Thermochimica Acta, 215 (1993) 291–296
Elsevier Science Publishers B.V., Amsterdam

Thermogravimetric study of the thermal stability of poly(vinyl chloride)/poly(vinyl acetate) blends

S.H. Goh

Department of Chemistry, National University of Singapore, Singapore 0511 (Singapore)

(Received 4 May 1992)

Abstract

The thermal stability of poly(vinyl chloride)/poly(vinyl acetate) blends was studied by thermogravimetry. Blends were prepared by solution-casting from tetrahydrofuran (THF) and 2-butanone (MEK). The stability of the blends is different from that predicted by the additivity rule. The dehydrochlorination and deacetylation of MEK-cast blends are faster than those of THF-cast blends because of the different degrees of mixing of the blends.

INTRODUCTION

The degradative behavior of a polymer in a binary blend is generally 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. A binary polymer blend can be a homogeneous miscible blend or a phase-separated immiscible blend depending on the thermodynamics of polymer–polymer interaction [4–6]. The effects of miscibility on the thermal stability of some polymer blends have been discussed in several recent papers [7–9]. In these studies, comparison was made between a miscible A/B blend and an immiscible A/C blend. We have recently reported that the thermal stability of a miscible A/B blend is quite different from that of an immiscible A/B blend [10, 11].

Poly(vinyl chloride) (PVC) is miscible with poly(ethylene-co-vinyl acetate) over a certain copolymer composition range, although there is disagreement as to the width of the miscibility range [12–17]. Several of these studies also reported that PVC is immiscible with poly(vinyl acetate) (PVAc). However, Bhawagar et al. [18] reported that the immiscibility of PVC/PVAc blends arises from a powerful solvent effect. PVC/PVAc blends cast from tetrahydrofuran (THF) are phase-separated, whereas those cast from 2-butanone (MEK) are miscible. Recently, De Jager and

---

Correspondence to: S.H. Goh, Department of Chemistry, National University of Singapore, Singapore 0511, Singapore.

Ten Brinke [19] re-examined the miscibility of PVC/PVAc blends and reported that both THF-cast and MEK-cast blends are immiscible.

Jamieson and McNeill [20] studied the thermal stability of PVC/PVAc blends by thermal volatilization analysis and direct measurements of acid production. The two polymers degrade in different temperature regions when heated separately, but the blend gives both HCl and CH_3COOH simultaneously. Thus, PVC and PVAc each mutually catalyze the degradation of the other. Moskala and Lee [9] studied the thermal stability of THF-cast PVC/PVAc blends by thermogravimetry. They also observed that the blends lose weight more rapidly than expected from the additivity rule. However, these two studies did not deal with the effect of miscibility. In the present work, the thermal stability of THF-cast and MEK-cast PVC/PVAc blends is studied by thermogravimetry.

EXPERIMENTAL

Materials

PVC with a weight-average molecular weight (M_w) of 58 000 was obtained from Diamond Shamrock; it was purified by precipitation from its THF solution in excess methanol. PVAc with an M_w of 124 000 was obtained from Union Carbide; it was purified by precipitation from its THF solution in excess *n*-hexane.

Preparation of blends

The polymer mixture (0.1 g) was dissolved in 10 cm^3 of THF or MEK, and the solution was poured into a disposable aluminum 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 60°C for 1 week and then at 110°C for 1 h.

Thermal analysis

The glass transition temperatures (T_g) of samples were measured with a Perkin–Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C min^{-1}. Each sample was scanned between −10 and 110°C several times to check the reproducibility of the T_g values. The initial onset of the change of slope of the DSC curve was taken as T_g.

The thermogravimetric curves of various samples in a nitrogen atmosphere were obtained using a Du Point 9900 thermal analysis system fitted with a 951 thermogravimetric analyzer. The nitrogen flow rate was 75 $cm^3\,min^{-1}$ 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

As mentioned earlier, the miscibility of PVC/PVAc blends is still a subject of controversy. Bhawagar et al. [18] showed the DSC curves of THF- and MEK-cast PVC/PVAc (25:75) blends. The THF-cast blend showed two glass transitions, at 32 and 75°C. The MEK-cast blend showed one glass transition, at 42°C, indicating miscibility. However, the glass transition behavior of blends of other compositions was not mentioned. De Jager and Ten Brinke [19] reported that two glass transitions were observed for all the THF- and MEK-cast blends, but they did not show the DSC curves.

Figure 1 shows the DSC curves of MEK-cast PVC/PVAc blends. The blend containing 25 wt% of PVC shows only one glass transition at 40°C. The T_g value is slightly higher than that of 37°C for purified PVAc. The present result supports the claim by Bhawagar et al. that the MEK-cast PVC/PVAc (25:75) blend is miscible. On the other hand, two glass transitions were observed for blends containing 50 and 75 wt% of PVC. The lower T_g values of the two blends are the same as that of the blend containing 25 wt% PVC. However, the upper T_g values of 70 and 65°C are substantially lower than that of 84°C for purified PVC. The results indicate that, even though blends containing 50 and 75 wt% of PVC are phase-separated, both PVC and PVAc are present in each of the two phases.

Figure 2 shows the DSC curves of THF-cast blends. Each of the blends shows two glass transitions, indicating phase separation. The T_g values are 38 and 76, 38 and 76, and 36 and 70°C for blends containing 25, 50 and 75 wt% of PVC, respectively. The upper T_g values also indicate the presence of PVAc in the PVC-rich phase, but the degree of mixing is not as high as that in the corresponding MEK-cast blend.

The TG curves of PVC and PVAc are shown in Fig. 3. Both polymers undergo a two-stage degradation: dehydrochlorination followed by chain

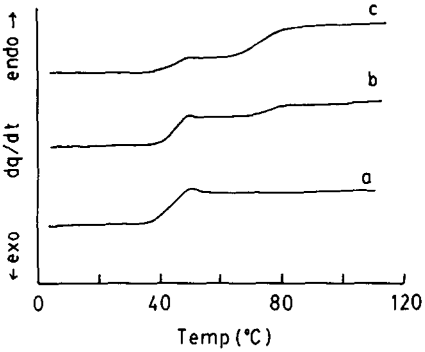

Fig. 1. DSC curves of MEK-cast PVC/PVAc blends: (curve a) 25% PVC; (curve b) 50% PVC; (curve c) 75% PVC.

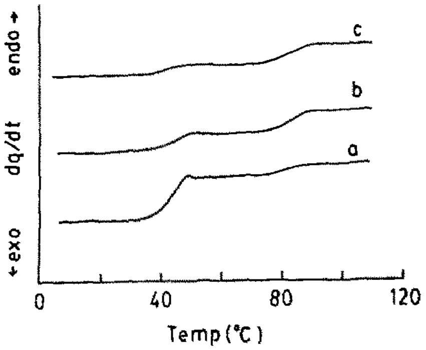

Fig. 2. DSC curves of THF-cast PVC/PVAc blends: (curve a) 25% PVC; (curve b) 50% PVC; (curve c) 75% PVC.

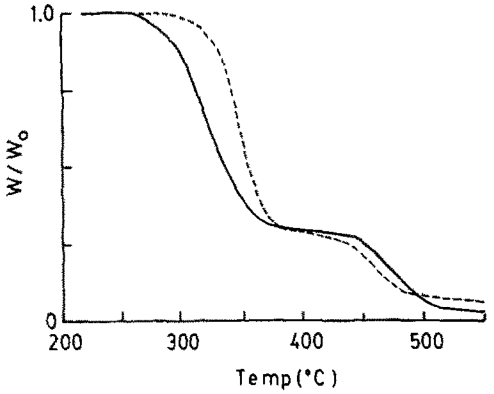

Fig. 3. TG curves of polymers: (——) PVC; (- - - -) PVAc.

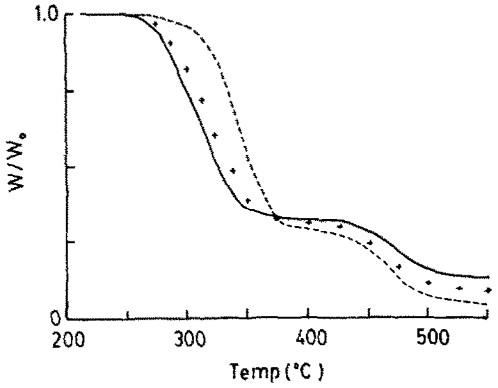

Fig. 4. TG curves of PVC/PVAc (25:75) blends (——) MEK-cast; (+) THF-cast; (- - - -) predicted by additivity rule.

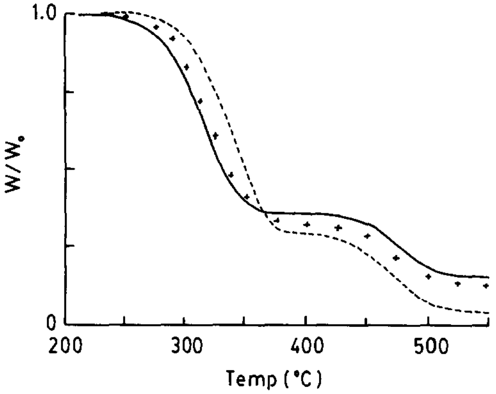

Fig. 5. TG curves of PVC/PVAc (50:50) blends (——) MEK-cast; (+) THF-cast; (----) predicted by additivity rule.

scission of the resulting structure for PVC and loss of acetic acid followed by chain scission for PVAc [2]. The TG curves of various PVC/PVAc blends are shown in Figs. 4–6. Also shown in the figures are the predicted TG curves based on linear additivity of the TG curves of unblended PVC and PVAc. The degradation behavior of the blends is different from that predicted by the additivity rule, in agreement with previous findings of other workers [9, 20]. The blends are less stable at lower temperatures but show better stability at higher temperatures. The poorer stability of the blends at lower temperatures reflects the mutual catalytic effect of degradation of the two polymers. Hydrogen chloride catalyzes the loss of acetic acid from PVAc; acetic acid catalyzes the loss of hydrogen chloride from PVC. Concerning the better stability of the blends at higher temperatures, it has been pointed out that the conjugated structure produced in one polymer can serve as a "radical sink" for radicals involved in the degradation of the other polymer [1, 3]. Since the

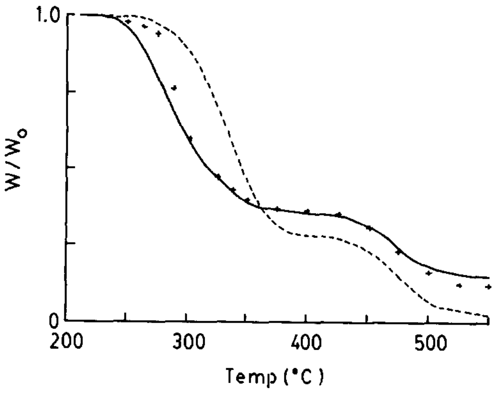

Fig. 6. TG curves of PVC/PVAc (75:25) blends (——) MEK-cast; (+) THF-cast; (----) predicted by additivity rule.

mechanism of degradation is considered to be of radical type for PVC and molecular type for PVAc [2], the conjugated residues of partially degraded PVC and PVAc help to stabilize PVC.

The TG curves also show that MEK-cast blends lose weight faster than THF-cast blends at lower temperatures. If the two polymers are in intimate contact with each other, as in a homogeneous miscible blend, the mutual catalysis of degradation will be more efficient, causing the blend to lose weight more readily than an immiscible blend. The T_g results reveal that the two polymers have a higher degree of mixing in an MEK-cast blend than in a THF-cast blend. Thus, the faster weight loss of MEK-cast blends at low temperatures is consistent with the higher degree of mixing of the blends. It is also noted that MEK-cast blends containing 25 and 50 wt% of PVC show better stability at higher temperatures than the corresponding THF-cast blends.

REFERENCES

1 I.C. McNeill, in N. Grassie (Ed.), Developments in Polymer Degradation, Applied Science, London, 1977, Vol. 1, Chap. 6.
2 N. Grassie and G. Scott, Polymer Degradation and Stabilization, Cambridge University Press, Cambridge, 1985, Chap. 2.
3 I.C. McNeill, in R.A. Pethrick (Ed.), Polymer Yearbook 3, Harwood Academic, Chur, 1986, p. 141.
4 D.R. Paul, in D.J. Walsh, J.S. Higgins and A. Maconnachie (Eds.), Polymer Blends and Mixtures, Martinus Nijhoff, Dordrecht, 1985, Chap. 1.
5 L.A. Utracki, Polymer Blends and Alloys, Hansers, Munich, 1989.
6 M.M. Coleman, J.F. Graf and P.C. Painter, Specific Interactions and the Miscibility of Polymer Blends, Technomic Publishing, Basel, 1991.
7 L. Goulet and R.E. Prud'homme, Eur. Polym. J., 22 (1986) 529.
8 J.I. Eguiazabal and J.J. Iruin, Mater. Chem. Phys., 18 (1987) 147.
9 E.J. Moskala and D.W. Lee, Polym. Degrad. Stabil., 25 (1989) 11.
10 S.H. Goh, Thermochim. Acta, 153 (1989) 423.
11 S.H. Goh, Thermochim. Acta, 173 (1990) 229.
12 C.F. Hammer, Macromolecules, 4 (1971) 69.
13 D. Feldman and M. Rusu, Eur. Polym. J., 10 (1974) 41.
14 C. Elmqvist and S.E. Svanson, Eur. Polym. J., 11 (1975) 789.
15 E. Nolley, D.R. Paul and J.W. Barlow, J. Appl. Polym. Sci., 23 (1979) 623.
16 M.M. Coleman, E.J. Moskala, P.C. Painter, D.J. Walsh and S. Rostami, Polymer, 24 (1983) 1410.
17 C.A. Cruz-Ramos and D.R. Paul, Macromolecules, 22 (1989) 1289.
18 D.E. Bhawagar, C.J. Serman, P.C. Painter and M.M. Coleman, Macromolecules, 22 (1989) 4654.
19 H. De Jager and G. Ten Brinke, Macromolecules, 24 (1991) 3454.
20 A. Jamieson and I.C. McNeill, J. Polym. Sci. Polym. Chem. Ed., 14 (1976) 387.