Compatibility and Thermal Stability Studies on PVC/Chlororubber-20-Graft Polyblend-Styrene–Vinyl Acetate–Acrylonitrile Blends.   II

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Synopsis

Compatibility and thermal stability studies have been performed on PVC blends with chlororubber-20-graft polyblend-styrene–vinyl acetate–acrylonitrile (1:1:1) [CR-20gp-SVAAN (1:1:1)]. The grafting of styrene, vinyl acetate, and acrylonitrile onto chlororubber-20 backbone chain generates some amount of heterogeneity in the system. The compatibility behavior of PVC/CR-20gp-SVAAN (1:1:1) blends has been reflected in the ultrasonic velocity and absolute viscosity vs. composition plots of the blend. These blends have been found to be thermally more stable than PVC/chlororubber-20 blends, but less stable than PVC/KM-365B blends. The rate of degradation is equal to that of the PVC/chlororubber-20 blends. The results have been discussed on the basis of compatibility, stabilizing, and destabilizing behavior of various component polymers with PVC matrix.

INTRODUCTION

Recently, Singh and Singh[1–3] have studied the thermal and compatibility behaviour of PVC/chlororubber-20-graft polyblend-ethyl acrylate–acrylonitrile (2:1) and PVC/chlororubber-20-graft polyblend-styrene–acrylonitrile (2:1) blends. It has been established that the thermal degradation in multiphase polymeric systems is a chemical process which generally takes place either through the reaction involving small molecules/radical species or through polymer molecules/long chain radical species which are produced in one phase and subsequently diffuse into other phase. Thus, compatibility of the system becomes prime factor which controls the thermal behavior of the polymer blends because of the involvement of various phases in thermal degradation process.

The present paper discusses the compatibility and thermal behaviour of PVC/chlororubber-20-graft polyblend-styrene–vinyl acetate–acrylonitrile (1:1:1) [PVC/CR-20-SVAAN (1:1:1)] blend system. This investigation may reveal some interesting aspects of the multiphase polymeric systems and may be helpful in correlation of other properties such as tensile and impact strengths.

EXPERIMENTAL

Materials

A powder grade SR-10 PVC (Shri Ram Chemicals Ltd., India; *K* value = 65) was used in the present investigation. A powder grade chlororubber-20 (Rish-
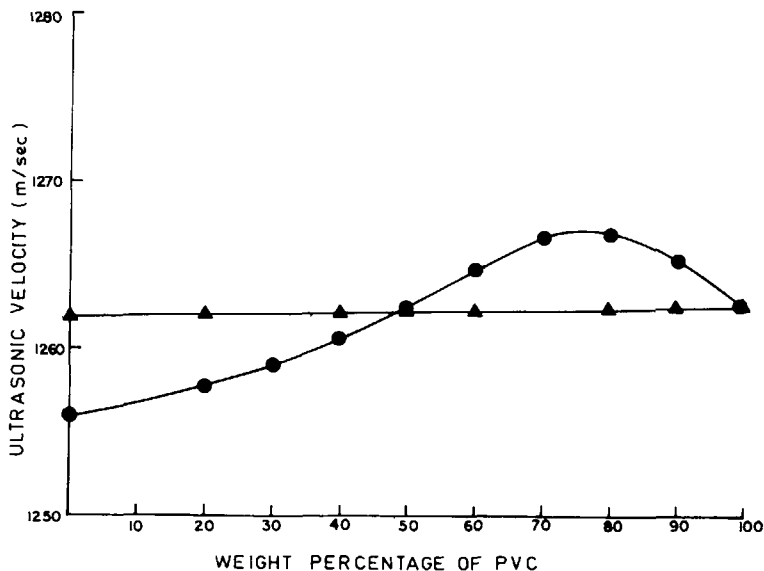
Fig. 1. Ultrasonic velocity vs. weight percentage of PVC (components 1): (▲) PVC/CR-20 blends; (●) PVC/CR-20gp-SVAAN (1:1:1) blends.

iroop Polymer, Ltd., Bombay, India) was used after purification. Chlororubber-20 was purified by dissolving it into ethyl methyl ketone and reprecipitating it by methanol. Barium Cadmium Laurate (Amrut Chemicals, Bombay, India) was used as thermal stabilizer. Tetrahydrofuran (AR, BDH; double distilled) was used in blend preparation for compatibility studies. CR-20gp-SVAAN (1:1:1) was synthesized in the author's laboratory. Details of synthesis have been given elsewhere.[4] All the solvents used were of BDH origin and of AR grade.

PVC blends with CR-20gp-SVAAN (1:1:1) for compatibility measurements were prepared by dissolving the requisite proportions of both the constituents in THF separately and then by thorough mixing of the polymer solutions.

The synthesized modifier [CR-20gp-SVAAN (1:1:1)] was mixed with PVC along with the requisite amounts of additives. The mixture was extruded in Brabender Plasticorder and Extrusiograph at 150–165°C. The extruded material, a cylindrical strand, was cut into small pieces. The pieces were ground after cooling in liquid nitrogen. The resulting material having approximate particle size of 200 μ was used in the thermal stability measurements. Equal amount of the material (1 g) was taken for each experiment.

Measurements

Compatibility Measurements. The compatibility was determined by the ultrasonic velocity at 2 MHz, and absolute viscosity of blend solutions at room temperature as discussed earlier.[5–7]

Thermal Stability Measurements. The thermal stability of polymer blends was determined by HCl evolution method and thermogravimetry under isothermal conditions as discussed earlier.[1,2] The thermal decomposition experiments were performed at 190 ± 1°C.
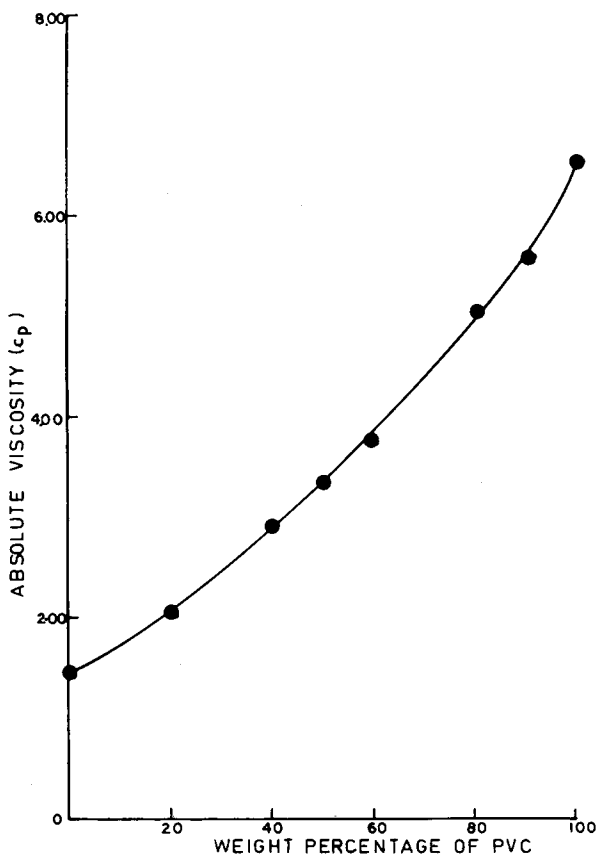
Fig. 2. Absolute viscosity vs. weight percentage of PVC (component 1).

RESULTS AND DISCUSSION

The compatibility of chlororubber with PVC has not been extensively studied. Friese[8] has only quoted his unpublished data on this subject which indicate that PVC forms compatible blends with polychloroprene while chlorinated polyisoprene blends with PVC were stated to be incompatible. However, the blends of grafted polyblends of chlororubber with PVC have not been studied so far. Singh et al.[5] and Singh and Singh[6,7] have observed that the ultraonic velocity and absolute viscosity vary linearly with composition in the solution of compatible blends while these quantities deviate from linearity for incompatible blends. The same techniques for compatibility measurements have been applied for the compatibility study of the present system. Figure 1 shows ultrasonic velocity vs. composition plot for the present system, i.e., PVC/CR-20gp-SVAAN (1:1:1) in the tetrahydrofuran solution. It depicts that the ultrasonic velocity curve deviates from linearity for this system while it shows linear behavior for PVC/CR-20 blends. The nature of the curve is indicative of polymer–polymer interactions at some compositions which is quite understandable with the presence of the polar groups in PVC/CR-20gp-SVAAN (1:1:1) blends. These polymer–polymer interactions are weak in PVC/CR-20gp-SAN (2:1) blends

TABLE I
Thermal Stability of PVC[a] Blends

| System | Composition of blends PVC/modifiers | Induction time (s) | | |
		Conductometric analysis	pH metric analysis	ITGA
PVC		3275	3100	3000
PVC/CR-20	95/5	2676	2250	2685
	90/10	2100	2000	2110
	85/15	1500	1200	1800
	80/20	910	825	—
	0/100	300	250	300
PVC/CR-20gp-SVAAN	95/5	2760	2760	2780
	90/10	1900	1810	1875
	85/15	1560	—	1525
	80/20	1350	1200	1375
	0/100	300	270	300
PVC/KM-365B	95/5	2050	2700	2800
	90/10	3150	2685	2700
	85/15	4600	3675	—
	80/20	—	—	2100
	0/100	no change	no change	4380

[a] PVC formulation: 90 parts PVC:SR-10, 2.5 parts lubricants, and stabilizer (Ba-Cd Laurate), 1.5 parts processing aid (PMMA), 8 parts DOP, and 8 parts TiO_2.

because the contribution of relatively less polar polystyrene is twofold in the blends in comparison to the present system. Similar behavior is also displayed in the ultrasonic velocity plot for PVC/CR-20gp-SAN (2:1) blends.[3]

Figure 2 shows the variation of the absolute viscosity versus composition of the PVC blends. The curve shows slight curvature for entire composition which may be due to presence of microheterogeneity. It may also be due to the stronger polymer–polymer interactions which are indicated by ultrasonic velocity vs. composition curve and by visual observations of the films obtained from THF solution. The cast films are found to be transparent and slightly yellowish. The transparency of the films show compatible nature of the system while the yellow color indicates specific interaction between constituent polymers.[9] At higher concentrations of modifiers, transparency of films reduces indicating the development of microheterogeneity. The yellow color of films intensifies with concentration of modifiers, which is an indication of stronger polar interactions. Differential thermal analysis of PVC/CR-20gp-SVAAN (1:1:1)[2] also supports the above-stated compatibility behavior.

Thermal Stability

The thermal stability of the blends was represented in the form of induction time of the degradation (the duration of the time in which the materials start degrading at a constant temperature). Table I depicts the results of thermal stability in terms of induction time. The values of the induction time for the present system obtained by all the three techniques are equal within the limit of experimental error. The following observations have been made on the basis of the analyses by all three techniques (Figs. 3–5).
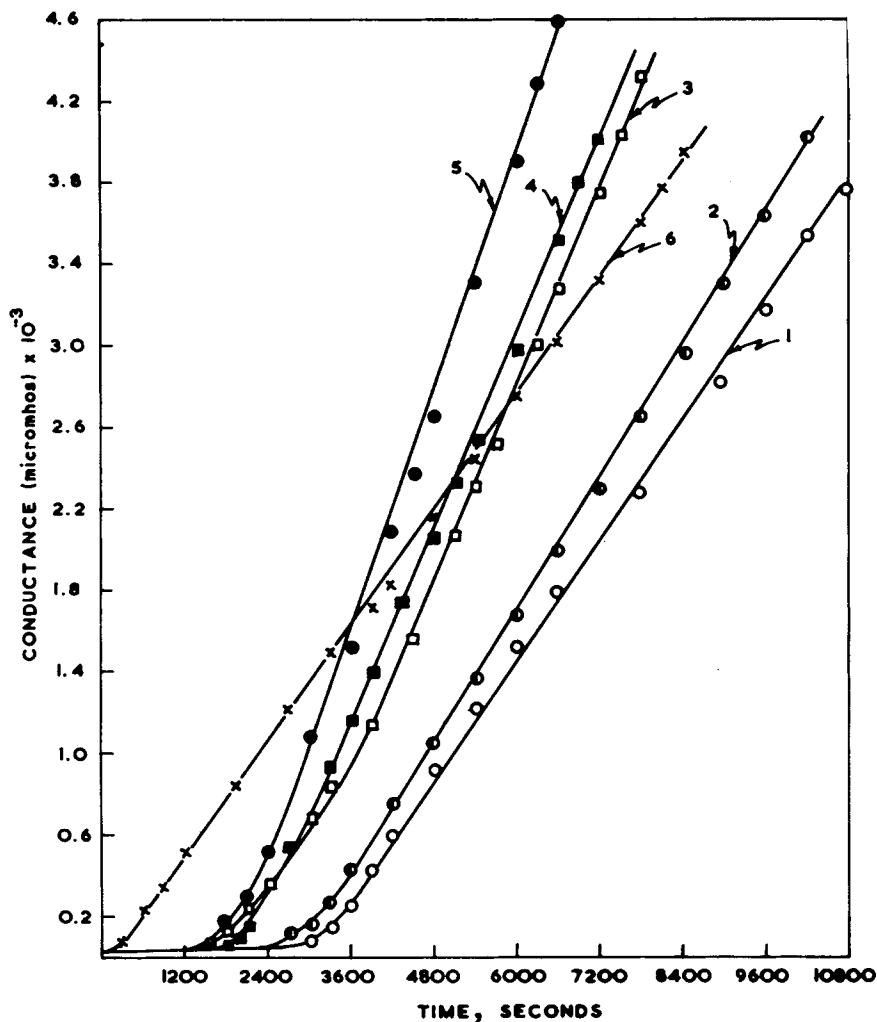
Fig. 3. Conductance of the dissolving medium vs. degradation time for PVC/CR-20gp-SVAAN blends.   (1) 100/0; (2) 95/5; (3) 90/10; (4) 85/15; (5) 80/20; (6) 0/100.

1. PVC/CR-20gp-SVAAN (1:1:1) blends are more stable than PVC/CR-20 blends but are less stable than PVC/KM-365B blends.

2. The thermal stability of this system decreases with the concentration of modifier.

3. The rate of degradation, i.e., the slope of the curve in the present system, is found to be more than that of the PVC/KM-365B blend, but almost equal to that of PVC/CR-20 blend, and is unaffected by the concentration of modifiers.

The systems, studied under the present investigation, are of complex chemical nature.   These multiphase polymeric systems are mixtures of graft copolymer of chlororubber-20 [chlororubber-20-graft copoly(styrene–vinyl acetate–acrylonitrile)], chlororubber-20, and PVC, and are found to be slightly heterogeneous
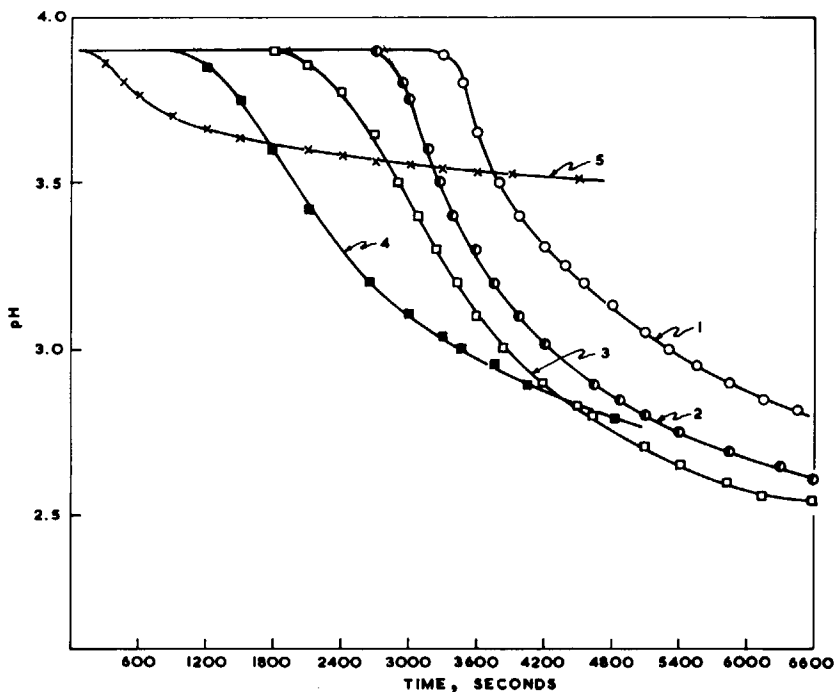
Fig. 4. pH of the dissolving medium vs. degradation time for PVC/CR-20gp-styrene–vinyl acetate acrylonitrile blends: (1) 100/0; (2) 95/5; (3) 90/10; (4) 85/15; (5) 0/100.

as discussed earlier. Earlier studies[10] on PVC/chlororubber blends indicate that chlororubber has negative effect on the thermal stability of PVC which is caused by the catalytic effect of its decomposition product, i.e., HCl on the degradation reaction of PVC. In the present studies also a similar negative effect of chloro-rubber-20 on the thermal stability of PVC has been observed. The higher thermal stability of PVC/CR-20gp-SVAAN (1:1:1) in comparison to PVC/CR-20 blends may be explained on the basis of the stabilizing effect of the styrene molecules on PVC matrix.[11–13] The grafted polystyrene macromolecule gets better opportunity for stabilizing the PVC matrix because of its proximity to the degradation reaction site. The grafted nature of polystyrene macromolecules helps the stabilization process due to their uniform distribution in PVC matrix, which is otherwise incompatible. Moreover, the grafted surface may also provide larger surface area for its stabilizing action. These cumulative effects may contribute to the stabilizing effect of PVC which leads to higher thermal stability of these blends in comparison with PVC/CR-20 blends. The lower thermal stability of the present system in comparison with PVC/KM-365B blends may be explained on the basis of higher stabilizing efficiency of polyacrylate phase and the presence of chlororubber-20 and polyacrylonitrile, as had been explained in the previous papers.[1,3] Polyacrylonitrile has negative effect on the thermal stability of PVC. It catalyzes the degradation reaction of PVC through its de-composition product, i.e., NH_3. The present investigations also conform the behavior observed by McNeill et al.[12,13] The concentration effect of modifier on thermal stability may be explained on the basis of the stabilizing effect of
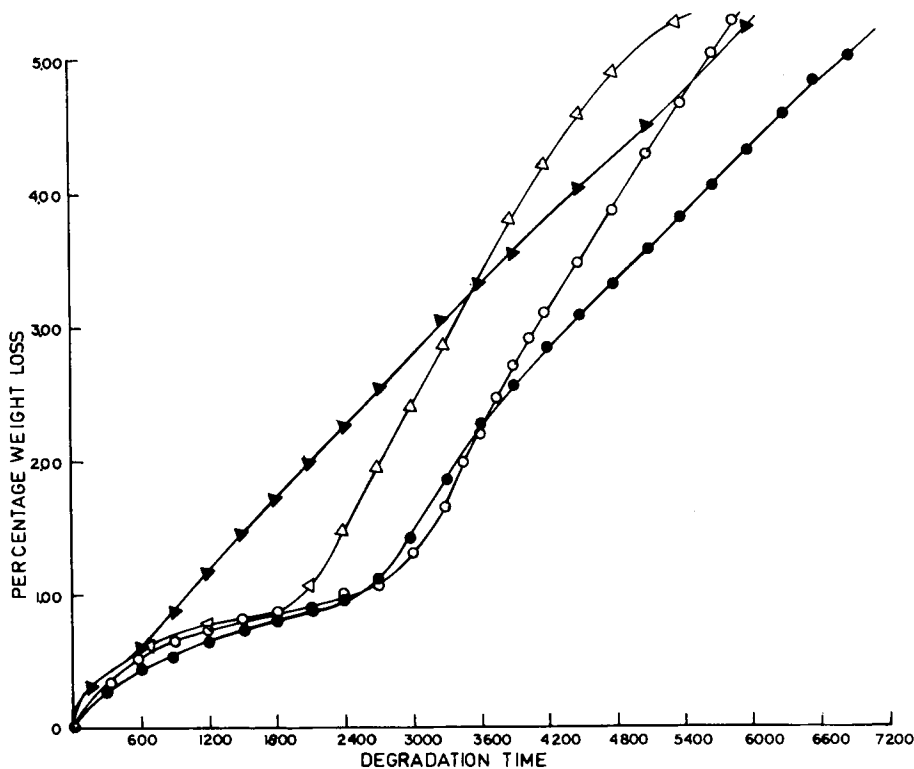
Fig. 5. Percentage weight loss of PVC/CR-20gp-styrene–vinyl acetate–acrylonitrile (1:1:1) blends vs. degradation time: (O) 100/0; (●) 95/5; (△) 90/10; (▲) 0/100.

polystyrene and destabilizing effect of chlororubber-20, polyacrylonitrile, and poly(vinyl acetate) onto PVC matrix as discussed by McNeill et al.[11–14] and by the present authors.[1,3]   Poly(vinyl acetate) also catalyzes the degradation reaction of PVC through its decomposition product, i.e., acetic acid, as has been discussed by McNeill et al.[14]

The rate of degradation, observed in the present system may lead to the following striking features.   In spite of the presence of poly(vinyl acetate) and polyacrylontrile chains onto chlororubber-20 backbone chain, the destabilizing and catalytic species for PVC degradation, the rate of degradation remains equal to that of PVC/CR-20 blends.   It appears that the degradation products of poly(vinyl acetate) and polyacrylonitrile (acetic acid and NH_3, respectively) get neutralized in the degradation process within the PVC matrix.   This process may be facilitated by the grafted nature of their molecules and the polymer–polymer interaction due to presence of polar groups.   As poly(vinyl acetate) and PAN macromolecules are present in equal quantity,[4] the rate of degradation is almost solely controlled by chlororubber-20.   Because of it, the rate of degradation in the present system is equal to that of PVC/CR-20 blends and is unaffected by its concentration as discussed in earlier communications.[1,3]   The time effect on the rate of degradation of the blends in thermogravimetry under isothermal conditions and pH measurements may be explained by considering the

combined destabilizing and stabilizing effects of polymeric constituents as discussed earlier.[1,3]

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