

Thermal Degradation of Ternary Blends of Poly(ϵ -caprolactone)/Poly(vinyl acetate)/Poly(vinyl chloride)

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Received 11 September 2003; accepted 29 February 2004

DOI 10.1002/app.20587

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The thermal degradation of ternary blends of poly(ϵ -caprolactone) (PCL), poly(vinyl acetate) (PVAC), and poly(vinyl chloride) (PVC) was studied using a thermogravimetry analyzer under dynamic heating in flowing nitrogen atmosphere. PCL degraded in a single stage, whereas the PVAC and PVC degraded in two stages during which acid is released in the first stage followed by backbone breakage in the second stage. The addition of PVC to either PCL or PVAC affected the thermal stability of the blend, whereas the addition of PVAC to PCL did not alter the thermal stability of the blend. In ternary blends, the addition of PVC affected the degradation of PVAC but did not influ-

ence the degradation of PCL in the range investigated. The increased addition of PCL to the binary blends of PVC/PVAC decreased the extent of thermal instability of PVAC because of the addition of PVC. The addition of even 10% PVAC to the PCL/PVC blend removed the thermal instability of PCL resulting from the addition of PVC and can be attributed to the ease of chlorine or hydrogen chloride capture of PVAC over PCL. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1378–1383, 2004

Key words: thermal properties; degradation; blends; acid removal; olefinic breakage

INTRODUCTION

When a binary polymer blend is degraded thermally, it is often found that the behavior of one or both polymers is modified.^{1–4} The low thermal stability and nonbiodegradability of poly(vinyl chloride) (PVC) demands the modification by either blending with other more stable polymers or addition of thermal stabilizers.^{1,2} There are many studies on the thermal stability of PVC with thermal stabilizers such as AlCl_3 , metal carboxylates, and organotin compounds.² PVC degrades in two stages. In the first stage, dehydrochlorination occurs, around 280°C, leading to the formation of a polyolefinic backbone, which in turn decomposes to lower molecular weight fragments at higher temperatures, around 450°C, by structural disintegration.^{1,2,5–7} Recently it was shown that the addition of PVC to poly(vinyl acetate) (PVAC) significantly affects the thermal stability of PVAC¹ and the formation of HCl during the dehydrochlorination of PVC catalyzes the degradation of PVAC and PVC. Various metal oxides did not show any effect on the thermal degradation of PVAC, whereas even a small addition of

PVC to the metal oxide/PVAC composite affected the thermal degradation of PVAC. This effect was attributed to the formation of metal chloride during the degradation of PVC that catalyzes the reaction.¹ PVC forms a completely miscible system with poly(ϵ -caprolactone) (PCL) because of the hydrogen bonding type of interaction.^{4,8–10} However, there are no published studies in the literature on thermal degradation of the PCL/PVC system.

In an attempt to increase the mechanical properties of PCL, the tensile property of the PCL/PVAC blend was investigated and the synergistic enhancement in the tensile strength over that of the pure polymers was observed.¹¹ The PCL/PVAC blends also showed a strong decrease in the enzymatic degradation of PCL for even less than 10% addition of PVAC.¹² Such a dramatic decrease in the biodegradation and synergism in the mechanical properties are observed for such polyesters such as PCL,^{11,12} poly(lactide),¹³ poly(ethylene oxide),¹⁴ and poly(hydroxybutyrate)¹⁵ with PVAC. This has been attributed to the hydrogen-donating and -accepting nature of the polymers and they form a completely miscible system.^{11–15} Surprisingly, the thermal degradation behavior of PCL/PVAC blends is ideal and follows the simple additive rule of polymer decomposition.¹¹ PCL degrades in a single stage, around 385°C, with simultaneous random scission and depolymerization from the chain end by specific chain scission.¹⁶ Because of the structural similarity of PVAC to PVC, PVAC degrades in two stages

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Contract grant sponsor: Department of Science and Technology, India.

Contract grant sponsor: General Electric Company, USA.

involving deacetylation ($\sim 328^\circ\text{C}$) followed by the structural disintegration of polyolefinic backbone ($\sim 450^\circ\text{C}$).^{1,17,18} Because of such interesting properties of PCL/PVAC blends, the thermal degradation of ternary blends formed by the addition of PVC to PCL/PVAC binary blends was investigated in an inert flowing nitrogen atmosphere under dynamic heating and compared with the degradation of binary blends.

EXPERIMENTAL

Materials

Poly(ϵ -caprolactone) (Sigma Aldrich, Mumbai, India), poly(vinyl acetate) (synthesized in the lab), poly(vinyl chloride) (Dhanpha Chemicals, Mumbai, India), and tetrahydrofuran (S. D. Fine Chemicals, Mumbai, India) were used.

Sample preparation

The solution-blending method was adopted for making the blends. In this method, the polymers in the required proportions are dissolved in a common solvent and the solvent is evaporated at low temperatures to avoid oxidative degradation. This forms films of the polymer blends (either binary or ternary). Further details of the solution blending are presented elsewhere.^{1,11}

Thermogravimetry studies

Thermal degradation studies were conducted in inert flowing nitrogen atmosphere ($150\text{ cm}^3/\text{min}$) under dynamic heating mode at the heating rate of $5\text{ K}/\text{min}$ in a thermogravimetry analyzer (TGA, Pyris Diamond; Perkin Elmer Cetus Instruments, Norwalk, CT). All the experiments were conducted from room temperature to 600°C and the reference material used was α -alumina. The sample weights were taken in the range of 25 to 30 mg.

Gel permeation chromatography analysis

The pure polymers were characterized by number-average molecular weight and polydispersity. The GPC consisted of an isocratic Waters (Milford, MA) model 501 pump, three styragel columns, a differential refractive index detector, and recording systems. Tetrahydrofuran (THF) was used as eluent for the analysis at the flow rate of $1\text{ cm}^3/\text{min}$ at 50°C . Samples were injected using a Rheodyne (Bensheim, Germany) valve with sample loop of $50\ \mu\text{L}$. The molecular weight was measured in terms of polystyrene equivalents and converted to original molecular weights using the Mark-Houwink relationship and the details of analysis are presented elsewhere.¹⁹ Before degradation of the ternary blends, polymeric materials were

characterized using GPC in terms of number-average molecular weight and polydispersity. The number-average molecular weights of PCL, PVAC, and PVC are 84,000, 53,500, and 164,700 g/mol, respectively, and the corresponding polydispersities are 1.51, 2.28, and 1.82. The PVAC has a broader range of molecular weights compared to that of other polymers.

Differential scanning calorimetry

The glass-transition temperatures of various blends were recorded in a differential scanning calorimeter (DSC-2; Perkin Elmer Cetus Instruments). The experiments were carried out in inert atmosphere (N_2), from -100 to 100°C , in an aluminum pan. The glass-transition temperatures were determined by differentiating the DSC signal. The blend containing equal percentages of the ternary mixture showed a single glass-transition temperature, indicating complete miscibility. The miscibility of the binary blends was investigated earlier. The miscibility of PCL with PVAC was studied using DSC and a single transition temperature was observed for the complete range.¹¹ The miscibility of PCL with PVC was extensively investigated using DSC and these materials were found to be miscible.^{20,21} The miscibility of PVAC and PVC was also investigated by DSC and their miscibility depends on the solvent used during solution blending.²²

Scanning electron microscopy

The miscibility of the PCL, PVAC, and PVC was examined using SEM (model S360 operated at 20 kV, Cambridge Instruments). The samples were coated with graphite using a vacuum evaporator (JEE-4X, JEOL, Tokyo, Japan) to aid the conduction during scanning. The magnification was $\times 500$ and Figure 1(a)–(d) show the SEM plots of the PCL/PVAC/PVC blends at compositions of 10/45/45, 50/10/40, 50/40/10, and 80/10/10, respectively. TG experiments were repeated several times from the different portions of the ternary blends and the results were reproducible within $\pm 2\%$. SEM studies in conjunction with TGA study suggest the complete miscibility of the polymers.

RESULTS AND DISCUSSION

The thermal degradation of poly(ϵ -caprolactone), poly(vinyl acetate), and poly(vinyl chloride) was investigated in several possible compositions in the ternary composition diagram. Figure 2(a) shows the thermal degradation profiles for PCL, PVAC, and PVC. There is no weight loss until 200°C for all polymers. The polymers degrade at higher temperature depending on their thermal stability. The thermal stability of polymers is in the order $\text{PCL} > \text{PVAC} > \text{PVC}$. The vinyl polymers (PVAC and PVC) decompose in two

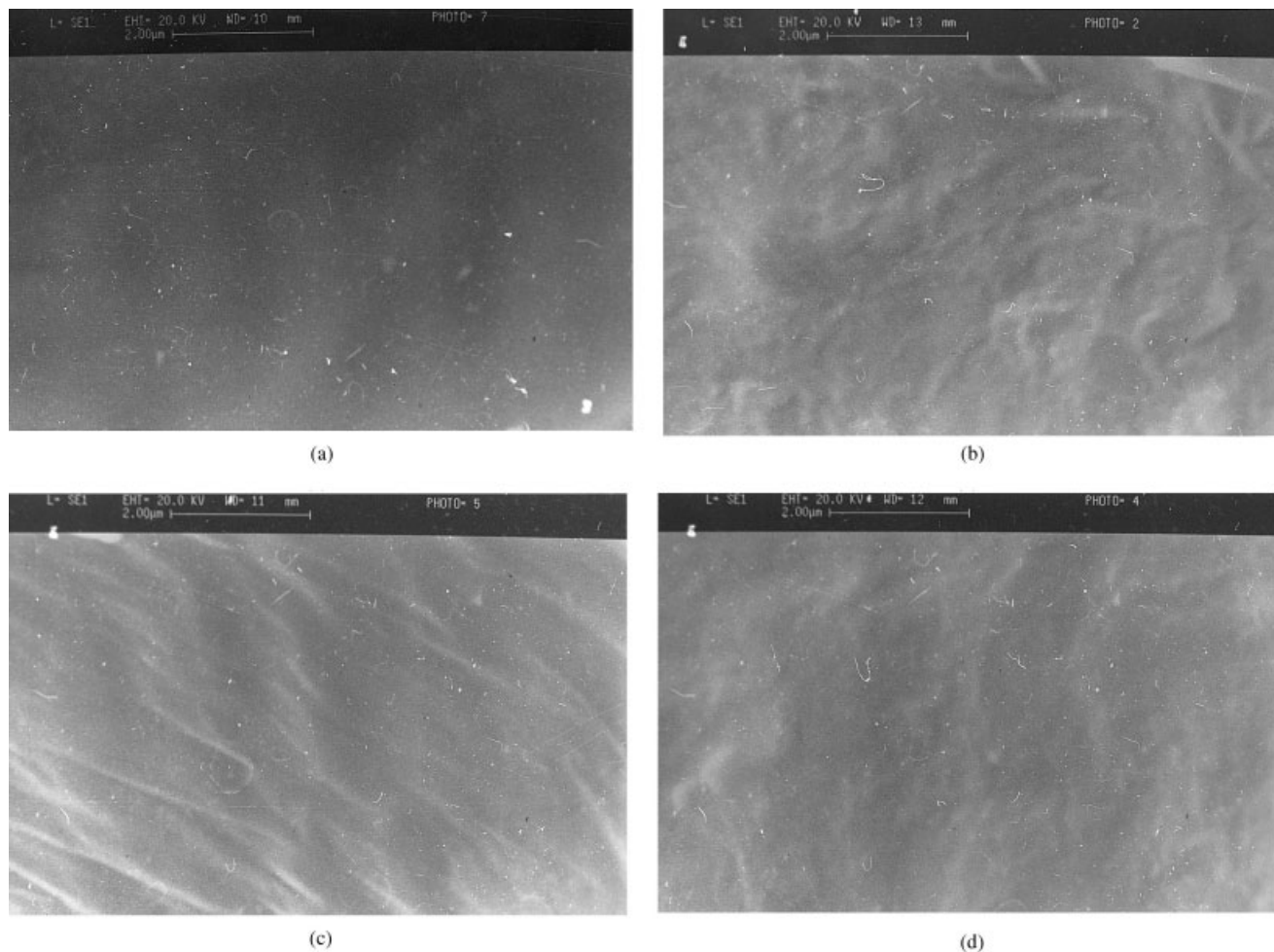


Figure 1 SEM micrographs for ternary blends in the order of PCL/PVAC/PVC: (a) 10/45/45; (b) 50/10/40; (c) 50/40/10; (d) 80/10/10.

stages, whereas PCL degrades in a single stage. Figure 2(b) shows the differential thermogravimetry profiles for all the polymers. The maximum temperature of

decomposition for PCL is 388°C, with simultaneous random chain scission and depolymerization from the hydroxyl chain end. The products of degradation

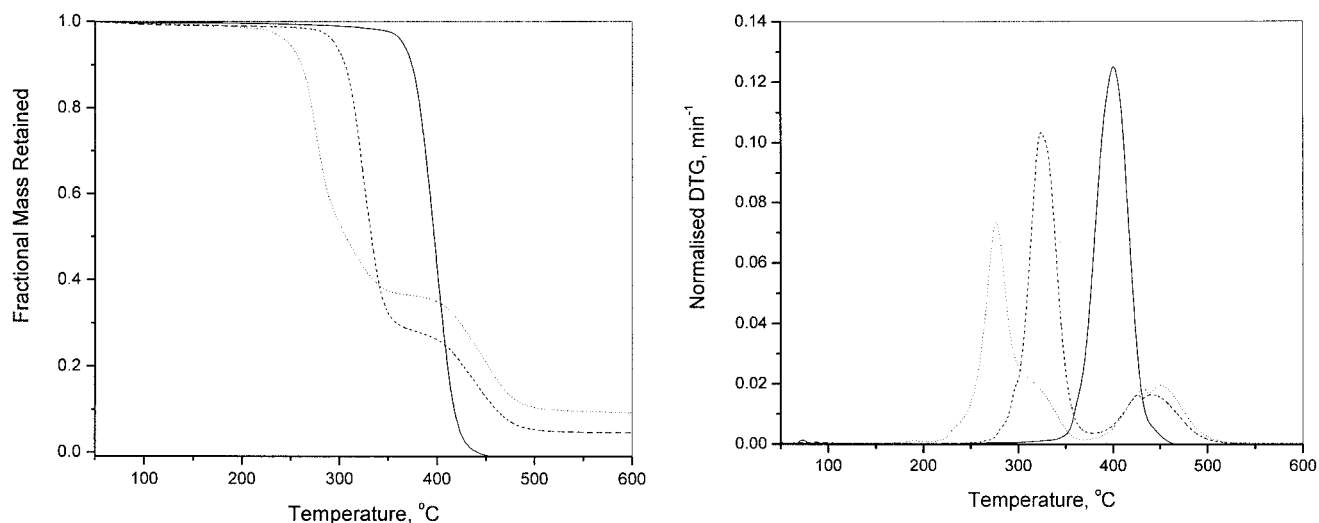
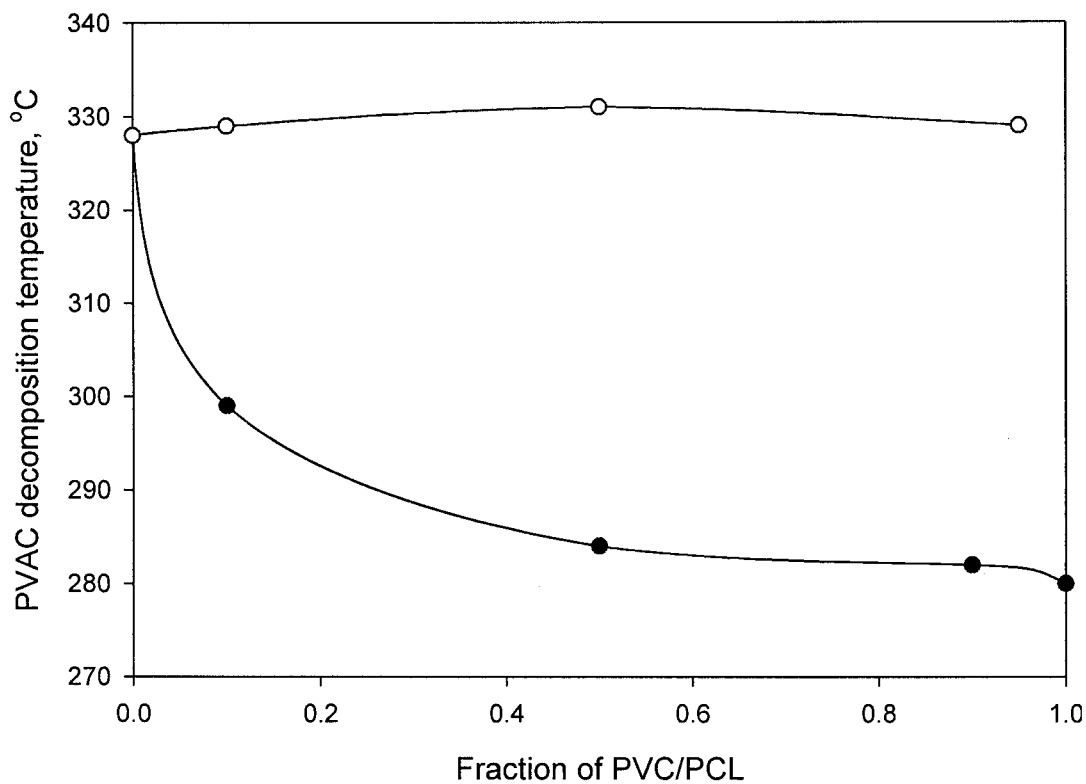
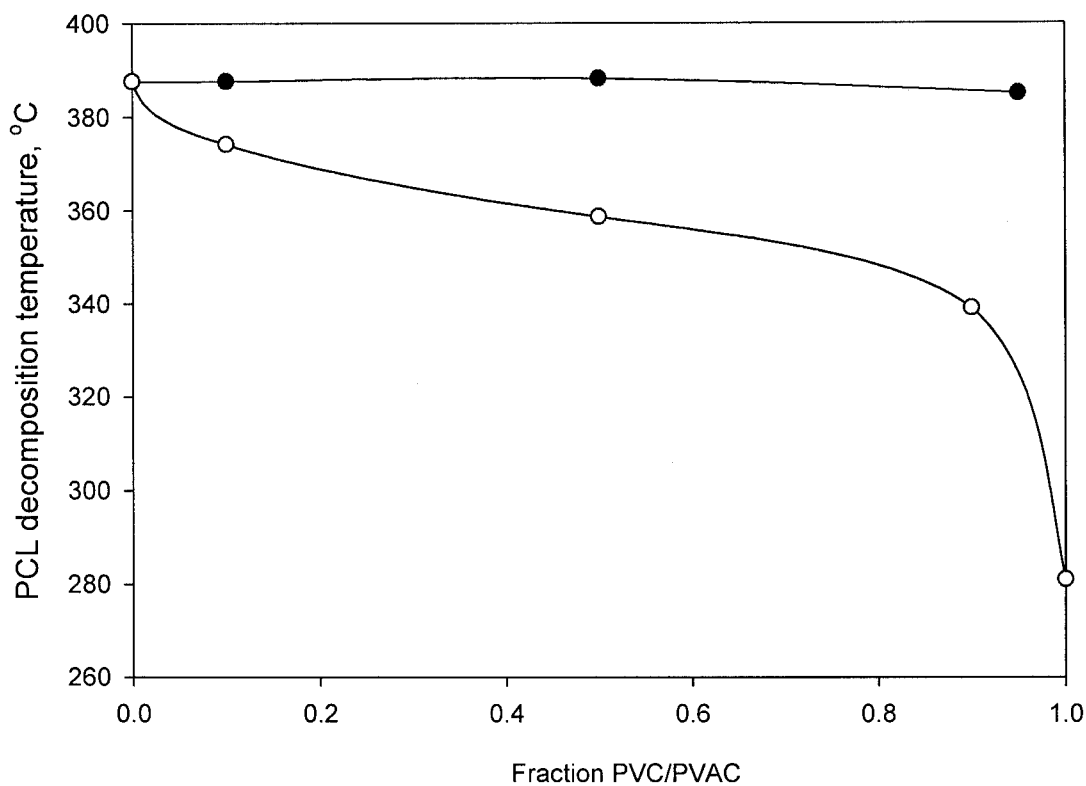


Figure 2 (a) Thermogravimetry profiles for the individual polymers: —, poly(ϵ -caprolactone); ···, poly(vinyl acetate); ---, poly(vinyl chloride). (b) Differential thermogravimetry profiles for the individual polymers. See (a) for legends.



(a)



(b)

Figure 3 (a) Variation of deacetylation temperature of PVAC as a function of PCL or PVC composition: ○, PCL; ●, PVC. (b) Variation of decomposition temperature of PCL as a function of PVAC or PVC composition. See (a) for legends.

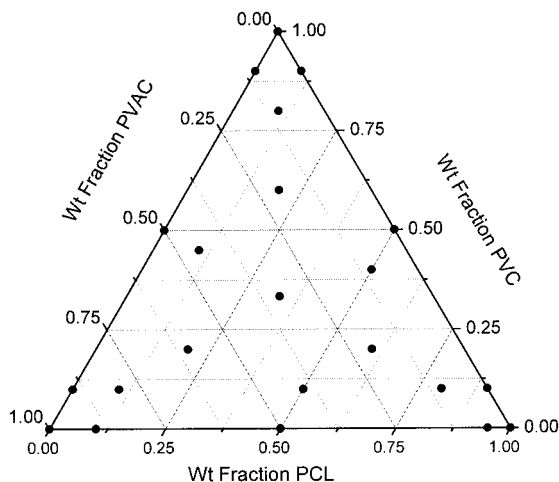


Figure 4 Ternary composition diagrams in terms of mass fractions of polymers. The circles represent the experimental composition.

are mainly ϵ -caprolactone and vaporizable dimers.¹⁵ The degradation mechanism of PVC is well documented,^{1,2,5-7} with degradation occurring in two stages. There are two peaks at 273 and 442°C, suggesting two stages in the degradation [Fig. 2(b)]. The first peak corresponds to the chlorine radical or hydrogen chloride formation leading to the dehydrochlorination of PVC. The second peak is attributed to structural disintegration of the polyolefinic series and further aromatization, isomerization, and so forth, leading to the formation of lower ring compounds.⁵⁻⁷ The degradation of PVAC is similar to the degradation of PVC, with two stages of degradation at 328 and 442°C, corresponding to the deacetylation and disintegration of the polyolefinic backbone, respectively [see Fig. 2(b)]. This analysis also indicates that the first stage of degradation occurs at higher temperatures for PVAC than for PVC.

Figure 3(a) shows the variation of maximum temperature for the thermal degradation of PVAC. The thermal degradation of PVAC is significantly influenced by even 10% addition of PVC and the thermal degradation of binary blend of 50/50 PVAC/PVC is similar to the thermal degradation of pure PVC. Recently, we reported the effects of various metal oxides on the thermal degradation of PVC and PVAC and their blends.¹ The decreased decomposition temperature of PVAC was attributed to the catalyzing action of chlorine radical liberated from the PVC chain. The chlorine radicals liberated from the PVC chain influence the degradation of PVAC.¹ The polyolefinic breakage was not affected because of the addition of PVC. The degradation of PVC occurs in two stages,^{2,5,7} with the peak at 273°C corresponding to the liberation of the chlorine radical or the formation of hydrogen chloride. The amount of HCl formed during degradation can be directly determined from the TGA curve

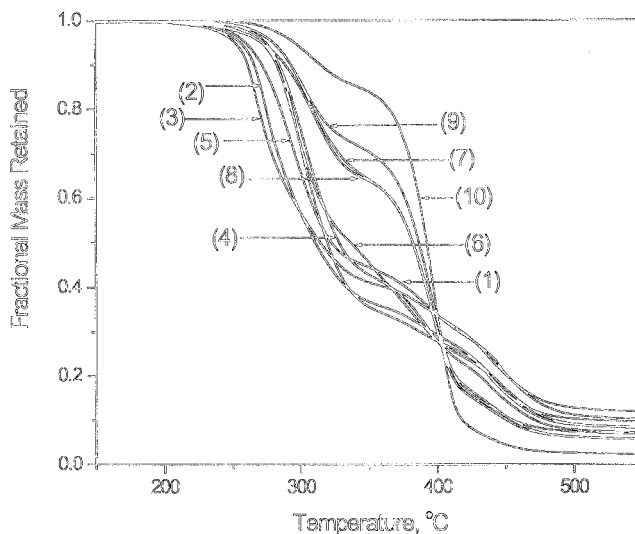


Figure 5 TG profiles for various possible combinations of ternary blends marked on Figure 4. Curves showing PCL : PVC in different fractions: (1) 10 : 10; (2) 10 : 45; (3) 10 : 80; (4) 20 : 20; (5) 20 : 60; (6) 33 : 33; (7) 50 : 10; (8) 50 : 40; (9) 60 : 20; (10) 80 : 10.

presented in Figure 2(b). Small amounts of HCl formed during the dechlorination step of PVC catalyze the degradation of PVAC.¹ The effect of HCl liberated during the degradation of PVC on the degradation of PVAC and PCL is similar to the effect of HCl on the degradation of PET.²³

Figure 3(b) shows the decomposition temperatures of the binary blends of PCL with PVAC and PVC. The addition of PVC influences the degradation of PCL by lowering its degradation temperature. However, this effect is much lower than the destabilization observed when PVC is added to PVAC. This can probably be

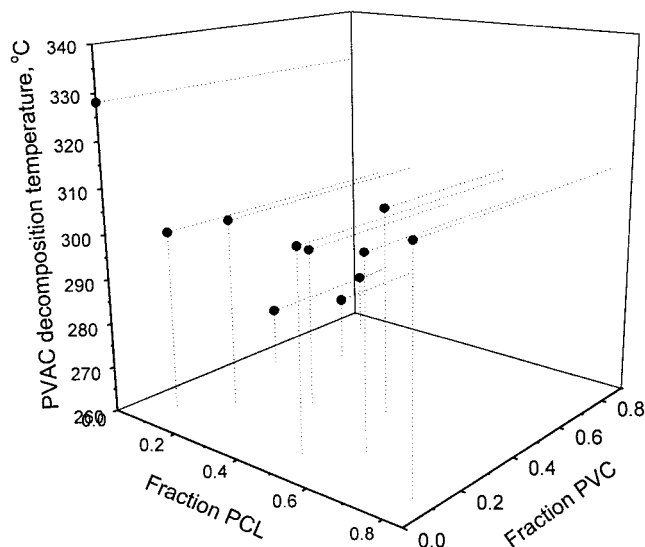


Figure 6 PVAC decomposition temperature as a function of PCL and PVC fractional composition in the ternary blend.

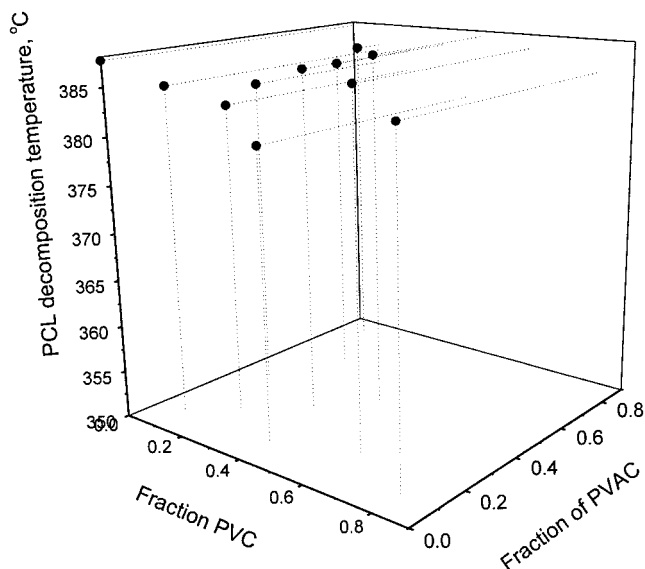


Figure 7 PCL decomposition temperature as a function of PVAC and PVC fractional composition in the ternary blend.

attributed to the higher decomposition temperature of PCL compared to that of PVAC. The thermal stability of PCL is relatively unaffected by the addition of PVAC and is possibly attributable to the weak decomposition nature of acetate radical compared to that of the chlorine radical.¹¹

Figure 4 shows the ternary mass fraction diagram of PCL, PVAC, and PVC and the circles on the plot show the experimental composition whose interactions were investigated. The points on the vertices and sides represent the composition of the pure and binary blends under study, and the circles inside the triangular area represent the composition of the ternary blends. Figure 5 shows the thermogravimetry profiles for the ternary blends. As discussed earlier, the addition of PVC substantially reduced the thermal stability of PVAC but only negligibly influenced the degradation of PCL. The addition of PVAC did not influence the degradation of PCL.

Figure 6 shows the variation of the deacetylation temperature of PVAC in the ternary blend as a function of PCL and PVC composition. At a fixed composition of PVC in the ternary blend, an increase in the PCL fraction reduced the destabilization of PVAC that occurs as a result of PVC addition. At a fixed composition of PCL in the ternary blend, the addition of PVC significantly enhanced the degradation of PVAC. Thus it can be concluded that, whereas the degradation of PVAC is increased in the presence of PVC in a binary blend, the addition of PCL to the binary blend reduces the degree of destabilization of PVAC attributed to PVC addition.

Figure 7 shows the maximum decomposition temperature of PCL resulting from the addition of PVC or

PVAC. The thermal stability of PCL remains unaffected, irrespective of the amount of PVC or PVAC present, whereas the binary blend of PCL/PVC showed a destabilization of PCL attributed to PVC addition. The chloride radicals liberated from the PVC chain might preferentially decompose the PVAC chain compared to PCL. The thermal stability of PCL in the ternary mixture is attributed to the presence of PVAC, which acts as a scavenger of chloride radicals or hydrogen chloride.

CONCLUSIONS

The thermal degradation of polymers such as PCL, PVAC, and PVC and their binary and ternary blends was investigated. The thermal stability of the polymers is in the order of PCL > PVAC > PVC. In the binary blends, the addition of PVC destabilized PCL to a lesser degree but the addition of PVAC did not influence the degradation of PCL. In ternary blends, the addition of PVC did not destabilize PCL but influenced the degradation of PVAC.

The authors thank the Department of Science and Technology, India for financial support. The first author thanks the General Electric Company, USA for a fellowship.

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