Thermal Stability of PVC/Chlororubber-20-Graft Polyblend–Styrene–Acrylonitrile Blends.   I

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Synopsis

Thermal stability of PVC blends with chlororubber-20-graft polyblend-styrene–acrylonitrile [CR-20gp-SAN (2:1)] was studied by HCl evolution techniques and thermogravimetry under isothermal condition.   The thermal stability of PVC/CR-20gp-SAN (2:1) blends has been compared with those of PVC/CR-20 and PVC/KM-365B blends.   It has been observed that the thermal stability of modified PVC is less than that of unmodified PVC.   The CR-20gp-SAN (2:1) modified PVC blends were found to be more stable than PVC/CR-20 blends but less stable than PVC/KM-365B blends.   The rate of degradation in PVC blends was observed to be unaffected by the concentration of the modifiers, but the PVC/KM-365B blends were found to be degrading slower in comparison with PVC/CR-20 and PVC/CR-20gp-SAN (2:1) blends.   The rate of degradation for PVC/CR-20 blends at lower concentrations (<10%) of modifiers is almost equal to that of PVC/CR-20-gp-SAN (2:1) blends, but more at higher concentrations of modifiers (>10%).   The experimental results have been explained on the basis of the chemical nature of the modifiers and their miscibility with PVC.

INTRODUCTION

Recently, a great deal of attention has been drawn to the studies of morphology and physical properties of the multicomponent polymeric systems.   The multiphase polymeric systems or polymer blends have become more important due to the variation of their morphology over a broad spectrum.   The physical properties of polymer blends have been studied extensively; however, comparatively less interest has been shown in the studies of their chemical properties such as thermal stability.   In last decade, the thermal degradation behaviour of few blends have been studied.   Richards and Salter[1] have studied the degradation of polystyrene/poly(α-methyl styrene) blends.   McNeill et al.[2–13] have studied a number of blends of poly(vinyl chloride), poly(methyl methacrylate), polystyrene, and poly(vinyl acetate).   Blanchard et al.[14] have studied the degradation of poly(oxy-ethyl-glycol)/polystyrene blends.   Mizutani et al.[15] have studied the degradation of polypropylene/vinyl polymer blends.   Recently, Piglowski and Laskawski[16] and Singh and Singh[17] have studied the thermal behaviour of PVC/polyurethane and PVC/chlororubber 20gp-ethyl acrylate–acrylonitrile (2:1) [PVC/CR-20-gp-EAN (2:1)] blends respectively.   It has been pointed out by Deanin[18] that, in general, thermal behavior obtained in polymer–polymer blends is the average of the thermal behaviors of the component polymers.   It has also been established[1–16] that the thermal degradation in multiphase polymeric system is a chemical process which generally takes place

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either through polymer molecules/long chain radical species or through the reaction involving small molecules/radical species which are produced in one phase and subsequently diffuse into other phase. The same conclusion has also been drawn on the basis of the authors' investigations on PVC/CR-20-gp-EAN (2:1) blends.[17]

It has recently been observed[19] that the graft polyblends of rubbers can be used as impact modifiers for PVC. The graft polyblends of chlororubber (CR-20) studied under the present investigation are of importance due to their limited compatibility with PVC.[20]

Our present investigation is mainly concerned with the thermal degradation behaviour of the blends of PVC with CR-20gp-SAN (2:1). These studies may reveal some aspects of the degradation behavior of multiphase polymeric systems.

EXPERIMENTAL

A powder SR-10 grade PVC (Shri Ram Chemicals, Kota, India, K value = 65) was used in the present investigation. A powder grade chlororubber-20 (Chlororub-20, Rishiroop Polymers Pvt., Ltd., Bombay, India) was purified by dissolving it in ethyl methyl ketone and precipitating in methanol prior to its use. An impact modifier, KM-365B (Indofil Chemicals, Ltd., Bombay, India) was used in its original powder form. Barium cadmium Laurate (Amrut Chemicals, Bombay, India) was used as a thermal stabilizer. All the solvents used were of BDH origin and AR grade.

Synthesis of Chlororubber-20-Graft Polyblend-Styrene Acrylonitrile-(2:1)

The styrene, acrylonitrile graft polyblends of CR-20 were synthesized by solution precipitation polymerization technique.[19,21,22] As a typical example, 50 g of CR-20 was dissolved in 400 mL of xylene. Styrene (33.7 g), acrylonitrile (16.7 g), and benzoyl peroxide (0.89 g) were added to the CR-20 solution which was heated at $80 \pm 1°C$ for 15 h in an inert atmosphere. The reaction products were precipitated in methanol and dried at 65°C under vacuum for 36 h. The homopolymers of styrene and acrylonitrile were separated from the graft polyblend of CR-20, prior to its use. The details of synthesis and characterization will be published elsewhere.[20,23]

Preparation of Blends

The synthesized modifier [CR-20gp-SAN (2:1)], CR-20, and KM-365B (commercial impact modifier) were mixed with PVC along with the requisite amounts of other 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. The resulting powdered material having approximate particle size of 200 μ was used in the thermal stability measurements in each case.

TABLE I
Thermal Stability of PVC[a] Blends

System	Composition of blends PVC/modifier	Induction time (s)		
		Conducto-metric	pH metric	Isothermal gravimetric analysis
PVC	—	3275	3100	3000
PVC/CR-20	95/5	2675	2250	2685
	90/10	2100	1800	2110
	85/15	1500	1200	1500
	80/20	910	825	—
	0/100	300	250	300
PVC/CR-20gp-SAN (2:1)	95/5	2750	2675	2675
	90/10	1950	2300	1950
	85/15	1625	1725	1800
	80/20	—	—	—
	0/100	600	600	800
PVC/KM-365B	95/5	2050	2700	2800
	90/10	3150	2685	2700
	85/15	4600	3675	—
	0/100	no change	no change	4350

[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.

Measurements of Thermal Stability

HCl Evolution Technique. The thermal stability measurements were carried out by continuously monitoring the conductivity and pH of the solutions in which the decomposition products of the PVC blends were being dissolved. $1 \times 10^{-4}N$ HCl (100 mL) solution was taken as the dissolving medium. The degradation measurements were carried out under isothermal conditions at 190 $\pm$ 1°C.

The experimental set up used for these studies has mainly two parts. The first part consists of the sample holder, a test tube (1.5 cm diameter) kept in a thermostat maintained at 190 $\pm$ 1°C. The second part consists of the absorbing vessel, containing 100 mL of dilute HCl solution. The temperature of the absorbing vessel was maintained at 25°C. Dry air was passed through whole assembly (air tight) at the rate of 275 cm^3/min. The changes in the conductivity and pH of the dissolving medium were measured with the conductivity and pH meters (Toshniwal Pvt., Ltd., India). A blank experiment, without sample was performed for 3 h. 1 g of powdered sample, as described earlier, was taken for each measurement.

Thermogravimetry under Isothermal Conditions. The thermogravimetric measurements under isothermal condition were performed by the thermogravimetric analyser (FCI, Ltd., India) at 190 $\pm$ 1°C. The sample holder, a circular boat made of nickel, was suspended into the furnace by platinum–rubidium wires. The furnace temperature was maintained at 190 $\pm$ 1°C. A thermocouple was adjusted 2 mm above the sample holder. The blank experiment (without sample) was carried out for 3 h. The results of these measurements were presented as the relationship between the percentage weight loss of the sample vs. the degradation time of the blends.
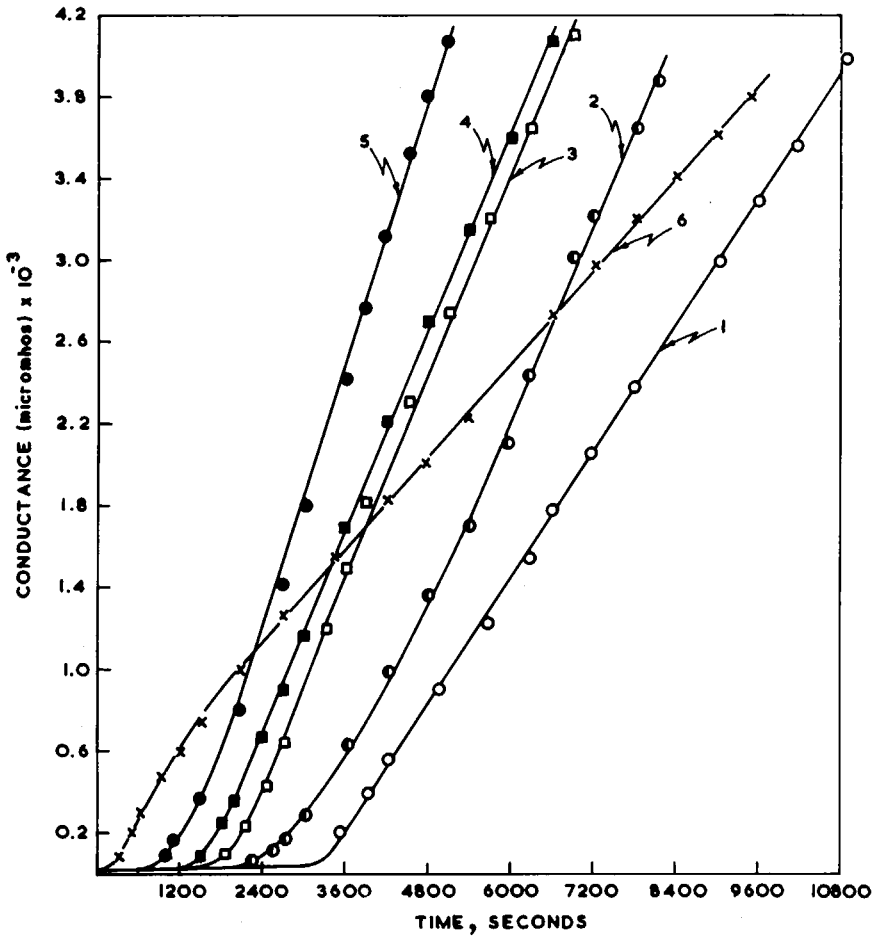
Fig. 1. Conductivity of the dissolving medium vs. degradation time for PVC/CR-20 blends: (1) 100/0; (2) 95/5; (3) 90/10; (4) 85/15; (5) 80/20; (6) 0/100.

RESULTS AND DISCUSSION

The induction time of degradation (the time taken by the blend for initiation of degradation at a constant temperature) represents the thermal stability of blends. The results of induction time obtained from various techniques are tabulated in Table I. The analysis of Table I clearly indicates that the induction time of degradation for various PVC blends varies with concentration and chemical nature of the modifiers, and the values of the induction time measured by conductometric and thermogravimetry under isothermal conditions are of the same order within experimental errors. The induction time is the lowest in case of pH metric measurements which may be due to more sensitive nature of the method. The average induction time of degradation for unmodified PVC was observed to be equal to 3150 s.

The conductivity and pH of the dissolving medium during blank experiment remain constant which indicates that the conductivity and pH changes observed
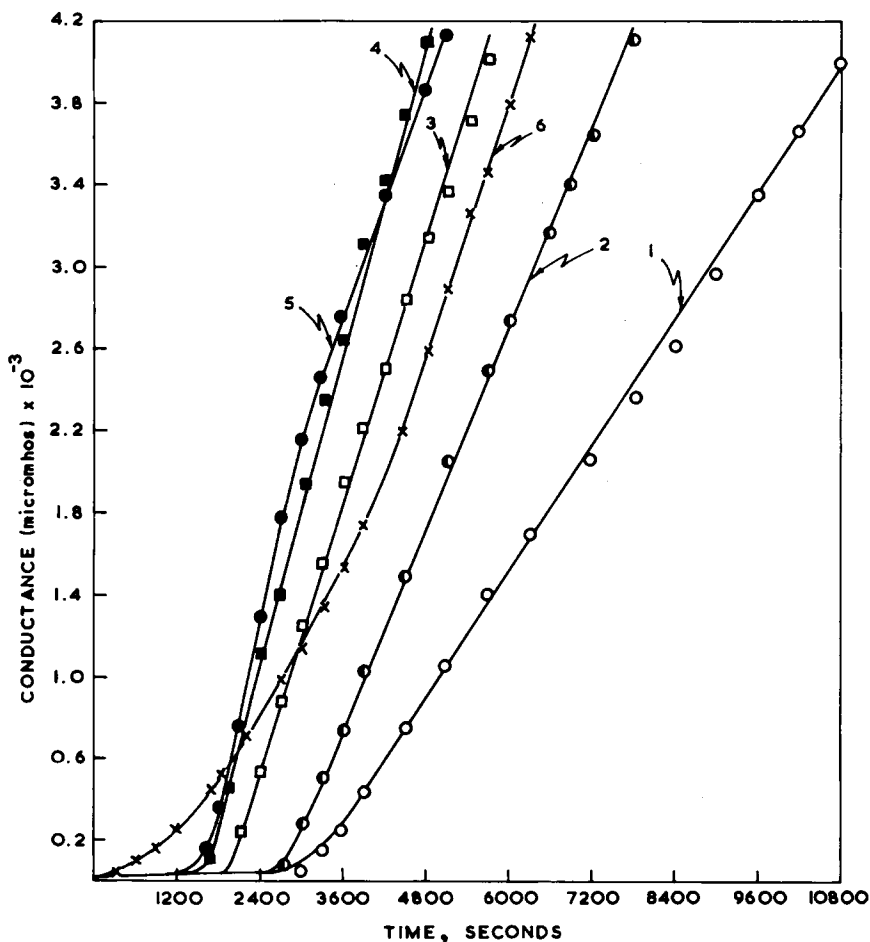
Fig. 2. Conductivity of the dissolving medium vs. degradation time for PVC/CR-20gp-SAN blends: (1) 100/0; (2) 95/5; (3) 90/10; (4) 85/15; (5) 80/20; (6) 0/100.

in the measurements are really due to the degradation of the PVC blends. The results of conductometric and pH measurements are shown in Figures 1–6. It may be inferred that the increasing concentration of modifiers [CR-20 and CR-20gp-SAN (2:1)] decrease the thermal stability of modified PVC blends. The analysis of Table I leads to the conclusion that PVC/KM-365B blends are the most stable amongst the modified PVC blends. The following trend of thermal stability of PVC blends is found to be unaffected by the concentrations of the modifiers in the blends: PVC/KM-365B > unmodified PVC > PVC/CR-20-gp-SAN (2:1) > PVC/CR-20.   Among the modifiers also, the following trend of thermal stability has been observed: KM-365B > CR-20gp-SAN (2:1) > CR-20.

The rate of degradation, represented by the slope of the conductivity and pH of dissolving medium vs. degradation time curve, has been compared for all the blends.   The rate of degradation of PVC/CR-20gp-SAN (2:1) blends is found to be increasing with the concentration of the CR-20gp-SAN (2:1) (see Fig. 2).
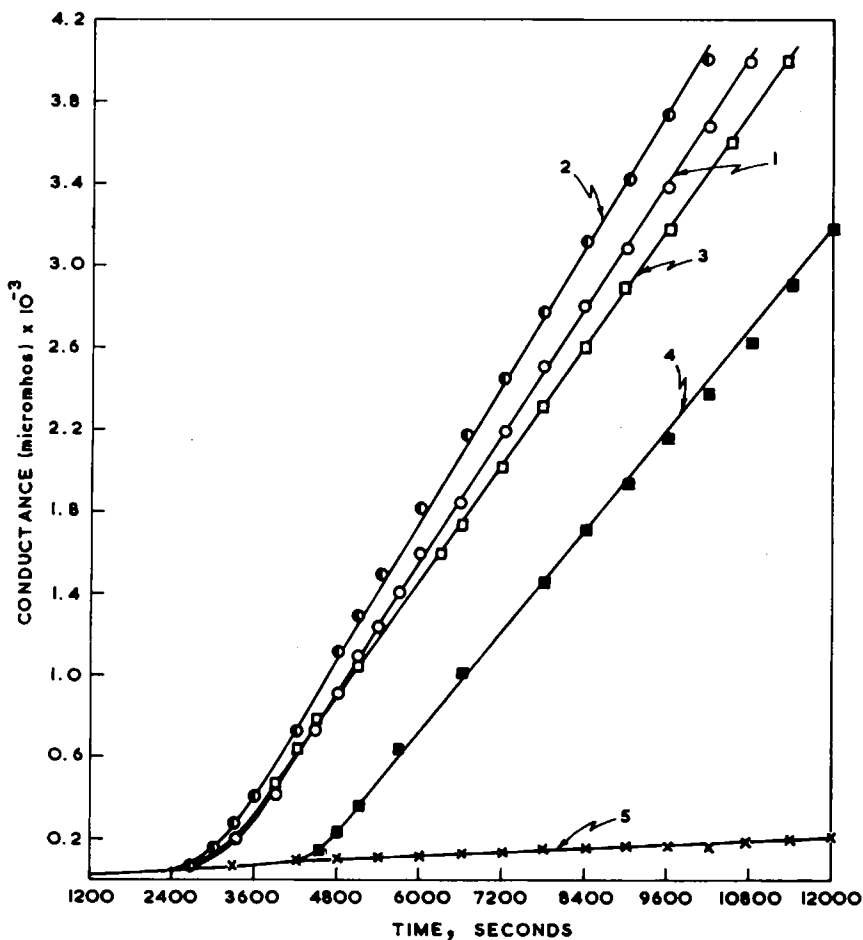
Fig. 3. Conductivity of the dissolving medium vs. degradation time for PVC/KM-365B blends: (1) 100/0; (2) 95/5; (3) 90/10; (4) 85/15; (5) 80/20; (6) 0/100.

But, the rate of degradation for PVC/KM-365B and PVC/CR-20 blends is found to be almost unaffected by the concentrations of modifiers (see Figs. 3 and 4). The PVC/CR-20 and PVC/CR-20gp-SAN (2:1) blends degrade faster than PVC/KM-365B blends and unmodified PVC, although the rates of degradation in PVC/CR-20gp-SAN (2:1) and PVC/CR-20 blends are found to be almost equal at the lower concentrations of modifiers (<10%), but at higher concentrations of these modifiers (>10%), the PVC/CR-20gp-SAN (2:1) blends degrade faster than PVC/CR-20 blends. Among the modifiers themselves, the rate of degradation is observed in the following order; KM-365B < CR-20 < CR-20gp-SAN (2:1).

The results of thermogravimetry under isothermal conditions are presented in Figures 7–9. This analysis also indicates the same order of thermal stability in PVC blends and modifiers, as observed by the former two techniques of HCl evolution. However, a few exceptions have been noticed in the present case (Table I). PVC/CR-20gp-SAN (2:1) and PVC/CR-20 blends have been found to be equally stable at 5–10% concentrations of the modifiers.
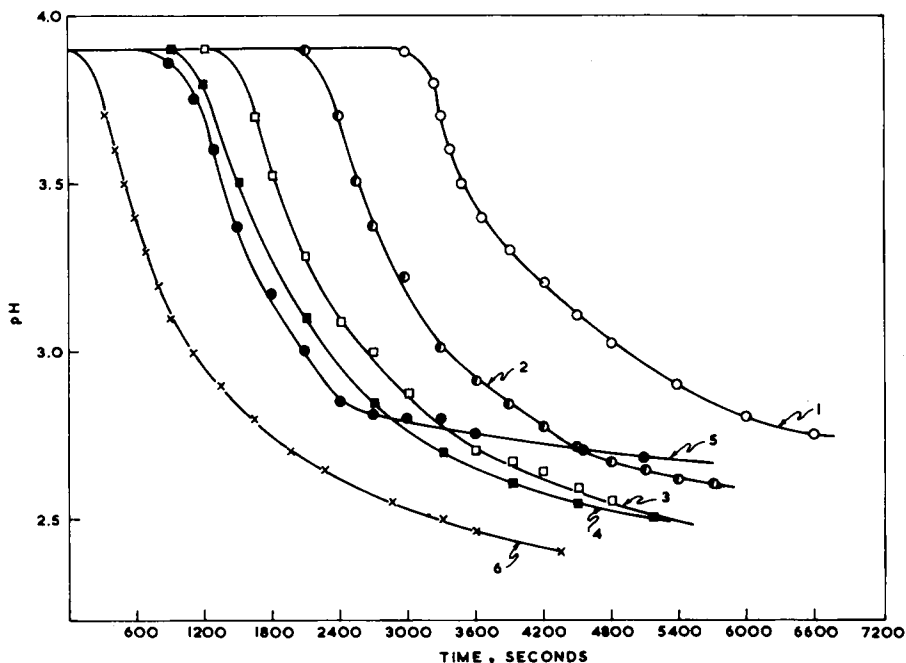
Fig. 4. pH of the dissolving medium vs. degradation time for PVC/CR-20 blends: (1) 100/0; (2) 95/5; (3) 90/10; (4) 85/15; (5) 80/20; (6) 0/100.

The systems studied under the present investigation are having a complex chemical structure. Among these, PVC/CR-20 blends are slightly heterogeneous in the studied range of compositions (0–25% of CR-20), and, thus, they form a semi-compatible system.[20] CR-20gp-SAN (2:1) is a chemical mixture of un-grafted chlororubber-20 and its graft copolymer [chlororubber-20-graft copoly-(styrene)acrylonitrile)] in which polystyrene and polyacrylonitrile components are present as grafted branches onto chlororubber-20 backbone chain. The details of the chemical nature and composition of CR-20gp-SAN (2:1) have been discussed elsewhere.[20,23] The blends of CR-20gp-SAN (2:1) with PVC have been observed to be more heterogeneous than PVC/CR-20 blends. KM-365B is an industrial impact modifier for PVC. The exact chemical nature of this modifier is not revealed; nevertheless, it is mentioned that it is an acrylate based modifier in which polyacrylates form major component. The thermal behavior of these blends, therefore, have to be viewed and discussed in context of their chemical nature.

Under the present investigation, the modified PVC is found to be more stable or to have longer induction time than CR-20 and CR-20gp-SAN (2:1) modified PVC blends. Earlier studies[7] on PVC/chlororubber blends indicate that chlororubber has negative effect on the thermal stability of PVC which is mainly due to the catalytic effect of its degradation product, i.e., HCl on the degradation reaction of PVC. In the present investigation also, similar negative effect of chlororubber-20 on the thermal stability of PVC was observed. It may be due to the destabilizing effect of chlororubber and polyacrylonitrile (PAN) phase. Their decomposition products, i.e., HCl and NH_3, respectively, catalyze the
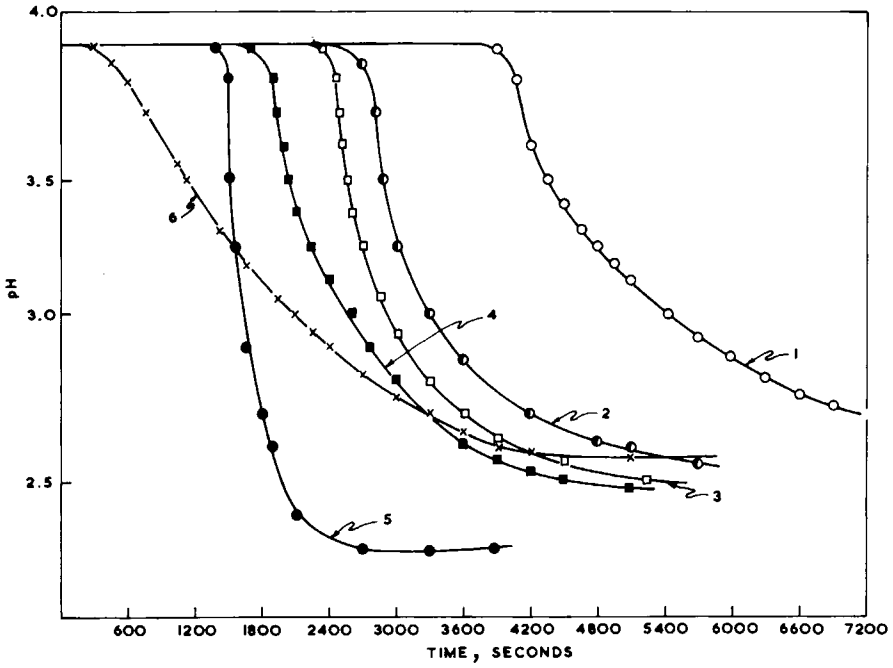
Fig. 5. pH of the dissolving medium vs. degradation time for PVC/CR-20gp-SAN (2:1) blends: (1) 100/0; (2) 95/5; (3) 90/10; (4) 85/15; (5) 80/20; (6) 0/100.
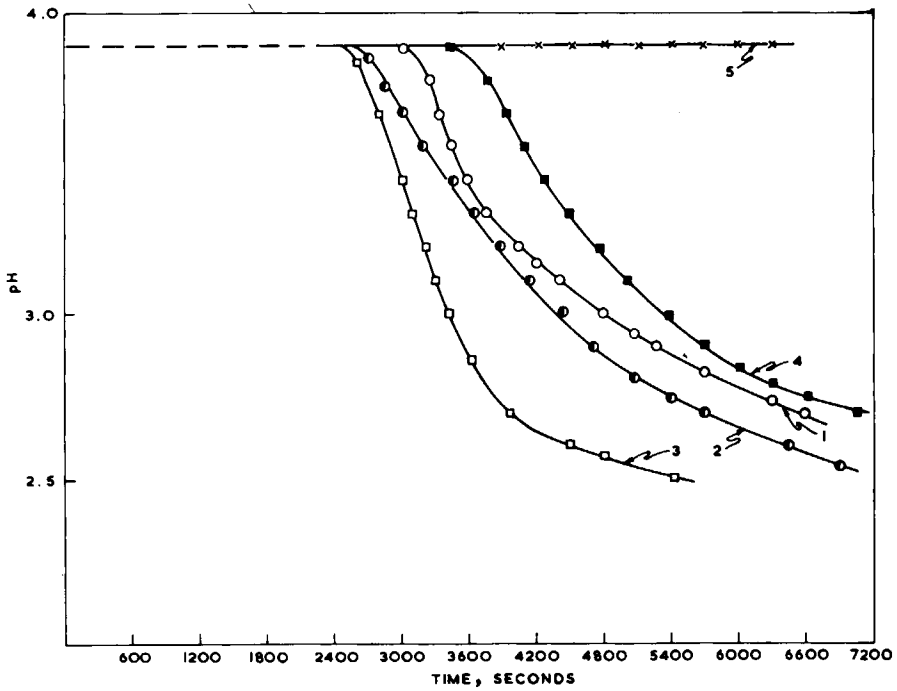

Fig. 6. pH of the dissolving medium vs. degradation time for PVC/KM-365 blends: (1) 100/0; (2) 95/5; (3) 90/10; (4) 85/15; (5) 0/100.
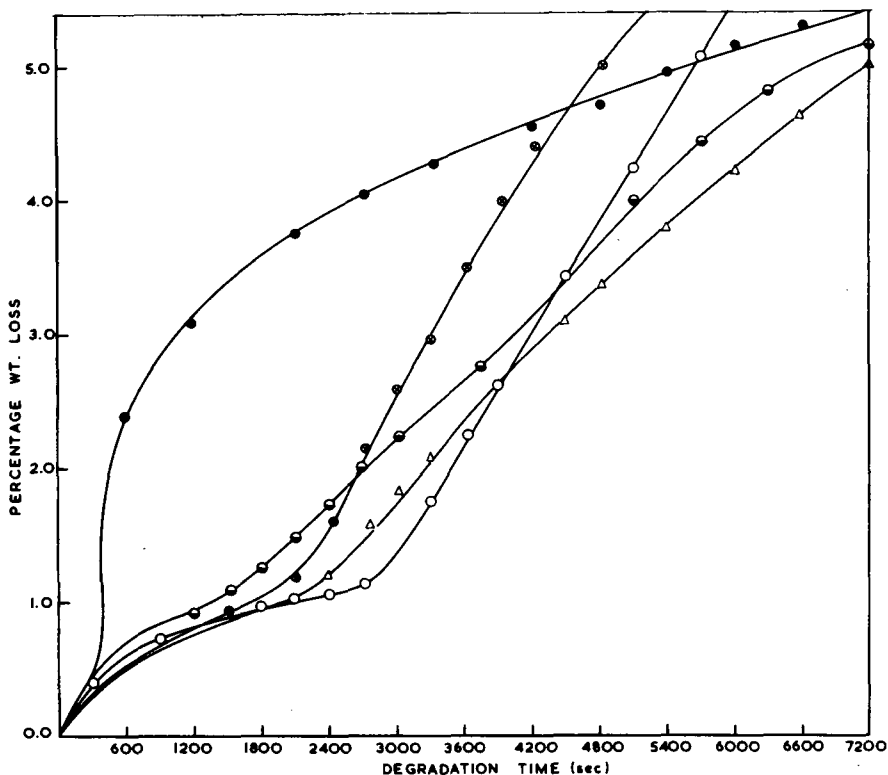
Fig. 7. Percentage weight loss of PVC/CR-20 blends vs. degradation time at constant temperature of 190 ± 1°C. (⊗) 100/0; (△) 95/5; (○) 90/10; (◓) 85/15; (●) 0/100.

degradation reaction of PVC.   The degradation reaction of PVC becomes more and more pronounced at higher concentrations of CR-20 and CR-20gp-SAN (2:1) because of the higher availability of NH_3 and HCl.   Moreover, the destabilizing effect of PAN increases due to the grafted nature of its molecule onto CR-20 backbone which makes its diffusion in PVC matrix much easier.

PVC/KM-365B blends are found to be the most stable amongst all the blends and unmodified PVC.   Since it is the acrylate group which is involved in the stabilization process of PVC matrix, its presence in KM-365B modifier, therefore, gives sufficient clue for the explanation of its above-mentioned stabilization action, though the exact chemical nature and composition of the compound is not known.   It may be due to the stabilizing action of acrylate phase which may be caused by two processes.[4,5]   First, when chlorine radicals from PVC dehydrochlorination site enter the polyacrylate phase and initiate its depolymerization which may compete with PVC for chlorine radicals; consequently, the evolution of HCl may be reduced.   Secondly, the interaction of the HCl with ester group of acrylate phase results in formation of anhydride rings in the polymer chains which may block further degradation.   At 5% concentration of KM-365B, the PVC/KM-365B blends are found to be less stable than unmodified PVC.   It may be due to the inhomogeneous distribution of the acrylate phase into PVC matrix because of its low concentration.
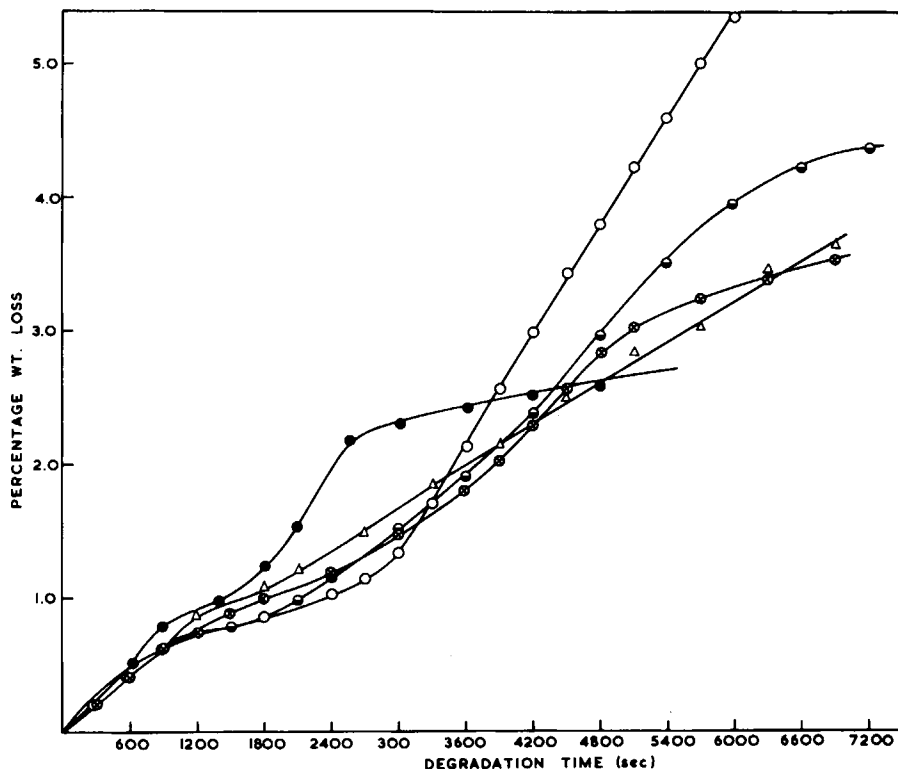
Fig. 8. Percentage weight loss of PVC/CR-20gp-SAN blends vs. degradation time at constant temperature of 190 ± 1°C. (O) 100/0; (⊗) 95/5; (△) 90/10; (⊖) 85/15; (●) 0/100.

PVC/CR-20gp-SAN (2:1) blends are found to be more stable than PVC/CR-20 blends, which may be due to the stabilizing effect of polystyrene phase on the PVC matrix as has been discussed by McNeill et al. for PVC/PS blends.[8,13] The presence of polystyrene phase as grafted branches onto CR-20 main chain provides it better opportunity to stabilize the PVC because of its proximity to the degradation reaction site. The grafted nature of polystyrene onto polar chlororubber backbone chain also provides it ample opportunity of diffusion into PVC matrix. Otherwise, polystyrene homopolymer is incompatible with PVC. Moreover, the grafted nature of polystyrene may also provide more surface area for increasing their stabilizing activities.

The rate of degradation of PVC/CR-20gp-SAN (2:1) blends has been observed to be increasing with the concentrations of CR-20gp-SAN (2:1) in the blends, but, in PVC/CR-20 and PVC/KM-365B blends, it is unaffected by the concentration of modifiers. This implies the following facts:

(i) Only one mechanism of stabilizing/destabilizing controls the degradation of PVC/KM-365B and PVC/CR-20 blends since the degradation rates in these blends are unaffected by the concentrations of modifiers.

(ii) The degradation rate of PVC/CR-20gp-SAN (2:1) blends is found to be increasing with concentration of CR-20gp-SAN (2:1). It indicates that, at higher concentrations, the destabilizing effects of CR-20 and PAN phases overshadow the stabilizing action of polystyrene, once the degradation starts.

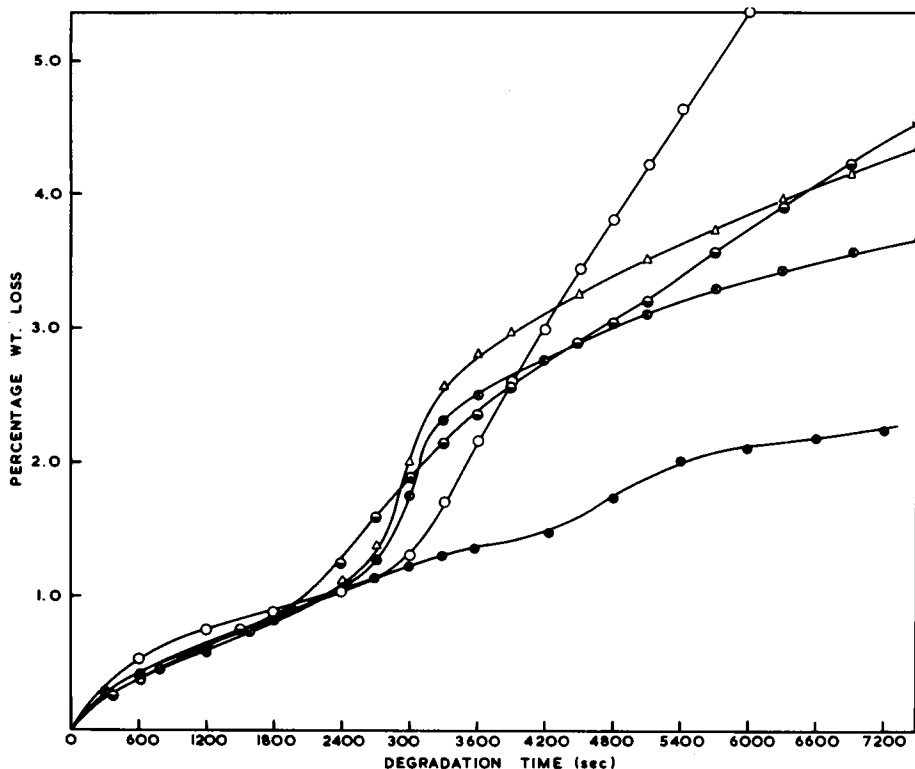(iii) If, at higher concentrations, the destabilizing effects of CR-20 and PAN

Fig. 9. Percentage weight loss of PVC/KM-365B blends vs. degradation time at constant temperature of 190 ± 1°C. (O) 100/0; (⊗) 95/5; (△) 90/10; (◓) 80/20; (●) 0/100.

overcome the stabilizing effect of polystyrene phase then PVC/CR-20 blends would have been more stable than PVC/CR-20-gp-SAN. But it is not true. It may, therefore, be inferred that PS also stabilizes the chlororubber-20 phase. After the initiation of degradation reaction, the catalytic effect caused by the decomposition products of chlororubber-20 and PAN, i.e., HCl and NH_3, respectively, becomes faster. Due to this mechanism, the degradation rate of PVC/CR-20gp-SAN (2:1) blends is more than that of the PVC/CR-20 blends.

It has been found by thermogravimetry under isothermal conditions that the rate of degradation at lower concentrations of modifiers in PVC blends is lesser than that of the unmodified PVC. This fact may be explained on the basis of stabilizing action of PS phase which is more pronounced at lower concentrations. But at higher concentrations, the destabilizing effect of CR-20 and PAN overcomes the stabilizing effect of PS. The rate of degradation and thermal behavior observed among the modifiers may also be explained on the basis of relative stabilizing effect of PS and destabilizing effects of CR-20 and PAN.

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