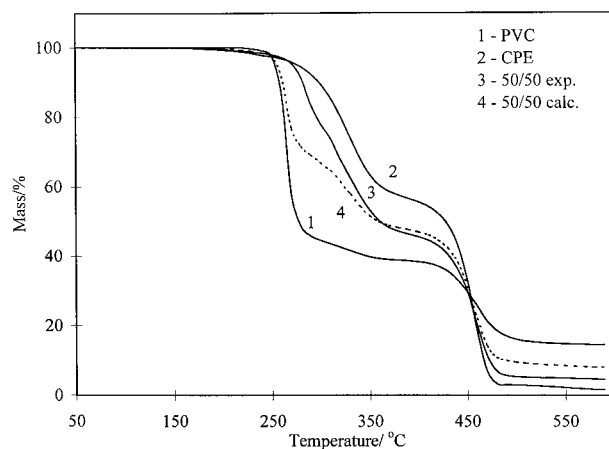


Figure 6 TG curves for (1) PVC, (2) CPE, (3) PVC/CPE 50/50 blend, and (4) predicted TG curve for PVC/CPE 50/50 blend; heating rate $2.5^\circ\text{C min}^{-1}$.

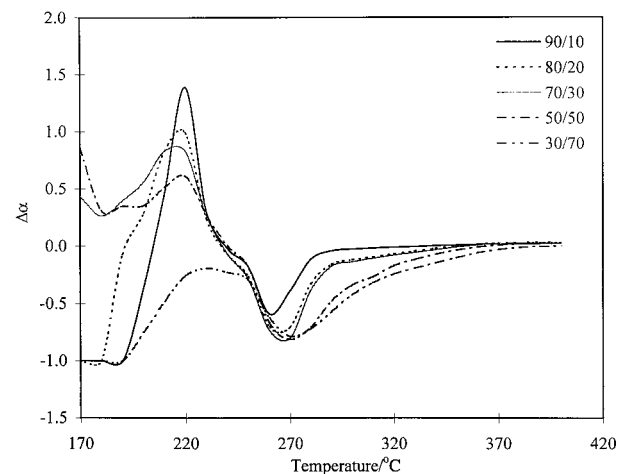


Figure 7 Dependence of the interaction $\Delta\alpha$ on the degradation temperature for PVC/CPE blends of different compositions; heating rate $2.5^\circ\text{C min}^{-1}$.

The degradation of PVC/CPE blends also occurs through two basic degradation steps at which the dehydrochlorination of polymers takes place in the first step, and the degradation of dehydrochlorinated sequences, in the second step. By increasing the quantities of CPE in the blends, the maximal rate of PVC dehydrochlorination decreases twice per each 20% of additional CPE, which is the result of the prevailing influence of statistical dehydrochlorination of CPE in the blends. At the same time, the peak temperature, at which the rate of PVC dehydrochlorination is maximal, shifts to higher values, while the corresponding peak temperature for CPE does not indicate any shift.

Some of the TG curve characteristics ($T_{1\%}$, $T_{5\%}$, Δm_1) may be regarded as the indicators of the PVC/CPE blend's thermal stability, while the temperature T_1^0 is not a good measure of thermal stability because of the tremendous dependence on the run conditions. Increasing the share of CPE (0–70%) in the blend, the temperature $T_{1\%}$ decreases, while the temperature $T_{5\%}$ increases. At the same time, the mass loss at the end of the first degradation step linearly decreases as the consequence of reducing the total quantity of chlorine in the blend and also due to the existence of interactions. In the temperature range associated with dehydrochlorination reactions (240–370°C), the mass loss occurs more slowly than expected on the basis of individual polymers. Generally, the thermal stability of PVC/CPE blends has been improved in relation to that expected in the temperature range where $\Delta\alpha < 0$. The apparent activation energy E and $\ln Z$ for the reaction of PVC dehydrochlorination in PVC/CPE blends of different compositions show the compensation dependence; therefore, the value E cannot be used as the criterion of the thermal stability.

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