STUDIES ON THE THERMAL CHARACTERISTICS OF POLYMER ALLOYS

A. N. Eboatu*, B. Animashaun, S.T. Spiff and F. M. Abdulrahman

CHEMISTRY DEPARTMENT, UNIVERSITY OF SOKOTO, NIGERIA

PVC: polystyrene alloys of varying compositions were prepared by the film casting technique. Thermogravimetric analysis of these materials showed that the decomposition patterns of the alloys are quite different from those of the constituent polymers. These results are explained in terms of polymer interaction phenomena.

The blending of two or more polymers to form novel materials is an operation that usually reduces composition non-uniformity [1]. This has important technological implications, as chemical, physical and mechanical properties, as well as appearance, all depend upon composition uniformity. In fact, it is known [2-4] that these alloys very often exhibit a synergism in properties achievable only through this technique. Blending methods usually [5] involve solid - to - liquid, solid - to -solid or liquid - to - liquid mixing.

The two polymers chosen for this investigation have extensive industrial and household applications. In a recent article [6], we showed by means of DSC that PVC and polystyrene (PSt) are a compatible macromolecular pair (single T_g when blended). The present paper reports the results of TG studies on this blend.

Experimental

Materials

The PVC and PSt samples were supplied by Aldrich Ltd., and have intrinsic viscosities of 0.75 and 0.86, respectively. Analytical grade tetrahydrofuran (TFH) solvent was procuced from BDH.

Methods

Mixtures of PVC and PSt solutions with varying compositions were made in TFH. Equal volumes of these mixtures were in turn cast as films, at 38° from the same mercury surface. Thermogravimetric analyses of these samples were carried out with the Mettler TA 3000 system. Each sample was subjected to a heating programme from 100° to 700° at a rate of 10 deg/min in air atmosphere. With the aid of a computer incorporated into the machine, step analyses of weight losses and peak temperatures of degradation were performed. At the end of heating, the material left in the TG crucible was regarded as char. The effects of the film composition on the
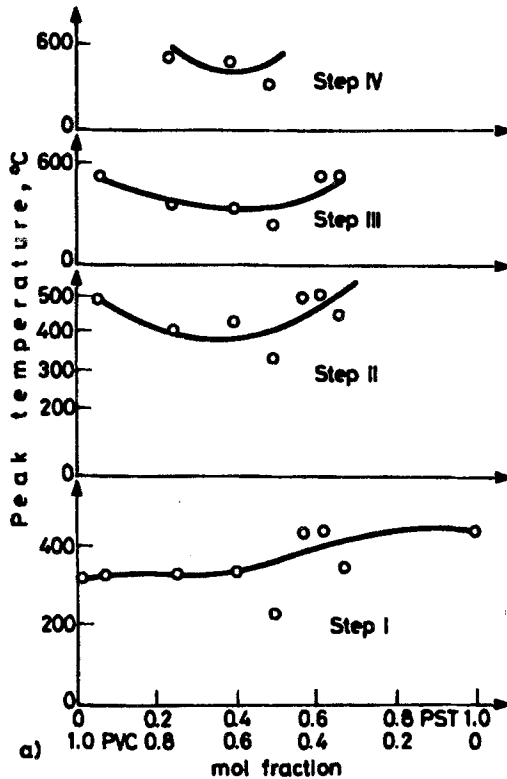

Fig. 1a Representative thermal curves I (PVC); II (Blend); III (PSt). Effect of alloy composition on peak temperature of degradation

weight losses and the peak temperatures of degradation and char were therefore examined.

Results and discussion

Representative thermal curves of the pure polymers and of the blend are illustrated in Fig. 1. From this and Fig. 1a, the following facts are evident: Qualitatively, it is notable that the decomposition pattern of the blend is quite different from that of either component: whereas the pure polymers
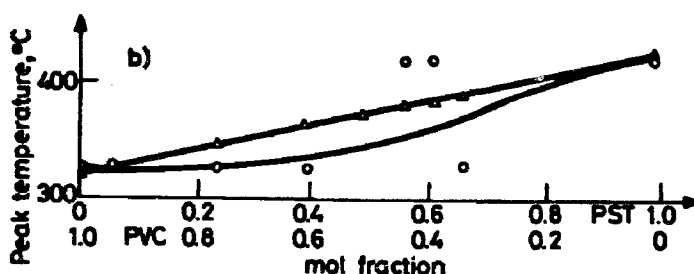

Fig.1b Representative thermal curves I (PVC); II (Blend); III (PSt).Effect of alloy composition on peak temperature of degradation (first step only) o--o--o (observed) Δ--Δ--Δ (calculated)

each show one-step decomposition, the polyblends in some cases have as many as 5 steps. It is also observed that, at least for the first step, blending does not drastically change the peak temperature of degradation.

The above observations can be explained as follows: PVC degradation is known [5] to be accompanied by cross-linking, resulting from dehydrohalogenation reactions. This means that the original polyblend is converted into an interpenetrating polymer network (I.P.N.) by topological linkage of the dehydrohalogenated PVC and PSt or a product of PSt degradation. It is therefore envisioned that it is this highly entangled species, whose complexity is expected to increase with temperature, that is progressively degraded in the various steps.

Figures 1b, 2b and 3b were constructed by using the well-known rule of mixtures [7] to calculate the theoretical values (1st step only). In Fig. 1b, it is seen that there is a slight but perceptible decrease in the observed peak temperatures as compared to the hypothetical values. This observation is similar to that of Congdon et al. [8], who studied the thermal stability of a PVC:ABS polyblend. As in their case, it is felt that the reduction in thermal
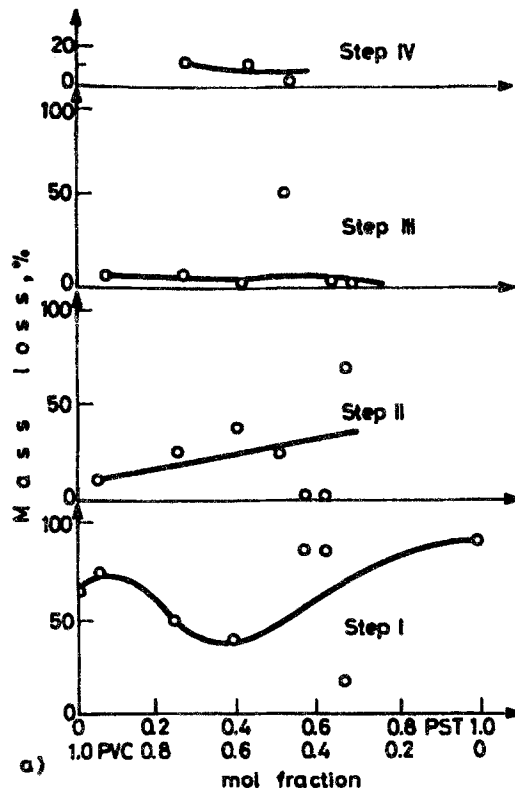
Fig. 2a Effect of alloy composition on percentage weight loss

stability on blending is attributable to shear heating effects, which may accelerate dehydrohalogenation and the subsequent cross-linking of PVC.

It is seen in Fig. 2a that, as in the case of peak temperatures, the thermal stability of the polyblends depends upon the species under consideration. The greatest weight loss is observed in the first step and the loss decreases progressively in the higher steps, indicating that the material(s) resulting from the initial I.P.N. formations tends to be more thermally stable. This is not unexpected, as the blend becomes richer in carbon skeleton due to the increased dehydrohalogenation and/or dehydration with rise in temperature. Nonetheless, it is clear that in the first step, where the bulk of the degradation occurs, the blends are less stable than the pure polymers. This is due to the reasons already adduced. A comparison of the theoretical and the observed weight losses presents a rather complicated picture. All that is ob-
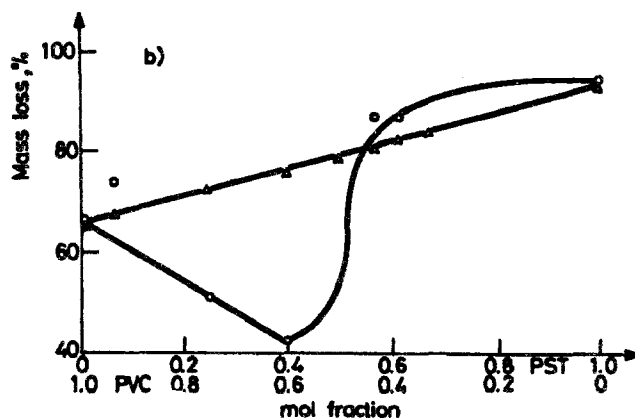
Fig. 2b Effect of alloy composition on percentage weight loss (1st step only) o--o-- (observed);
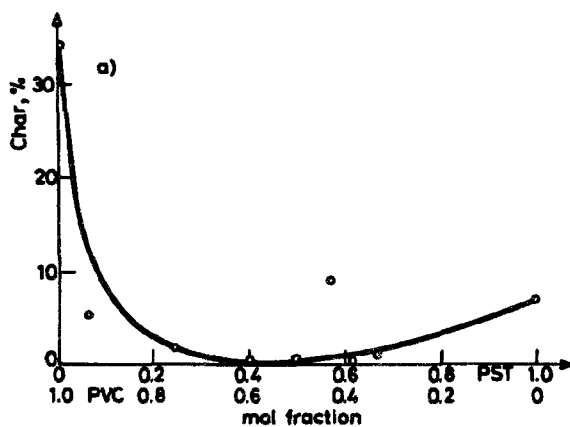Δ--Δ--(calculated)

Fig. 3a Effect of alloy composition on char formation

vious is that, as the alloy becomes richer in PSt, the more stable it tends to
be.

Figure 3a illustrates the effect of the blend composition on the amount of
char left at the end of the heating programme. It is obvious that less material
is volatilized from PSt than from PVC, while the blends leave less char than
either. As has already been observed (Fig. 2a), the bulk of the volatilization
process occurs in the first step. It is possible to envisage some synergistic
chemical interaction, apart from mere I.P.N. formation, which might lead to
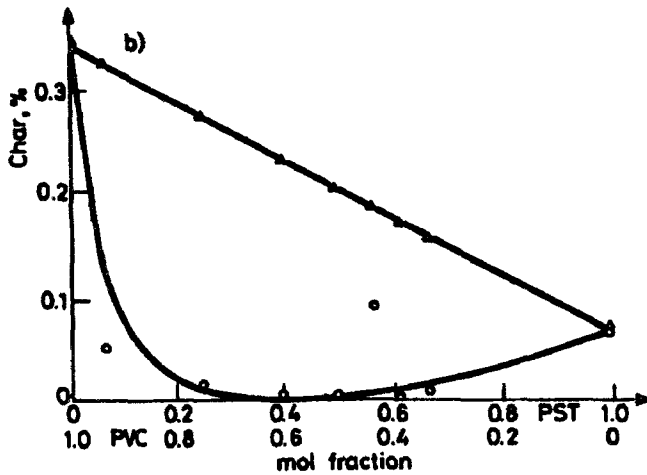
Fig. 3b Effect of alloy composition on char formation o--o--o--(observed) Δ--Δ--(calculated)

the premature degradation of PSt. Thus, it is seen (Fig. 3b) that the observed char left is far lower than the calculated values. Alternatively, since the blends, unlike the pure samples, are degraded progressively in each step, it is expected that they will leave less char at the end of heating than do the pure components.

Conclusions

The following conclusions can be drawn from this investigation:

i/ PVC and PSt form intimate mixtures, the components of which are not separated even at high temperatures.

ii/ Blending leads to degradation taking place in discrete stages.

iii/ The alloying of PVC and PSt does not seriously alter the peak temperature of degradation in the first step.

iv/ The component polymers lose weight only in one step. On the other hand, for the blends, though the weight loss is maximum in the first step. observable weight losses do occur during subsequent stages.

References

1 T. Zeher and G. G. Costas, Principles of Polymer Processing, John Wiley & Sons, N.Y., (1979) p. 196.
2 A. J. Curtis, M. J. Covitch, D. A. Thomas and L. H. Sperling, Polym. Eng. Sci., 12 (1972) 101.
3 S. C. Kim, D. Klempner, K. C. Frisch, H. L. Frisch and H. Ghiradella, Polym. Eng. Sci., 15 (1975) 339.
4 S. C. Kim, D. Klempner, K. C. Frisch and H. L. Frisch, J. Appl. Polym. Sci., 21 (1977) 1289.
5 B. D. Gessner, J. Appl. Polym. Sci., 9 (1965) 370.
6 A. N. Eboatu, D. Olojo and M. Momo, Accepted for publication 3rd March 1988 in J. Appl. Polym. Sci.
7 L. E. Nielson, Mechanical Properties of Polymers and Composites, Marcel Dekker Inc. N.Y., (1974) p. 397.
8 W. L. Congdon, H. E. Bair and S. K. Khanna, Polymer Alloys, Plenum Press, N.Y. 1980., Vol. II. pp 255-262.

Zusammenfassung - Mittels eines Feinfoliengiebverfahrens wurden PVC-Polystyrol-Mischungen verschiedener Zusammensetzung gefertigt. Eine thermogravimetrische Analyse dieser Stoffe zeigte, daß sich der Typ der Zersetzung der Mischungen vollständig von dem der reinen Komponenten unterscheidet. Diese Ergebnisse werden als Folge von Polymer-wechselwirkungen interpretiert.