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Thermogravimetric analysis of PVC/NR-b-PU blends

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Abstract Thermal stability of solution-cast blends of poly(vinylchloride) and NR-b-PU block copolymers of three different chain extender diols was studied by thermogravimetry. Thermal degradation of individual components and their blends were investigated with special reference to blend ratio. As the block copolymer content in the blends increased their thermal stability was also found to increase. Enhanced thermal stability of PVC is believed due to the favorable interaction with PVC and the PU hard segments of the block copolymer. DTG curves were used for the determination of different stages involved in the degradation. Activation energy for degradation was determined from Coats–Redfern plot.

Keywords Polymer blends · Thermogravimetry · Degradation kinetics · Activation energy · Block copolymers · PVC

Introduction

Thermogravimetry of a polymeric material gives an idea about the composition and its thermal stability. Furthermore, a detailed understanding of the degradation of polymers on heating is relevant for the designing of materials with improved properties for specific application. It measures the change in mass of the material when it is heated at a constant temperature in an inert atmosphere or in the presence of air or oxygen. Blending of different polymers has introduced a new zone of technically important materials. For developing durable industrial products it is necessary to investigate the thermal stability of these blends. Thermogravimetry can be used as a way to measure the thermal stability of polymer due to the simplicity of this mass loss method.

The reaction between diisocyanates and a mixture of diols of different molecular masses provides thermoplastic polyurethane elastomers with a block segment structure. The preparation of thermoplastic polyurethane elastomers with a wide range of properties can be carried out by changing the combining ratios of reactive intermediates with variations in molecular structure. Typical polyurethanes are known to exhibit small resistance to heat. This low heat resistance is the main reason for limitation in technical application of polyurethanes. The thermal degradation of polyurethanes has been studied by various methods. Mass loss and activation energy of the degradation as a function of soft segment length and concentration was studied by thermogravimetry (TG) [1]. Rajalingam and Radhakrishnan [2] determined the oxidative stability of the polyurethanes by DSC. Apart from degradation of chemical bonds at high temperatures, the degradation of hydrogen bonds in hard segments of polyurethane in the temperature range 80–180 °C has been extensively studied by Sung and Schneider [3], Teo et al. [4], and Seymour and Cooper [5] using Fourier transform infrared (FTIR) spectroscopy.

Although there are many polymer blends, those containing poly(vinylchloride) (PVC), one of the most common commercial thermoplastics, are among the most important from both a scientific and a commercial point of view. PVC is, therefore, often blended with other polymers [6–9], including polyurethanes [10, 11].

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Afzal etal. [12] studied a series of blends of dodecylbenzenesulfonic acid (DBSA)-doped polyaniline (PANDR) and PVC were synthesized by solution blending technique and investigated by heat flow microcalorimetry (HFC) for thermal and oxidative stability and for PVC–PANDR compatibility. FTIR results provided evidence for strong dipole–dipole interactions between PANDR and PVC. Poly(vinyl chloride) (PVC), plasticized by di(2-ethylhexyl) phthalate (DEHP), medium molecular mass polyester urethane (PU), or by both plasticizers, was thermally degraded under dynamic thermogravimetric conditions and the kinetics of decomposition was studied by isoconversional methods by Pielichowski and Świerz-Motysia [13]. It has been found that the initial decomposition temperature is higher for PVC plasticized with PU, as compared with PVC plasticized with di(2-ethylhexyl)phthalate (DEHP) or plasticized with PU/DEHP, and thermal degradation shows features of a multi-step complex process. Thermal decomposition of three common plastics, polyethylene (PE), polystyrene (PS), and poly(vinylchloride) (PVC) has been studied and reported by some authors [14]. The thermal behavior of polyamide 6 nanocomposites (NC) and PA6/TPU/clay nanocomposite blends (NCB) were examined by non-isothermal thermogravimetry (TG, DTG), differential scanning calorimetry (DSC), and dynamic-mechanical thermal analysis (DMTA) [15]. Polyurethanes were prepared from 4,4′-methylenebis (phenyl isocyanate) (MDI), 1,4-butanediol (BD), and poly(tetrahydrofurane) polyether polyol (PTHF) by melt polymerization and their thermal characteristics were evaluated [16]. Thermal and mechanical characterization of the bio-compatible polymers, e.g., olefins, nylon, polyacetals, poly(vinylchloride), and polyesters are carried out using differential scanning calorimetry (DSC), thermogravimetry (TG), thermal mechanical analysis (TMA), and dynamic-mechanical analysis (DMA) [17]. A series of cross-linked polyurethane acrylate solids with glass transition temperatures ranging from −49 to +65 °C was prepared by photopolymerization of specially formulated solvent-free resins. The kinetics of thermooxidative and thermal (in N_2) degradation of these cross-linked acrylate networks at temperatures ranging from 100 to 400 °C was studied as a function of crosslink density using thermogravimetry [18].

In our laboratory, we have achieved the synthesis of low molecular mass NR-b-PU block copolymers [19, 20]. These materials are expected to act as a polymeric additive to PVC due to specific intra- and intermolecular interactions between PVC and PU segments leading to better thermal stability. The present study focuses on the thermal behavior of a few series of blends consisting of poly (vinylchloride) and NR-b-PU block copolymers. Thermal decomposition of these block copolymers and their blends were analyzed from TG and DTG curves. Activation energy for degradation was determined from Coats–Redfern plots.

Experimental

Materials

Poly(vinyl chloride) with K value 65, $\overline{M}_{\mathrm{W}} = 1.4 \times 10^5$, with density 1.37 g cm^{-3} supplied as powder by Chemicals and Plastics (Chennai, India). Natural crumb rubber (ISNR-5) $\overline{M}_{\mathrm{W}} = 8.2 \times 10^5$, intrinsic viscosity in benzene at 30 °C = 4.45 dL/g, was received from Rubber Research Institute of India (RRII) (Kottayam, India). Liquid natural rubber with $\overline{M}_{\mathrm{v}} = 4,600$ (LNR) is obtained by depolymerisation of NR [21]. THF soluble block copolymers from toluene diisocyanate (TDI), with chain extender diols, viz., propylene glycol (PG), 1,4-butane diol (1,4-BDO), and 1,3-butane diol (1,3-BDO), were synthesized by solution polymerization. Toluene diisocyanate (TDI) was an 80/20 mixture of 2,4- and 2,6-isomers. This was supplied by Merck (Germany) and used as received. Propylene glycol (PG) obtained from E. Merck, India and 1,4-Butane diol (1,4-BDO) supplied by Fluka (Switzerland). 1,3-Butane diol (1,3-BDO) was supplied by Riedel-dettaën (Germany). These diols dried with anhydrous CaO and then distilled under reduced pressure before use. Dibutyl tin dilaurate (DBTDL) was supplied by Fluka (Switzerland) and used as catalyst without further purification. Chloroform was laboratory grade, which was supplied by Merck. India Ltd., Bombay (India). It was dried with anhydrous calcium oxide and then distilled before use. Methanol (Reagent grade) was obtained from Merck India Ltd. It was used without further purification. Hydrogen peroxide (30%) was obtained from Merck India Ltd. Toluene and tetrahydrofuran (THF) (Reagent grade) supplied by Merck India Ltd. was distilled before use.

Synthesis of block copolymers

Soluble block copolymers from toluene diisocyanate (TDI), with chain extender diols, viz., propylene glycol (PG), 1,4-butane diol (1,4-BDO), and 1,3-butane diol (1,3-BDO), were synthesized by solution polymerization and characterized by a pre-reported procedure [22]. All the block copolymer samples were prepared with fixed NCO/OH ratio 1.08.

Preparation of blends

Three series of blends of PVC and three different NR-b-PU block copolymers were prepared from the common solvent

THF as follows. A 3% (w/v) solution of PVC in THF was prepared. This solution was then added to the block copolymer solution in THF at various compositions. It was thoroughly mixed using a magnetic stirrer for 12 h at 50 °C and cast on glass plates. The samples were then dried in vacuum at 70 °C for 2 days to remove the traces of residual solvent.

Thermogravimetric studies

Thermogravimetry (TG) was carried out on a DuPont 2000 TGA in N_2 atmosphere at a heating rate of 10 °C/min. The samples were scanned from 30 to 600 °C.

Designation of block copolymers and blends

Samples of block copolymers are designated as NR-b-PU_1, NR-b-PU_2, and NR-b-PU_3 representing NR-b-PU (PG), NR-b-PU (1,4-BDO), and NR-b-PU (1,3-BDO), respectively. The blends were designated as follows. PVC/NR-b-PU_1 (80/20) means a blend of 80 parts PVC and 20 parts NR-b-PU_1; PVC/NR-b-PU_2 (80/20) means a blend of 80 parts PVC and 20 parts NR-b-PU_2; PVC/NR-b-PU_3 (80/20) means a blend of 80 parts of PVC and 20 parts NR-b-PU_3, etc.

Results and discussion

Characterization of the block copolymers

The synthesized block copolymers were characterized by IR, NMR, and solution viscosity methods. The molecular masses of the block copolymers were determined by GPC using THF as the solvent and the characteristics described in Table 1.

Thermal analysis

The degradation temperature of PVC, NR-b-PU block copolymers and PVC/NR-b-PU blends has been analyzed by thermogravimetric method.

Thermal characteristics of blend components

Thermogravimetric traces of PVC, NR-b-PU_1, NR-b-PU_2, and NR-b-PU_3 are given as in Fig. 1a–d. The

Table 1 Composition and characteristics of NR-b-PU block copolymers

Sample	NCO/OH ratio	Mass% of hard segment	Mass% of soft segment	Intrinsic viscosity/dL g^{-1}	$\overline{M}_n$	$\overline{M}_W$	Dispersity
NR-b-PU_1	1.08	31.14	68.86	0.2603	14000	31400	2.242
NR-b-PU_2	1.08	31.88	68.12	0.2752	14877	33640	2.261
NR-b-PU_3	1.08	31.88	68.12	0.2656	14113	31810	2.253

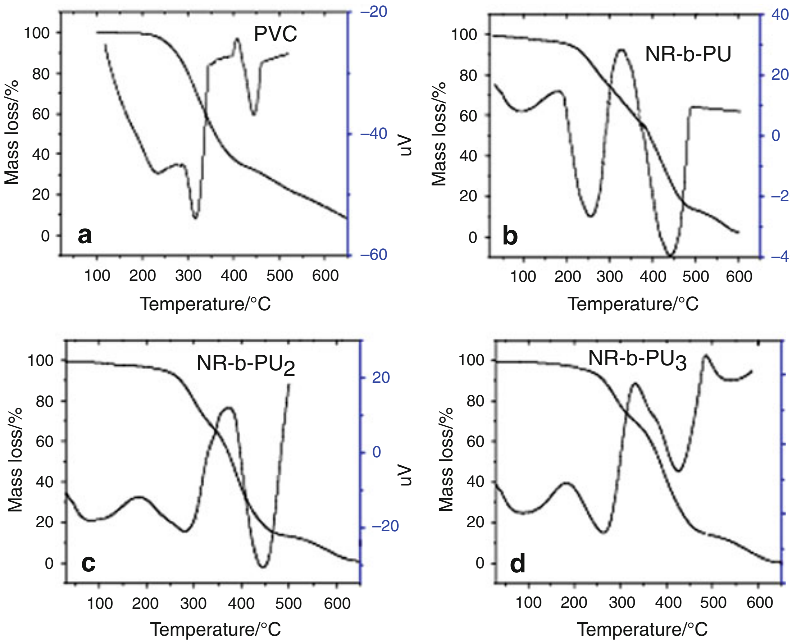


Fig. 1 Thermogravimetric curves of **a** PVC, **b** NR-b-PU_1, **c** NR-b-PU_2, and **d** NR-b-PU_3

Table 2 Phenomenological data for the thermal decomposition of PVC, NR-b-PU_1, NR-b-PU_2, and NR-b-PU_3

Sample	First stage				Second stage		
	Onset temp./°C (T_0^1)	Temp. range/°C	Peak temp./°C (T_{max}^1)	Mass loss/%	Onset temp./°C (T_0^2)	Peak temp./°C (T_{max}^2)	Mass loss/%
PVC	180	180–375	316	59.8	375–550	447	29.7
NR-b-PU_1	180	180–330	253	29.4	330–600	438	69.2
NR-b-PU_2	220	220–330	288	30.6	330–600	441	66.2
NR-b-PU_3	205	205–330	261	29.4	330–600	439	68.0

phenomenological data of thermal decompositions are tabulated in Table 2. A two stage degradation pattern is seen in the case of PVC. The first stage begins at 180 °C (T_0) and ends at 375 °C with a peak temperature at 306 °C (T_{max}^1). This corresponds to a mass loss of 59.8%, which is attributed to the elimination of HCl molecules leaving behind longer polyene chains. Second stage of degradation begins at 375 °C (T_0^2) and ends at 490 °C with a peak temperature of 466 °C (T_{max}^2). Thermal degradation of the polyene sequences occurs during this stage yielding volatile aromatic and aliphatic compounds by the intramolecular cyclization of the conjugated sequences [23]. The total mass loss at this stage is found to be 89.5%.

NR-b-PU block copolymers also exhibit two stage degradation indicating a two-phase morphology. All samples decomposed in two stages (Fig. 1b–d), indicating the coexistence of two components. The onset of mass loss, the temperature of complete decomposition, the DTG peak temperatures, and the percentage of mass loss in each stage are summarized in Table 2.

The onset of mass loss in the first stage occurs between 180 and 220 °C for the three block copolymers. The percentage of mass loss in this stage corresponds to the hard segment content, which indicates that the first stage of decomposition is due to hard segments. Obviously, the second stage of decomposition is due to the soft segments, since the percentage of mass loss here corresponds to the soft segment content as shown in Table 2. The first stage of decomposition is completed in the temperature range 180–330 °C. The second stage of decomposition is rather rapid. It begins around 300 °C and is completed in the range 550–600 °C. Two stage decomposition is a clear indication of the heterophase nature of block copolymers.

Among the block copolymers 1,4-BDO-based sample, viz., NR-b-PU_2 have higher onset of mass loss indicating higher thermal stability. This can be attributed to the methylene straight $(CH_2)_4$ chain in 1,4-BDO which leads to some extent of chain alignment in the block copolymer. Among the PG and 1,3-BDO samples, viz., NR-b-PU_1, and viz., NR-b-PU_3, the latter has more stability as per data. This can be attributed to a more extended structure of 1,3-BDO than PG.

Evaluation of the peak temperatures observed in the DTG curves also provides ample data in determining the thermal stability. Table 2 shows a comparison among the average peak temperatures of the three block copolymer samples. Corresponding to the two-step decomposition there are two peaks in the DTG curves of all the samples. The first peak represents the decomposition of the hard segment and the second peak represents the decomposition of the soft segment. Variation of peak temperatures with the structures of the chain extenders follow more or less in the same pattern of the onset of mass loss. The average peak temperatures of the various compositions corresponding to the first stage of thermal decomposition for the various block copolymers are 253, 288, and 261 °C, respectively, for NR-b-PU_1, NR-b-PU_2, and NR-b-PU_3 indicating that 1,4-BDO-based sample has maximum thermal stability as per the peak temperature. It is to be noted that irrespective of the nature of the chain extender diol the average peak temperature in the second stage of thermal decomposition is almost invariant and occurs around 440 °C. This is expected since the NR soft segment used is the same in all the block copolymers.

Thermal characteristics of blends

The blends were prepared in three series, viz., PVC/NR-b-PU_1, PVC/NR-b-PU_2, and PVC/NR-b-PU_3. Samples were made in different compositions such as 80/20, 60/40, 40/60, and 20/80 of PVC and the three block copolymers. All the samples were subjected to thermogravimetry and the data were used to assess the effect of block copolymer content on the degradation pattern of PVC.

Thermogravimetric curves of PVC/NR-b-PU_1 blends at 80/20, 60/40, 40/60, and 20/80 compositions are given in Fig. 2. The phenomenological data obtained are noted in Table 3. All the samples undergo a two stage degradation pattern. The first stage degradation with a peak temperature around 260 °C for the different compositions corresponds to the parallel decompositions PU hard segment and the dehydrochlorination of PVC. Mass loss at this stage appropriated to the PU hard segment and PVC content in

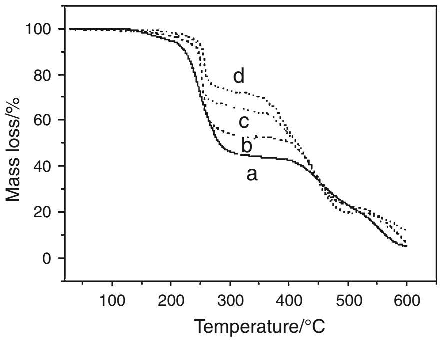


Fig. 2 Thermogravimetric curves of PVC/NR-b-PU_1 blends (*a*) 80/20, (*b*) 60/40, (*c*) 40/60, and (*d*) 20/80 compositions

the blend was found to be 56.1, 47.1, 35.3, and 29 for the 80/20, 60/40, 40/60, and 20/80 compositions, respectively, as against the calculated values of 53.7, 47.6, 41.6, and 35.4. The peak temperature increases with the increase in the PU content. Observed mass loss for the blends with higher PU content progressively decreased than the calculated values. Increase in peak temperature and reduction in mass loss is an indication of greater thermal stability. This may be explained by the increased polar interactions between the PU hard segment and PVC.

Table 3 shows that the peak temperature for the second stage degradation occurs around 450 °C which is again the degradation temperature corresponding to that of the NR and the residual polyene formed after the dehydrochlorination of PVC. Over 90% mass loss occurs at this stage indicating the completion of the degradation process. Compared to the first stage there is no considerable variation in the peak temperature with increase in the blend ratio. Mass loss occurred in the second stage degradation are 34.0, 41.5, 52.2, and 55.5, respectively, for the 80/20, 60/40, 40/60, and 20/80 compositions. These values reflect almost the same trend as that of the first stage with nominal reduction in mass loss values. This may be followed by the fact that there are no stabilizing interactions involved in this stage. But the overall thermal stability of all the three series of blends stands modified by increasing the PU content.

Similar results are obtained for the other two series also. Thermogravimetric curves for the PVC/NR-b-PU_2 and PVC/NR-b-PU_3 blends are given in Figs. 3 and 4, respectively. The phenomenological data obtained are noted in Table 3. For the PVC/NR-b-PU_2 series blends the peak temperatures for the decomposition of the blends occurred at higher temperatures compared to the first series. For example, the peak temperature for the 80/20 blend

Table 3 Phenomenological data for the thermal decomposition of PVC/NR-b-PU_1, PVC/NR-b-PU_2, and PVC/NR-b-PU_3 blends

Blend	First stage				Second stage			Total mass loss/%
	Onset temp./°C (T_0^1)	Temp. range/°C	Peak temp./°C ($T_{\max}^1$)	Mass loss/%	Temp. range/°C	Peak temp./°C ($T_{\max}^2$)	Mass loss/%	
PVC/NR-b-PU_1 (80/20)	185	185–380	243	56.1	380–600	458	34.03	90.1
PVC/NR-b-PU_1 (60/40)	190	190–380	250	46.0	380–600	466	41.5	87.5
PVC/NR-b-PU_1 (40/60)	200	200–335	259	35.2	335–600	469	52.19	87.4
PVC/NR-b-PU_1 (20/80)	205	220–335	263	29.0	335–600	472	55.5	84.6
PVC/NR-b-PU_2 (80/20)	195	195–380	266	53.4	380–600	468	29.3	82.8
PVC/NR-b-PU_2 (60/40)	206	186–380	277	45.3	380–600	472	35.8	81.2
PVC/NR-b-PU_2 (40/60)	210	210–380	281	26.3	330–600	478	50.1	76.4
PVC/NR-b-PU_2 (20/80)	216	216–330	290	20.1	330–600	484	54.0	74.1
PVC/NR-b-PU_3 (80/20)	190	190–380	250	55.1	380–600	462	30.0	85.1
PVC/NR-b-PU_3 (60/40)	195	195–380	256	46.3	380–600	468	38.8	85.1
PVC/NR-b-PU_3 (40/60)	205	205–350	263	34.1	350–600	471	50.2	84.3
PVC/NR-b-PU_3 (20/80)	210	210–350	269	29.0	350–600	475	54.0	83.0

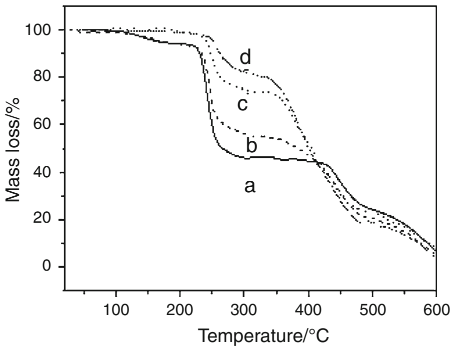


Fig. 3 Thermogravimetric curves of PVC/NR-b-PU$_1$ blends (*a*) 80/20, (*b*) 60/40, (*c*) 40/60, and (*d*) 20/80 compositions

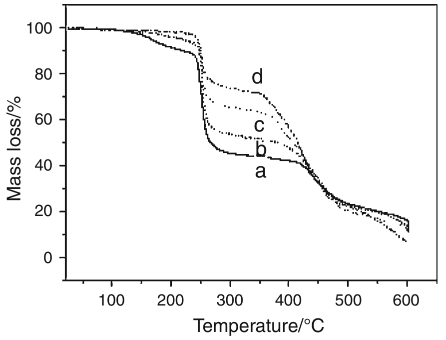


Fig. 4 Thermogravimetric curves of PVC/NR-b-PU$_1$ blends (*a*) 80/20, (*b*) 60/40, (*c*) 40/60, and (*d*) 20/80 compositions

occurred at 266 and that of 20/80 at 290 °C compared to 243 and 263 °C, respectively, for the first series. This indicates better thermal stability of this series. The third series showed intermediate values as indicated in Table 3. For comparison the calculated and observed mass losses for the all blends are listed in Table 4. Second stage decompositions also showed same trend with increased reduction in mass losses compared to the first series. Figure 5 shows the variation of the observed and calculated mass loss values with block copolymer content for the first stage of degradation for the all three series of blends. Among the three series PVC/NR-b-PU$_2$ shows maximum thermal stability.

The temperature at which 50% mass loss happens is tabulated in Table 5. It is noted that the values are highest for the PVC/NR-b-PU$_2$ blends reflecting maximum thermal stability. Percentage mass loss at three different temperatures selected at random, viz., 200, 300, 350, 400, and 500 °C (Δm_1, Δm_2, Δm_3, Δm_4, Δm_5) for all the three series of blends were shown in Table 5. These data are intended to follow the stability of the blends in terms of the mass loss. Values are lowest for the different compositions involving NR-b-PU$_2$ indicating its role in the thermal stabilization of PVC.

Table 4 Variation of calculated and observed mass loss for the blends

Blend	I Stage mass loss/%		II Stage mass loss/%	
	Calculated	Observed	Calculated	Observed
PVC/NR-b-PU$_1$ (80/20)	53.7	56.1	37.6	34.0
PVC/NR-b-PU$_1$ (60/40)	47.6	46.0	45.5	41.5
PVC/NR-b-PU$_1$ (40/60)	41.6	35.2	53.4	52.1
PVC/NR-b-PU$_1$ (20/80)	35.4	29.0	61.3	55.5
PVC/NR-b-PU$_2$ (80/20)	53.9	53.4	37.0	29.3
PVC/NR-b-PU$_2$ (60/40)	48.1	45.3	44.3	35.8
PVC/NR-b-PU$_2$ (40/60)	42.3	26.3	51.6	50.1
PVC/NR-b-PU$_2$ (20/80)	36.3	20.1	58.9	54.0
PVC/NR-b-PU$_3$ (80/20)	53.7	55.1	37.3	30.0
PVC/NR-b-PU$_3$ (60/40)	47.7	46.3	45.0	38.8
PVC/NR-b-PU$_3$ (40/60)	41.6	34.1	52.1	50.2
PVC/NR-b-PU$_3$ (20/80)	35.4	29.0	60.3	54.0

Thermal degradation kinetics

The kinetic parameters for the thermal degradation of PVC, the block copolymers synthesized and their blends with PVC were derived from the TG curves by applying an analytical method proposed by Coats and Redfern [24]. In solid state thermal decomposition reactions, which are generally homogenous in nature, the mechanism is governed by three fundamental aspects, viz., the laws of diffusion, nucleus formation, and its growth and phase-boundary movements. Overall rate of decomposition is controlled by these processes. The most prominent rate controlling process operating in a particular case is chosen and used for deriving the rate equations. The integral equation was used in the form:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

where $g(\alpha)$ is the kinetic model function, α is the decomposed fraction at any temperature, T, ϕ is the heating rate, A is a numerical constant, and E stands for activation energy. A plot of the above integral equation against $1/T$ gives a straight line with slope $= E/R$ and intercept $= \ln(AR/\phi E)$.

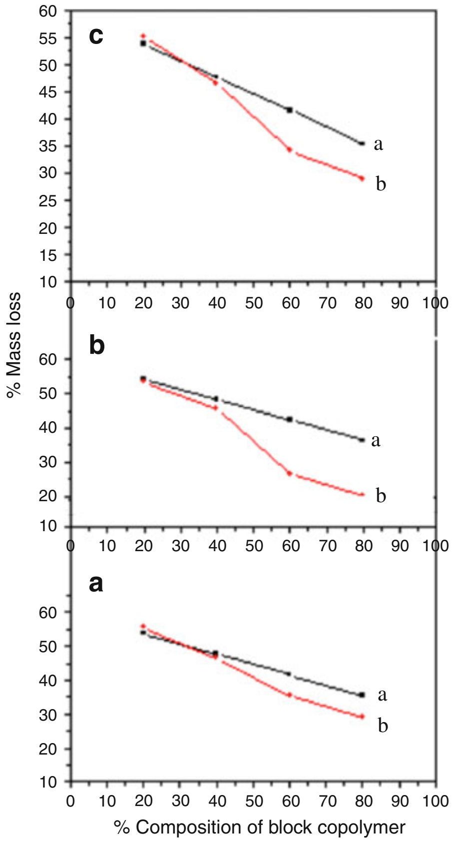


Fig. 5 Variation of calculated and observed mass loss for the first stage thermal decomposition for **a** PVC/NR-b-PU$_1$, **b** PVC/NR-b-PU$_2$, and **c** PVC/NR-b-PU$_3$ blends

Table 5 Mass losses at different temperatures and 50% mass loss temperatures due to the blends

Blend	Mass loss/%					T_{50}/°C
	Δm_1 200 °C	Δm_2 300 °C	Δm_3 350 °C	Δm_4 400 °C	Δm_5 500 °C	
PVC/NR-b-PU$_1$ (80/20)	5.9	54.3	56.1	57.3	77.1	260.3
PVC/NR-b-PU$_1$ (60/40)	4.0	45.4	47.7	49.4	77.2	376.6
PVC/NR-b-PU$_1$ (40/60)	2.9	34.1	36.9	45.4	80.6	397.3
PVC/NR-b-PU$_1$ (20/80)	2.3	27.8	29.6	45.4	80.0	406.0
PVC/NR-b-PU$_2$ (80/20)	5.9	54.1	54.1	56.0	76.4	282.4
PVC/NR-b-PU$_2$ (60/40)	3.8	44.9	46.1	52.9	75.1	398.6
PVC/NR-b-PU$_2$ (40/60)	1.1	25.7	28.1	47.3	75.0	410.7
PVC/NR-b-PU$_2$ (20/80)	0.9	17.6	23.2	51.7	74.1	418.5
PVC/NR-b-PU$_3$ (80/20)	5.9	55.1	56.8	58.4	77.2	267.9
PVC/NR-b-PU$_3$ (60/40)	4.0	47.1	48.8	51.7	77.6	389.6
PVC/NR-b-PU$_3$ (40/60)	2.8	36.4	36.9	49.4	78.9	398.6
PVC/NR-b-PU$_3$ (20/80)	2.3	20.7	29.0	44.3	80.0	407.3

All the TG data were analysed using the nine mechanistic equation proposed by Satava [25] and their kinetic parameters were calculated. The kinetic parameters for the two stage thermal decomposition of the homopolymers and the blends are shown in Table 6.

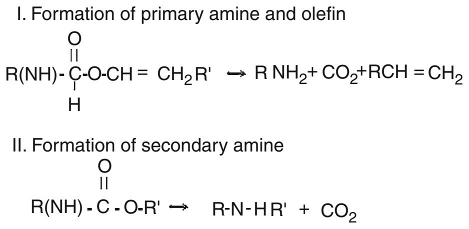
The observed mechanisms of decomposition of the homopolymers are as follows. It can be assumed that thermal decomposition of block copolymers proceeds through the formation of volatile products as indicated by Scheme 1. The degradation of PVC has been studied extensively and literature reveals that in the initial stage of the thermal decomposition of PVC, compounds with conjugated double bonds (polyenes) are produced in the polymer main chain by removal of hydrogen chloride via a zipper reaction. The removal of labile chlorine atoms in PVC induced the zipper reaction [26, 27]. At relatively higher temperatures (above 400 °C), the dehydrochlorinated PVC was converted to benzene, toluene, alkyl benzene, and polycyclic aromatic compounds [28]. Hydrogen chloride has been reported to catalyze the dehydrochlorination of PVC [29, 30]. Miranda et al. proposed that PVC decomposition occurred in three steps: dehydrochlorination at 200–320 °C, production of hydrogen chloride and benzene at 250–375 °C, and polycondensation of dehydrochlorinated PVC to form polycyclic aromatic compounds at 375–520 °C [31, 32]. This radical chain mechanism involves initiation by C–Cl bond scission and propagation by H abstraction from the adjacent carbon atom simultaneously with the formation of another chlorine atom and regeneration of the organic radical.

Dehydrochlorination of PVC which is an autocatalytic process follows, one dimensional diffusion mechanism according to the mechanistic equation obtained in the form $(\alpha)^2 = kt$. Second stage involved the scission of the polyene chains the Mampel equation $-\ln(1-\alpha) = kt$ best represents the experimental data which gives the mechanism, viz., random nucleation with one nucleus on each particle. Same pattern is followed in the decomposition of the block copolymers, the first stage, viz., the decomposition of the PU hard segments occurred by the one dimensional diffusion path way and the second stage, the decomposition of the soft segment by the random nucleation mechanism.

It can be assumed that the decomposition mechanism for PVC/PU blends proceeds through formation of typical volatile products as in the case of the homopolymers, but the characteristic decomposition temperatures are shifted towards higher temperatures. It was found that the Mampel equation $-\ln(1-\alpha) = kt$ best represents the experimental

Table 6 Kinetic parameters of blend components and the blends

Sample	Activation energy		Arrhenius parameter		Entropy of activation	
	E/kJ mol^{-1}		A/s^{-1}		ΔS/J deg^{-1} mol^{-1}	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
PVC	73	103	2	7	−246	−236
NR-b-PU$_1$	42.7	68	530	584	−243	−206
NR-b-PU$_2$	43.5	125	649	740	−248	−211
NR-b-PU$_3$	79	120	943	780	−271	−215
PVC/NR-b-PU$_1$ (80/20)	29.6	86	189	416	−265	−223
PVC/NR-b-PU$_1$ (60/40)	40.4	114	634	574	−265	−199
PVC/NR-b-PU$_1$ (40/60)	80.5	126	715	651	−270	−228
PVC/NR-b-PU$_1$ (20/80)	93.7	145	800	858	−271.8	−235
PVC/NR-b-PU$_2$ (80/20)	40.2	98	284	529	−238	−186
PVC/NR-b-PU$_2$ (60/40)	73.1	123	496	653	−241	−201
PVC/NR-b-PU$_2$ (40/60)	95.1	154	750	958	−247	−228
PVC/NR-b-PU$_2$ (20/80)	110.9	198	1396	1875	−247	−218
PVC/NR-b-PU$_3$ (80/20)	34.4	95	265	506	−218	−183
PVC/NR-b-PU$_3$ (60/40)	51.9	121	487	634	−243	−202
PVC/NR-b-PU$_3$ (40/60)	93.2	147	745	965	−256	−234
PVC/NR-b-PU$_3$ (20/80)	98.9	195	1296	1765	−234	−201



$$\mathrm{R(NH)\text{-}C(=O)(H)\text{-}O\text{-}CH=CH_2R'} \rightarrow \mathrm{R\,NH_2 + CO_2 + RCH=CH_2}$$

$$\mathrm{R(NH)\text{-}C(=O)\text{-}O\text{-}R'} \rightarrow \mathrm{R\text{-}N\text{-}H\,R' + CO_2}$$

Scheme 1 Scheme of decomposition of NR/PU block copolymers

$$\mathrm{R\,NH_2 + HCl} \rightarrow \mathrm{R\,NH_2\,HCl}$$

$$\mathrm{R\,NH\,R'} \rightarrow \mathrm{R\,NH\,R'\,HCl}$$

Scheme 2 HCl absorption mechanism

data and gives a mechanism of the first stage degradation reaction in all the blend samples, which corresponds to random nucleation with one nucleus on each particle mechanism for the solid state thermal decomposition. This change in the mechanism in comparison to the blend components suggests that the dehydrochlorination and decomposition of the PU segments now follows another interrelated route, which slows down autocatalytic dehydrochlorination of PVC. This can be explained by the trapping of HCl by the products of PU decomposition as per suggested Scheme 2. From this it is obvious that the blend characteristics undergo a change with respect to the PU content which could be due to the greater interaction between the blend components enabled by the higher PU content.

Activation energy for the first stage degradation of PVC, NR-b-PU$_1$, NR-b-PU$_2$, and NR-b-PU$_3$ was 72.9, 42.7, 42.8, and 53.2 kJ/mol, respectively. Regarding the blends, the activation energy for the first stage degradation of PVC/NR-b-PU$_1$ is in the order 29.6, 40.4, 81.5, and 93.7 kJ/mol for the 80/20, 60/40, 40/60, and 20/80 blends, respectively. For PVC/NR-b-PU$_2$ blends the values are 40.2, 73.2, 95.0, and 110.9 kJ/mol for the four compositions. PVC/NR-b-PU$_3$ blends showed intermediate values, viz., 34.4, 51.8, 93.2, and 98.9 kJ/mol, respectively. However, in the first stage of degradation E seems to be low for the 80/20 composition in which polyurethane content is the lowest, where much intermolecular attraction is not expected due to the formation of shorter chains. The marked increase in activation energy values is in agreement with the observation that the blends with higher PU content indicate greater degree of interaction between the blend components which slows down the dehydrochlorination process causing stabilization of PVC against the dehydrochlorination.

Activation energy for the second stage degradation of PVC is 102.9 kJ/mol. The values remain high for all the blend systems as indicated in Table 6. Higher activation energy is construed by the fact that this stage involves chain breaking. The soft segment is devoid of polar interaction and thus no gradation in the activation energy is observed.

The entropy of activation (ΔS) was also calculated for each stage of thermal decomposition for the various blends using the relationship:

$$A = (k\,T_{\mathrm{s}}/h)\, e^{\Delta S/R}$$

where A is the Arrhenius parameter, k the Boltzmann constant, T_{s} the peak temperature, ΔS the entropy of activation, and R the gas constant. Table 6 shows that ΔS has negative values. Entropy of activation in the first stage ranges from −238 to −272 J/deg/mol. Second stage values are little lower and ranges from −186 to −263 J/deg/mol. The negative values of the entropy of activation (ΔS) in both stages of the thermal decomposition of the copolymers suggest that the segments undergo some chain alignment at elevated temperatures forming the activated complex. This interim order is more pronounced in the hard segment decomposition and relatively less in the soft segment decomposition. The reason for this is the higher interaction through hydrogen bonding and dipolar interaction in the polyurethane part, leading to greater ordering in the activated complex compared to the soft segment. This is reflected in the magnitude of the entropy change which is more in the first stage than in the second stage. Arrhenius parameter, A, exhibits a regular trend. Values for second stage degradations are much higher than the first stage values as shown in Table 6. Higher values for the second stage could be accounted by the higher collision frequencies at the degradation temperatures.

Conclusions

Thermal degradation of the blends is found to occur through a two step route in which the first step corresponds to the parallel decomposition PVC and the PU hard segments of the block copolymer. The second step is attributed to the decomposition of the NR soft segment of the block copolymer and the polyenes formed from the dehydrochlorination of PVC. Thermal stability of PVC is found to be enhanced by the addition of NR-b-PU block copolymers and increases with blend ratio. Enhanced thermal stability of these blends is attributed to specific intra- and intermolecular interactions of PU hard segments with PVC. It was found that the Mampel equation $-\ln(1-\alpha) = kt$ best represents the experimental data and gives a mechanism of the first stage degradation reaction in all the blend samples, which corresponds to random nucleation with one nucleus on each particle mechanism for the solid state thermal decomposition.

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