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THERMOGRAVIMETRIC STUDY OF THE THERMAL STABILITY OF POLY(VINYL CHLORIDE)/POLY(α-METHYLSTYRENE-CO-ACRYLONITRILE) BLENDS

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ABSTRACT

The thermal stability of poly(vinyl chloride) (PVC)/poly(α-methylstyrene-co-acrylonitrile) blends was studied by thermogravimetry. The stability of the blends is different from that predicted by the additivity rule. In general, the blends are less stable at lower temperatures but more stable at higher temperatures than expected. The stability of PVC-rich blends is also affected by their miscibility behavior.

INTRODUCTION

It has been observed that the degradation behavior of a polymer in a binary blend is different from that of the pure polymer [1–3]. The degradation product of one polymer may stabilize or destabilize the other polymer in the blend. For example, depolymerization of poly(methyl methacrylate) (PMMA) in a poly(vinyl chloride) (PVC)/PMMA blend begins at 225 ° C, which is 50 ° C lower than the depolymerization temperature of PMMA [4,5]. The destabilization of PMMA by PVC arises from the attack of chlorine radicals on the backbone CH_2 or CH_3 groups of PMMA, leading to chain scission and depolymerization.

Several recent papers discussed the effect of miscibility on the thermal stability of polymer blends by comparing a miscible A/B blend and an immiscible A/C blend [6–8]. Since the degradation product of a polymer can affect the stability of the other polymer, the observed difference may not be attributable solely to the miscibility of the blend.

It is more appropriate to compare the thermal stability of a miscible A/B blend with that of an immiscible A/B blend. In an earlier communication, we reported that the thermal stability of a miscible bisphenol-A polycarbonate (PC)/PMMA blend is quite different from that of an immiscible PC/PMMA blend [9]. However, miscible PC/PMMA blends undergo phase separation at high temperatures and, therefore, the kinetics of phase

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separation may have some effect on the thermal stability of the miscible blend.

In this communication, we report a thermogravimetric study of the thermal stability of PVC/poly(α-methylstyrene-co-acrylonitrile) (αMSAN) blends. Kim et al. [10] reported that the miscibility of PVC/αMSAN blends depends on the method of preparation. Blends prepared by solution casting from tetrahydrofuran (THF) are immiscible, but those prepared by precipitation from the THF solutions in excess methanol are miscible. Furthermore, the miscible PVC/αMSAN blends do not undergo phase separation up to the degradation temperature [10]. Therefore, this system is ideal for studying the effect of miscibility on the thermal stability of polymer blends.

EXPERIMENTAL

Materials

PVC with a weight-average molecular weight (M_w) of 58,000 was obtained from Diamond Shamrock. αMSAN with a M_w of 160,000 was obtained from BASF; the acrylonitrile content is 30 wt.%. The two polymers were purified by precipitation from their THF solutions in excess methanol.

Preparation of blends

Miscible blends

Polymer mixture (0.5 g) was dissolved in 25 cm^3 of THF. The solution was then poured slowly into 250 cm^3 of methanol, with vigorous stirring. The precipitated polymer blend was washed with methanol and dried in vacuo, first at 70 ° C for 72 h and then at 110 ° C for 1 h.

Immiscible blends

Polymer mixture (0.1 g) was dissolved in 10 cm^3 of THF, and the solution was poured into a disposable aluminium dish. Solvent was allowed to evaporate slowly at room temperature over a period of 1–2 days. The film was then dried in vacuo, first at 70 ° C for 72 h and then at 110 ° C for 1 h.

Thermogravimetric measurements

The TG curves of various samples in a nitrogen atmosphere were obtained using a Du Pont 9900 thermal analysis system fitted with a 951 thermogravimetric analyzer. The nitrogen flow rate was 50 cm^3 min^{-1} and the heating rate was 20 ° C min^{-1}. Duplicate runs were made for each sample to check the reproducibility of the TG curves.

RESULTS AND DISCUSSION

The TG curves of PVC and αMSAN are shown in Fig. 1. PVC undergoes a two-stage degradation: dehydrochlorination followed by scission of the resulted polyene structure [2,3]. αMSAN undergoes a single-stage degradation. It has been suggested that the degradation of αMSAN is initiated either by proton extraction from the tertiary carbon or by random scission [11].

The TG curves of various PVC/αMSAN blends are shown in Figs. 2–4. Also shown in the figures are the predicted TG curves based on linear additivity of the TG curves of unblended PVC and αMSAN. The degradation behavior of the blends is clearly different from that predicted by the additivity rule. The blends are less stable at lower temperatures, implying that the dehydrochlorination of PVC in blends proceeds faster than expected from the additivity rule. Our recent study on the surface composition of PVC/αMSAN blends by X-ray photoelectron spectroscopy revealed that the surfaces of the blends, particularly the immiscible blends, were enriched with PVC [12]. For example, for a PVC/αMSAN (50 : 50) blend, the amounts of PVC in the surface regions are 70 and 84 wt.% for the miscible and immiscible blend, respectively. The enrichment of PVC on the surfaces of immiscible PVC/PMMA blends has also been reported [13]. It has been suggested that the dehydrochlorination of PVC involves a free radical mechanism [2]. The initiation is the liberation of chlorine atoms from labile centers and the propagation involves the reactions of chlorine atoms with adjacent methylene hydrogen atoms, leading to a conjugated structure. Because of the surface enrichment of PVC in PVC/αMSAN blends, more chlorine atoms are generated initially than expected. The chlorine atoms are then involved in various chain reactions. As a result, the weight loss arising

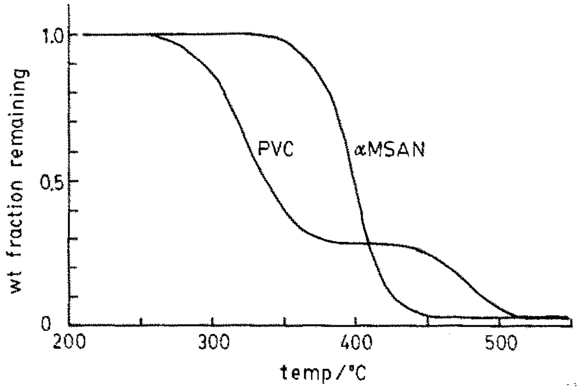

Fig. 1. TG curves of PVC and αMSAN.

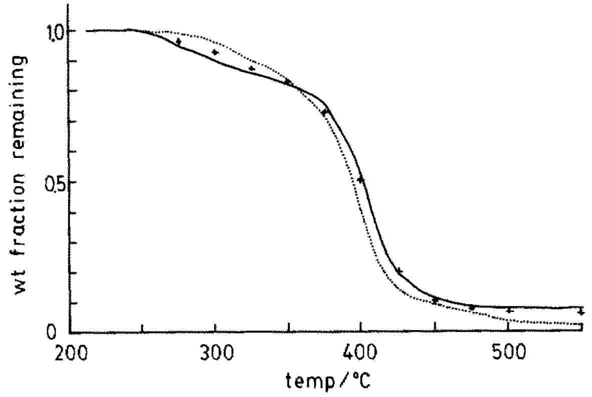

Fig. 2. TG curves of PVC/αMSAN (25:75) blends: ———, immiscible blend; +, miscible blend; (······), predicted by the additivity rule.

from dehydrochlorination of PVC in a blend is more than that predicted by the additivity rule based on the bulk composition.

On the other hand, the blends at higher temperatures are more stable than expected from the additivity rule. It has been pointed out that the conjugated structure produced in one polymer as a result of partial degradation can act as a 'radical sink' for radicals involved in the degradation of the other polymer [1,3,14]. For example, the degradation of polystyrene (PS) was retarded in a mixture of PS and partially degraded PVC [14]. It is plausible that the conjugated structure of dehydrochlorinated PVC serves as a radical sink for αMSAN, leading to a stabilization effect. This stabilization effect is most noticeable for PVC/αMSAN blends containing 50 and 75 wt.% of PVC.

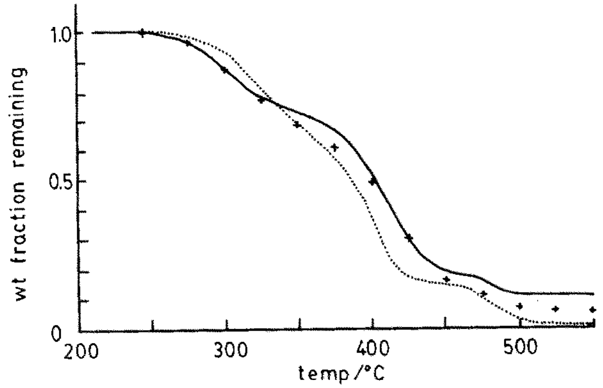

Fig. 3. TG curves of PVC/αMSAN (50:50) blends: ———, immiscible blend; +, miscible blend; ······, predicted by the additivity rule.

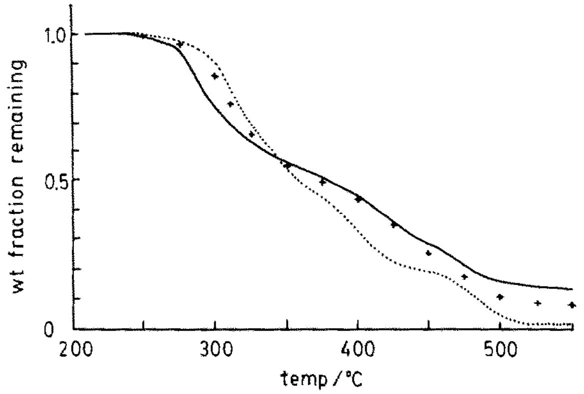

Fig. 4. TG curves of PVC/αMSAN (75:25) blends: ——, immiscible blend; +, miscible blend; ······, predicted by the additivity rule.

The miscibility appears to have no significant effect on the thermal stability of PVC/αMSAN (25:75) blends, in which PVC is the minor component. For PVC/αMSAN (50:50) blends, no significant effect is observed at the dehydrochlorination stage, but the immiscible blend appears to have a slightly better stability at higher temperatures.

The effect of miscibility is most pronounced for PVC/αMSAN (75:25) blends, in which PVC is the major component. The weight loss due to dehydrochlorination for the immiscible blend is more than that for the miscible blend. This in turn gives rise to a more conjugated structure in the immiscible blend to serve as a radical sink and thus to stabilize the αMSAN.

In summary, the thermal stability of PVC/αMSAN blends is different from that predicted by the additivity rule, and the effect of miscibility is most pronounced for blends with PVC as the major component.

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