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Thermal degradation and stability of HTPB-based polyurethane and polyurethaneureas

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Abstract

Thermal degradation profile of hydroxyterminated polybutadiene (HTPB)-based polyurethane and polyurethaneureas has been studied as function of chain extender concentration. Thermogravimetric analysis revealed the degradation as a two-step weight loss process. The cross-link density of polyurethane was seen to restrict the extent of weight loss during the depolycondensation of urethane bonds at higher temperature. Degradation in polybutadiene segment was associated with fragmentation, cyclization followed by rapid chain scission. Polyurethanes experienced a lower weight loss in first step during thermo-oxidative degradation over that in presence of nitrogen. The step-wise activation energies of degradation were calculated by *Coats–Redfern* and *Chatterjee–Conrad* methods. Accelerated aging of polyurethanes in air results in lowering of tensile strength with time.

Keywords: HTPB; Polyurethaneurea; Thermo-oxidative degradation; Cross-link; Kinetics

1. Introduction

Hydroxyterminated polybutadiene (HTPB)-based polyurethanes is used as solid composite propellants in space application [1–3]. HTPB-based polyurethanes are also useful as coatings, adhesives and sealants [4,5]. Hence a thorough study of the thermal degradation of these types of polyurethanes at high temperature is important to detect its service temperature as well as the probable degradation products to take measures against toxicity and pollution. The thermal degradation of polyurethanes has been studied by various methods. Weight loss and activation energy of the degradation as a function of soft segment length and concentration was studied by thermogravimetric analysis (TGA) [6]. Rajalingam and Radhakrishnan [7] 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 [8], Yamamoto et al. [9], Hayashi et al. [10], Teo et al. [11] and Seymour and Cooper [12] using Fourier transform infrared (FTIR) spectroscopy. Layton [13] and Christiansen et al. [14] have studied the thermal aging of HTPB-based polyurethane propellants at relatively low temperature and found that the mechanical property changed linearly with logarithmic aging time. Variation in thermal stability of HTPB-based polyurethanes made from different diisocyanates and NCO:OH ratio was shown by Desai et al. [15]. Harris et al. [16] analyzed

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the products of thermo-oxidative degradation of HTPB–TDI-based polyurethane by NMR. Barikani and Hepburn [17,18] reported some improvement of thermal stability in polyurethanes with the addition of low molecular weight diol chain extender. Liaw [19] used 4,4′-dihydroxydiphenylsulfone (bisphenol-S) chain extender in order to obtain better thermal stability. But Lee and Ko [20] have shown that the increase in chain extender concentration lowered the initial degradation temperature as revealed from TGA. On the other hand, an optimized hard segment concentration is required to get maximum tensile strength of segmented polyurethane. Hence it is important to study the thermal stability of polyurethane with the variation of chain extender concentration. In an earlier communication [21] we have shown that HTPB-based diamine chain extended cross-linked polyurethane attains maximum tensile strength and highest chemical cross-link density using 50 mol% diamine chain extender. Beyond 50 mol% chain extender cross-link density as well as tensile strength decreases. In the present communication we report the thermal degradation characteristics of HTPB-based polyurethane and polyurethaneureas with varying concentration of aromatic chain extender 4,4′-diaminodiphenylsulfone (DADPS). In order to study the variation in thermal endurance of polyurethanes as a function of diamine concentration and the cross-link density, TGA/DSC analyses were carried out both in inert atmosphere and in air. The degradation and weight loss characteristics obtained in TGA analysis have been correlated with the heat change profile obtained in DSC measurements. Moreover, we have carried out the step-wise degradation kinetics of the synthesized polyurethanes by two established methods [22] dealing with decomposition kinetics of HTPB-based polyurethanes. The thermal stability and mechanical properties of the synthesized polyurethanes have also been correlated with their structures.

2. Experimental

2.1. Materials

HTPB (functionality = 2.4, hydroxyl value = 43.2 mg KOH/g) with a number average molecular weight of 2580 ($\bar{M}_n$) was received from VSSC (India) and was used as received. 2,4-Toluene diisocyanate (TDI) (Fluka AG) was used without further purification. DADPS (Fluka AG) was first dehydrated under vacuum overnight and was then sublimed. The catalyst dibutyltin dilaurate (DBTDL) was used as received. Tetrahydrofuran (THF) and hexane (S.D. Fine Chemicals, India) were purified as per standard procedure.

2.2. Synthesis of prepolyurethane (PPUD) and polyurethaneureas

The PPUD used in this study was prepared from solution polymerization of HTPB and TDI (NCO:OH = 2:1) at 30 °C using 0.05 wt.% DBTDL as catalyst. The details of the synthesis have been reported earlier. For synthesis of polyurethaneureas (PUUSD20, PUUSD50 and PUUSD100) DADPS was added to the PPUD solution at varying concentrations (20, 50 and 100 mol%, respectively, with respect to $\bar{M}_n$ of HTPB). The PPUD and polyurethaneurea sheets were cast from the degassed viscous polymer solution on a clean flat-base Petri dish and moisture cured for overnight. The compositions of synthesized polyurethane and polyurethaneureas are listed in Table 1.

2.3. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

TGA/DSC analysis has been performed for polyurethanes in Mettler TG50 and DSC25 module attached to a Mettler TC II 4000 thermal analyzer using alumina crucible with a pinhole. The analyses were performed at a heating rate of 10 °C/min under nitrogen/air flow rate of 100 ml/min.

2.4. Fourier transform infrared (FTIR) spectroscopic analysis

FTIR spectroscopic analysis was carried out with a Nicolet Magna (Series II) (FTIR) with a DTGSBr detector and KBr as beam splitter with 100 scans for a wavelength range of 400–4000 cm^{-1}. Thin films of polyurethanes were cast on a Teflon® plate with the help of an applicator. The films were moisture cured as reported previously [21]. For thermal treatment, the film samples were heated in a tube furnace with a constant heating rate of 10 °C/min up to the desired

Table 1
Compositions, physical characteristics and cross-link densities of synthesized polyurethane and polyurethaneureas

Sample code	Diamine[a] (mol%)	Density (g/cm^3)	Hard segment (%, w/w)	Chemical cross-link density ($\times 10^4$ mol/g)	Appearance
PPUD	00	0.9007	11.67	2.95	Transparent
PUUSD20	20	0.9278	13.09	5.25	Transparent
PUUSD50	50	0.8549	15.13	5.75	Opaque
PUUSD100	100	0.9181	18.35	1.65	Opaque

[a] With respect to M_n of HTPB.

temperature. The films were allowed to attain room temperature before FTIR study.

2.5. Gel content (GC)

In order to estimate the GC, the previously weighed thermally aged samples were refluxed in THF for 4 h followed by drying in an air oven at 80 °C until they attained constant weights. The GC was calculated as

$$GC = 100\frac{W_f}{W_i}$$

where W_i is the sample weight after aging and W_f is sample weight after it attains constant value after refluxing in THF followed by drying.

2.6. Tensile strength and elongation at break

Accelerated aging tests were performed for polyurethanes by heating each sample in an oven at constant temperature for a prolonged period followed by the measurement of tensile strengths and percentage of elongation at break. Tensile strength of each sample was measured according to ASTM D 638. For this, a dumbbell-shaped specimen was cut from the cured sheet and stretched against a uniform cross-head separation speed of 50 mm/min in a KMI tensile testing machine. The elongation at break for each sample was also measured simultaneously.

2.7. Cross-link density

Chemical cross-link density of PPUD, PUUSD20 and PUUSD50 was measured following the swelling of the respective films in THF and toluene and calculation was done according to the method followed earlier [21].

2.8. Wide angle X-ray diffraction (WAXD)

WAXD study of PPUD and polyurethaneurea films (with or without thermal treatment) was studied in the range $2\theta = 10–50^\circ$ in a Philips PW-1710 X-ray diffractometer and PW-1729 X-ray generator with a Cu Kα target and nickel filter. Scan rate of $0.05^\circ\ s^{-1}$ (2θ) was maintained in all cases.

3. Results and discussion

3.1. Short-term thermal endurance

TGA was performed for PPUD and polyurethaneureas to study the short-term thermal endurance both in nitrogen and in air. In the presence of nitrogen all samples showed two-step degradation as a common feature. The start, peak and end degradation stages were obtained from the derivative of TG curves and the results are given in Table 2. All polyurethanes showed first degradation at 195–380 °C and PUUSD50 suffered a minimum weight loss (11.50%) in the first step. PPUD and PUUSD20 showed weight loss of 13.6 and 13.2%, respectively, in the first step. As the hard segment content of these polyurethanes varies from 11.67% in PPUD to 18.35% in PUUSD100, a correlation can be drawn between weight loss and hard segment content. Polyurethane undergoes depolycondensation (Scheme 1) at higher temperature with the formation of volatile diisocyanate and isocyanate terminated fragments along with the degradation of allophanate, biurate and urea linkages into various nitrogenous compounds [23]. In PPUD the dissociation of urethane linkages directly generates volatile diisocyanates as it already contains higher amounts of isocyanate terminated chains (Scheme 1). For polyurethane PPUD, the weight loss in the first

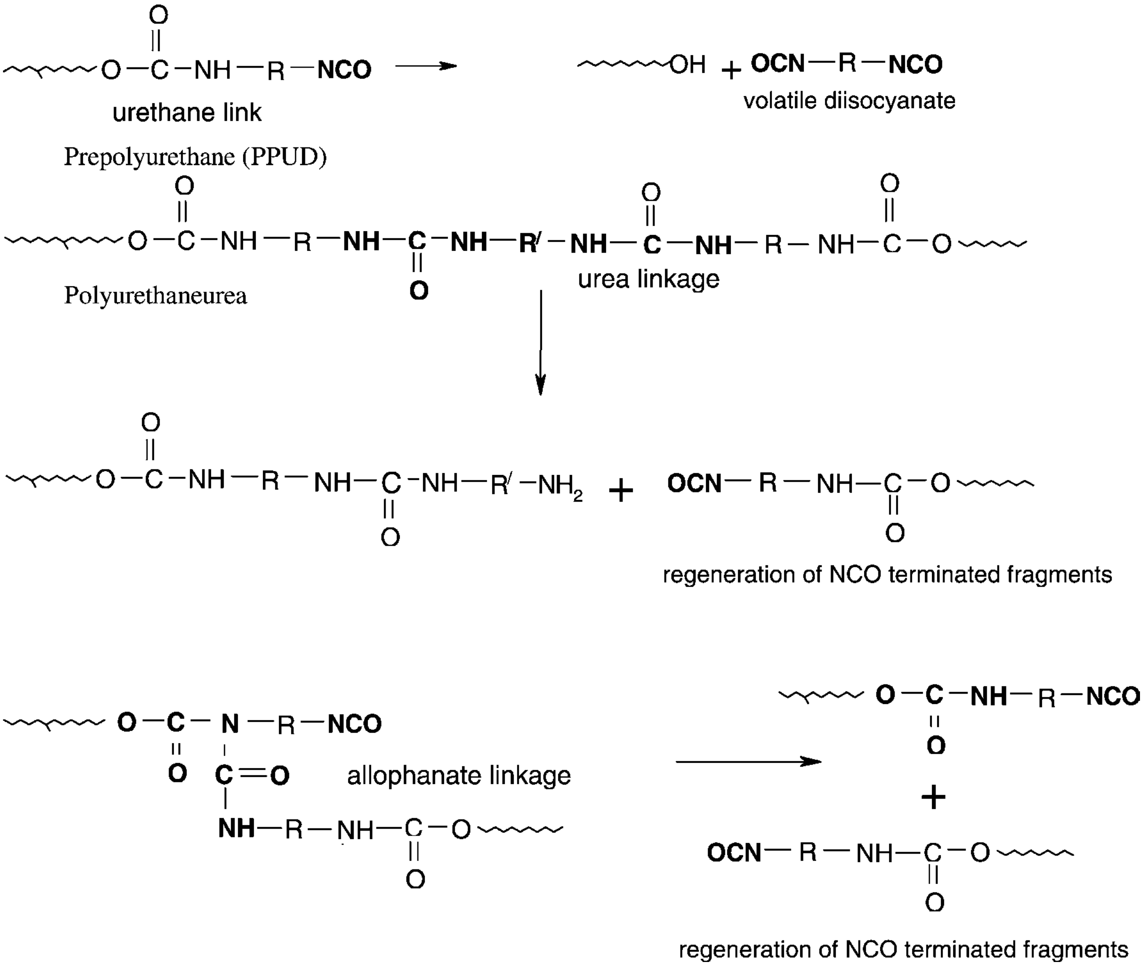
Table 2
Short-term thermal endurance study (TGA) of PPUD and polyurethaneureas[a]

Sample code	First degradation temperature (°C)				Second degradation temperature (°C)				Third degradation temperature (°C)				Char residue (%)
	Start	Peak	End	Percentage of weight loss	Start	Peak	End	Percentage of weight loss	Start	Peak	End	Percentage of weight loss	
PPUD[b]	204	310	358	13.6	358	468	523	85.4	–	–	–	–	1.00
PUUSD20[b]	198	307	356	13.2	356	468	516	85.1	–	–	–	–	1.70
PUUSD20[c]	208	295	355	8.3	355	460	502	76.9	502	562	658	14.7	0.10
PUUSD50[b]	196	308	345	11.5	345	468	518	86.3	–	–	–	–	2.20
PUUSD100[b]	195^{IA} 322^{IB}	289^{IA} 371^{IB}	322^{IA} 384^{IB}	18.6^{T}	389	442	487	80.2	–	–	–	–	0.60

[a] The superscripts IA and IB stand for the sub-step of first degradation of PUUSD100. Superscript T defines total weight loss in the first degradation of PUUSD100.

[b] Sample heated in nitrogen.

[c] Sample heated in air.



Scheme 1. Degradation of urethane, urea and allophanate linkages at 200–350 °C.

step (13.6%) is higher than that of its hard segment content (11.67%). Probably, chain scission in soft segments also takes place simultaneously generating some volatile organics. For PUUSD20 the weight loss (13.2%) matches well with its hard segment content (13.09%). PUUSD50 with a higher hard segment (15.13%) rather shows a lower weight loss. As the cross-link density of PUUSD50 is highest (Table 1), it exercises a higher tolerance against thermal degradation. Reegen and Frisch [24] established the fact that polyurethane with high cross-linking density has good thermal stability. Generation of isocyanate groups due to degradation of urethane group in the first step of thermal degradation was assessed by the change in peak area of isocyanate group in FTIR spectrum upon heating the samples. For PPUD the isocyanate peak area (at 2272 cm^{-1}) decreases with increase in temperature (Fig. 1). This is because of degradation of urethane bonds followed by the loss of diisocyanates (Scheme 1). However, PUUSD20 experiences a marginal increase in isocyanate peak area upon heating up to 200 °C (Fig. 2). This may be explained due to the generation of isocyanate terminated fragments as a result of degradation of the cross-linked polyurethane network rather than diisocyanate elimination as is found in the case of PPUD having lower cross-linking density (Scheme 1 and Table 1). The depolycondensation reaction in PPUD was corroborated by the decrease in N–H stretching frequency with temperature (Fig. 3). Since polybutadiene starts liberating volatile components only above 310 °C [25] the weight loss in the first degradation step occurs mainly due to the depolycondensation of urethane groups. It is evident from the results in Table 2 that starting temperature of degradation in nitrogen atmosphere is highest (204 °C) for PPUD with minimum hard segment content, whereas the value is lowest (195 °C) for PUUSD100 with maximum hard segment content. Hence higher the soft segment content in the polyurethane matrix, higher will be the starting temperature of degradation. Grassie et al. [26] concluded that the threshold degradation temperature of a polyester polyurethaneurea increases with increasing soft segment content. The first degradation of PUUSD100 is actually a combination of two sub-steps of degradation. The sub-steps are well defined in derivative thermogram (Fig. 4). Most probably, PUUSD100 contains two types of hard-segments in its morphology. One type degrades at 195–322 °C and the other degrades at 322–384 °C along with the liberation of some volatile matters. The total weight loss for two sub-steps was calculated to be 18.6 wt.%

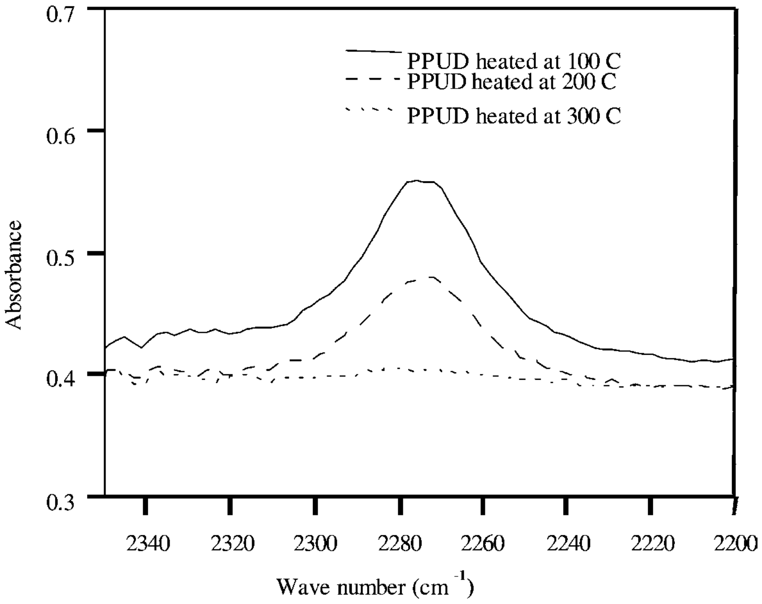


Fig. 1. Variation of isocyanate (NCO) band in FTIR spectroscopy with temperature for PPUD.

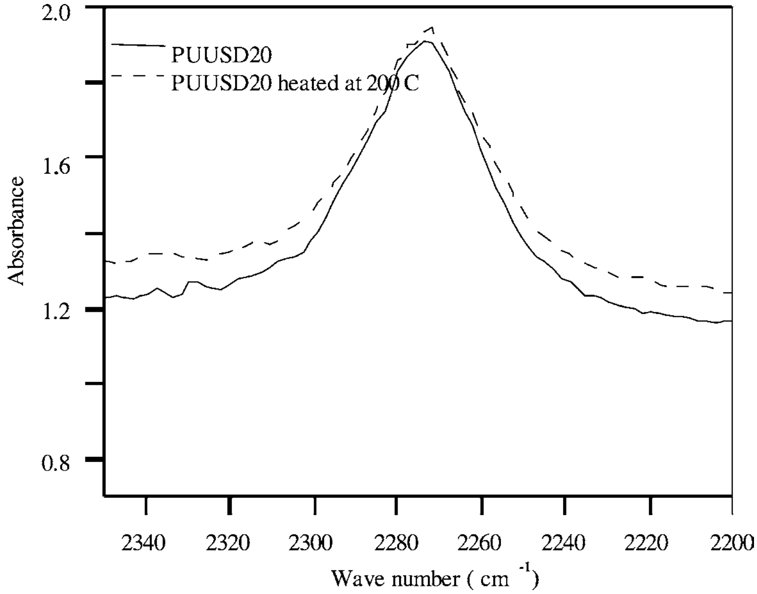


Fig. 2. Variation of isocyanate (NCO) band in FTIR spectroscopy with temperature for PUUSD20.

which is close to the hard segment content (18.35 wt.%) of PUUSD100.

A second degradation step in nitrogen for all the three HTPB-based polyurethanes was observed at around ∼468 °C except PUUSD100 (Table 2). The 80–86% weight loss in the second degradation step of polyurethanes is correlated well to their soft segment content (81.85–89.4%). Here the polyurethane with highest soft segment experiences highest weight loss (85.4% for PPUD) against the polyurethane with lowest soft segment showing lowest weight loss (80.2% for PUUSD100). Tingfa [27] reported

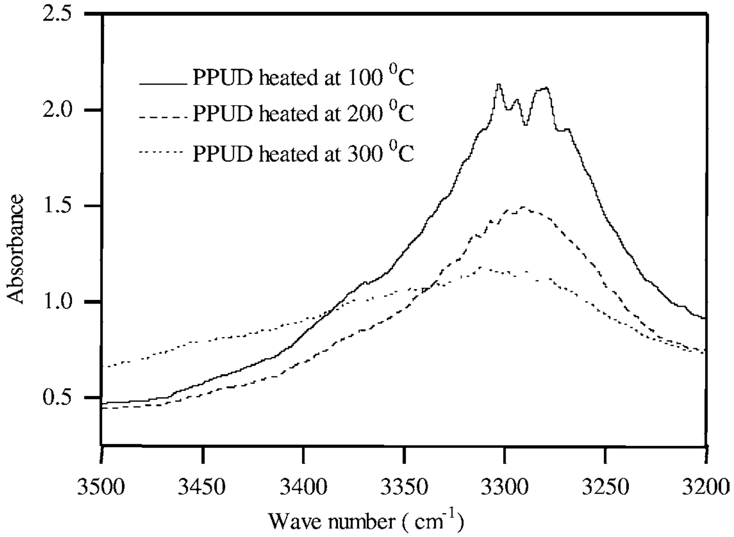


Fig. 3. The variation of N–H stretching peak area of PPUD with temperature.

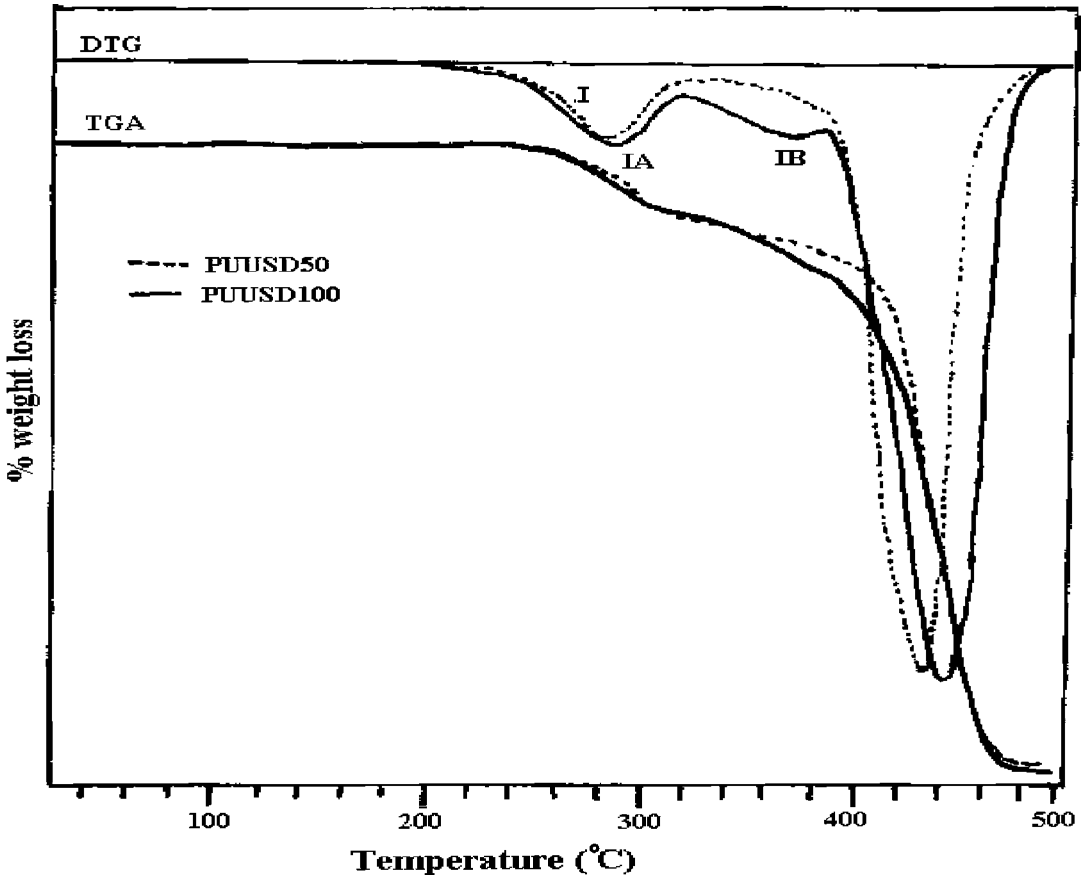


Fig. 4. TGA and DTG of PUUSD50 and PUUSD100 in nitrogen atmosphere.

a two-step degradation of pure HTPB in helium atmosphere, first step at around 394 °C and the second in the range 451–550 °C. On the basis of the above reports and correlation between weight loss and hard segment content of polyurethanes, the second step of degradation of PPUD, PUUSD20 and PUUSD50 in nitrogen with a maximum weight loss at ∼468 °C is presumed to be associated with the degradation of polybutadiene segment. The degradation temperature of polyurethane-bound polybutadiene segment is higher in the present case over that observed by Brazier and Nickel [28] for pure polybutadiene. Probably, the polybutadiene chain gained some extra stability in cross-linked polyurethane matrix so that a higher temperature is required to release the volatile fragments.

A three-step thermo-oxidative degradation was observed for PUUSD20. Its degradation temperatures and percentage of weight loss are given in Table 2. Only 8.3% weight loss has been recorded for the first step at 295 °C (Table 2). Polyurethaneurea provides higher thermo-oxidative stability. The additional cross-links generated in polybutadiene rich surface in presence of oxygen resists the expulsion of volatile fragments from the dissociation of hard segment in the first step. The same observation was also reported by Shieh et al. [29] in course of their thermal degradation study of MDI based polyurethanes. The formation of extra cross-links in polybutadiene soft segment was verified by the estimation of GC of thermally aged samples. Fig. 5 shows the GC of polyurethanes heated in the presence of air and nitrogen separately at 225

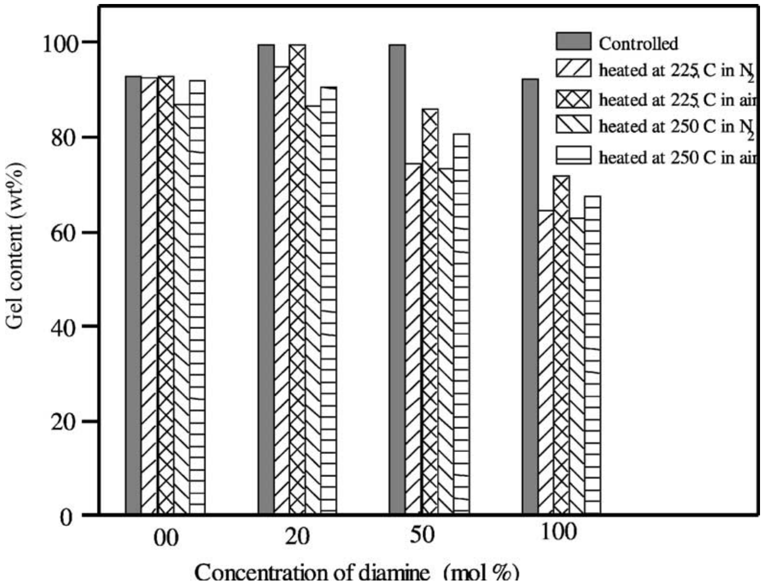


Fig. 5. Change in GC of polyurethanes (urea) on thermal aging.

and 250 °C for 15 min. The PPUD and polyurethaneureas aged in presence of air were seen to conserve more gel over that aged in presence of nitrogen against identical temperature and duration of aging. The second step of thermo-oxidative degradation of PUUSD20 also showed less weight loss (76.6%) than that in the presence of nitrogen (85.1%) (Table 2). Here also, the cross-linking reaction in polybutadiene soft segments competes with the simultaneous chain scission in the presence of oxygen.

3.2. Activation energy of decomposition

The activation energy of decomposition of PPUD and polyurethaneureas were estimated from the TGA in nitrogen atmosphere. We calculated the activation energy for each step of degradation by two established methods: Coats–Redfern and Chatterjee–Conrad.

Coats and Redfern [30] used the following equation for the first-order degradation reaction:

$$\log\left[-\frac{\log(1-\alpha)}{T^2}\right] = \log\left[\frac{AR}{(\beta E)(1-2RT/E)}\right] - \left[\frac{E}{2.303RT}\right]$$

where α is the fraction of weight lost at temperature T (absolute scale), β the heating rate, A is a numerical constant and E stands for activation energy. From the slope of the plot of $\log[-\log(1-\alpha)/T^2]$ vs. $1/T$, the activation energy was calculated (Fig. 6). The values of step-wise activation energies were listed in Table 3.

In Chatterjee–Conrad method [31] $\{\ln(\mathrm{d}\alpha/\mathrm{d}t) - \ln\alpha\}$ is plotted against $1/T$ and the activation energies of different stages of degradation was identified and calculated from slopes. Fig. 7 represents the Chatterjee–Conrad plots and the estimated kinetic data are listed in Table 3.

Analysis of the plots obtained in both the methods reveals that the polyurethane and polyurethaneureas undergo three-step decomposition rather a two-step decomposition observed in original TGA without any mathematical treatment. The first step definitely associated with depolycondensation of urethane groups as mentioned earlier. The activation energy for first step degradation calculated by *Coats–Redfern* method is higher than that estimated by *Chatterjee–Conrad* method. Moreover, the activation energy of the first step increases from PPUD to PUUSD100, due to the increase in polyurethane hard segment. The second step degradation, which is associated with desorption of volatile fragments, show lower activation energy

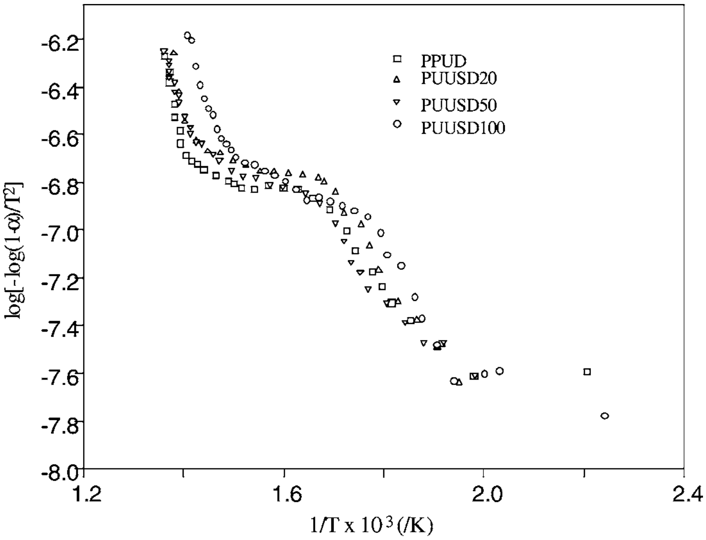


Fig. 6. Coats–Redfern plots for polyurethane and polyurethaneureas.

[32]. The major decomposition takes place at third step as obtained in Coats–Redfern method. The minimum activation energy was obtained as 80.6 kJ/mol for PUUSD100, which contains lowest soft segment. Here, the activation energy decreases with the increase in hard segment content. The third step degradation is associated with the bond cleavage in soft polybutadiene segments.

3.3. Differential scanning calorimetry

Differential scanning calorimetry studied for all the polyurethanes above room temperature in the presence of nitrogen showed the presence of a broad exothermic peak followed by a broad endotherm (Table 4). In no case an early endotherm associated with T_m of hard segment was observed. Hence it is affirmed that the soft segment degrades fast before melting of hard segment. The exothermic DSC peaks in nitrogen were observed at about 368–370 °C for PPUD, PUUSD20 and PUUSD50. These peaks correspond to the energy released due to the cross-linking and cyclization of HTPB over the chain scission during degradation of HTPB. Exothermic DSC peak for PUUSD100 appears at 385 °C. The exothermic energies calculated from DSC peaks are given in Table 4. Brazier and Norman [33] estimated the exothermic energy associated with the pure HTPB decomposition to be 0.95 kJ/g of polybutadiene. In the present investigation we calculated the degradation exotherm for HTPB fraction in polyurethane and the values are found to be 1.15, 1.19 and 1.16 kJ/g in PPUD, PUUSD20 and PUUSD50, respectively. The values are slightly higher over that for pure polybutadiene. For PUUSD100, exothermic

Table 3
Activation energies of decomposition of polyurethane and polyurethaneureas

Sample code	Coats–Redfern activation energy, E_a (kJ/mol)			Chatterjee–Conrad activation energy, E_a (kJ/mol)		
	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3
PPUD	59.6	20.9	185.6	50.1	26.5	159.1
PUUSD20	66.6	25.9	175.6	56.2	28.0	113.0
PUUSD50	83.3	34.5	109.4	58.3	33.2	106.9
PUUSD100	103.8	18.4	80.6	61.8	30.9	103.1

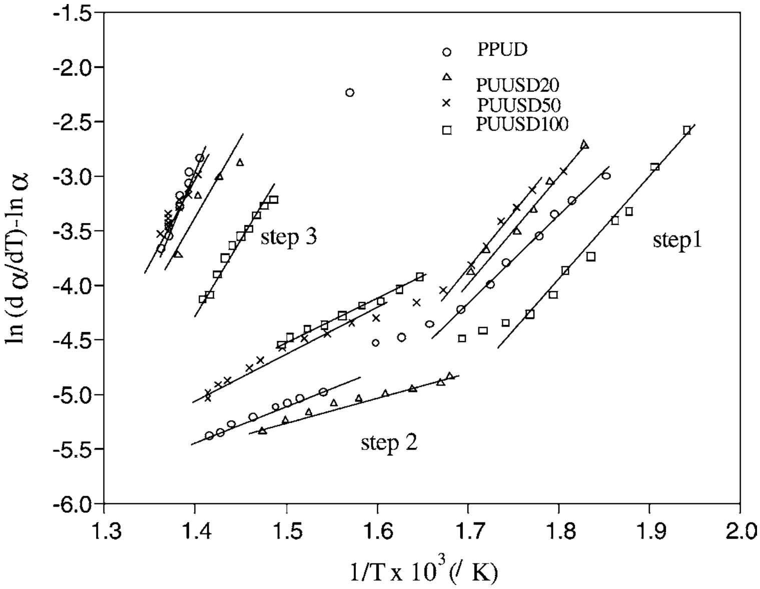


Fig. 7. Chatterjee–Conrad plots for polyurethane and polyurethaneureas.

energy calculated for HTPB fraction is 0.965 kJ/g, which is in close proximity to the value that obtained for pure polybutadiene. DSC analysis further shows the appearance of an endothermic peak at 454 °C in all polyurethanes except for PUUSD100 (Table 4). This endothermic peak appeared due to the energy absorption by polymer with subsequent rapid chain scission as well as cyclization reaction in soft segment at such high temperature. Endothermic peak of PUUSD100 appears at 483 °C. The presence of hard segment at higher concentration in PUUSD100 probably restricts the soft segmental chain scission and cyclization reaction to some extent.

DSC studied for PUUSD20 in the presence of air showed no endotherm but a broad exotherm consisting of multiple peaks (Table 4). Hence degradation with rapid chain scission takes place at higher temperature in air.

3.4. Long-term thermal endurance

In order to study long-term thermal endurance, the PPUD and polyurethaneurea samples were subjected to accelerated aging at 100 and 200 °C for 24 h in the presence of air and the percent retention of tensile strength and elongation at break were measured after aging. The results of thermo-oxidative aging carried out at 100 °C are given in Table 5. It is evident from Table 5 that thermo-oxidative degradation of PPUD and polyurethaneureas leads to the lowering

Table 4
Assignment of exothermic and endothermic peaks in DSC

Sample code	Sample atmosphere	Exothermic peak (°C)	Exothermic energy (kJ/g)	Endothermic peak (°C)	Endothermic energy (kJ/g)
PPUD	N_2	368	1.013	454	0.675
PUUSD20	N_2	370	1.047	454	0.740
PUUSD20	Air	404, 455, 532	3.685[a]	–	–
PUUSD50	N_2	369	0.986	454	0.714
PUUSD100	N_2	385	0.810	483	0.510

[a] Expressed in terms of total heat of exotherms.

Table 5
The retention of tensile strength for PPUD and polyurethaneureas after isothermal aging at 100 °C in air

Sample code	Aging time (h)	Tensile strength (kgf/cm^2)	Percentage of retention of tensile strength	Percentage of elongation at break
PPUD	–	37.6	–	350
PPUD	12	35.0	93	290
PPUD	24	26.4	70.2	225
PUUSD20	–	58.0	–	375
PUUSD20	12	54.8	94.5	290
PUUSD20	24	42.4	73.1	230
PUUSD50	–	63.0	–	350
PUUSD50	12	59.3	94.1	270
PUUSD50	24	50.3	80	240
PUUSD100	–	38.0	–	325
PUUSD100	12	30.0	78.9	250
PUUSD100	24	21.1	55.5	225

of their tensile strengths. Tarakov et al. [34] explained that the degradation process is associated with the breaking of N–C and C–O bonds of urethane group. Hence, the tensile strengths of polyurethanes under investigation decrease on accelerated thermal aging due to the degradation of N–C and C–O bonds as well as allophanate and biurate cross-links. Another important observation is that the retention of tensile strength is higher for polyurethanes having higher initial chemical cross-link density (Tables 1 and 5). This indicates that the degradation process is definitely associated with the breaking of cross-links at high temperature.

After 24 h aging at 100 °C PUUSD50 with higher cross-linking density retained 80% of its original tensile strength, whereas PPUD, having a lower cross-linking density retained 70.2% of original tensile strength. PUUSD100 with lowest cross-link density in the series retained only 55.5% of tensile strength after 24 h. Hence, the increase in cross-link density increases the long-term thermal stability in these polyurethanes. Desai et al. [15] reported the same

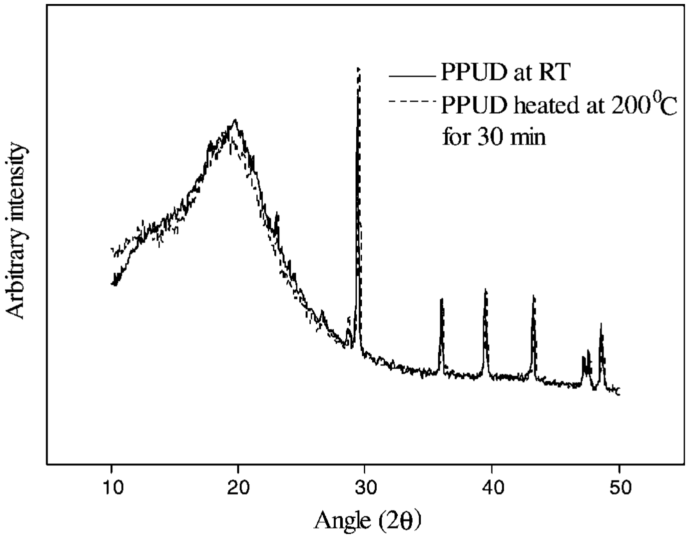


Fig. 8. Change in wide angle X-ray diffraction on heat treatment of PPUD.

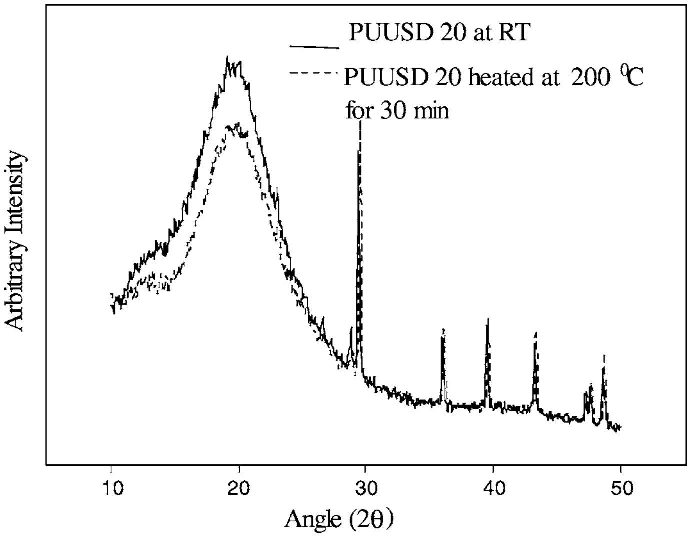


Fig. 9. Change in wide angle X-ray diffraction on heat treatment of PUUSD20.

correlation for HTPB–TDI-based polyurethanes. The percentage of elongation at break also decreases with the aging time (Table 5). All the polyurethanes on thermal aging at 200 °C became brittle after 1 h with rapid development of yellow color. This is because of rapid degradation of urethane groups as suggested by Pearson and Dyson [35] along with the development of conjugated double bonds in degradation process. Yakybivich et al. [36] earlier reported that changes in physical property of aromatic diisocyanate based polyurethane coatings took place during first 10 h of photochemical aging but the properties remained unchanged on further irradiation. But we observed that the tensile strength of PPUD and polyurethaneureas changed significantly between 12 and 24 h of thermal aging (Table 5).

3.5. WAXD study

WAXD study was carried out with polyurethane and polyurethaneurea samples before and after heat treatment at 100 and 200 °C in order to assess some structural change, if any, after thermal aging. Both preheated PPUD and PUUSD20 show a broad peak at $2\theta = 19.8^\circ$. No significant change in WAXD curves was observed for PPUD and polyurethaneurea (PUUSD20) after prolonged heating at 100 °C and for short exposure to 200 °C. But the peak areas at $2\theta = 19.8^\circ$ were decreased for PPUD and PUUSD20 heated at 200 °C for 30 min (Figs. 8 and 9). This indicates a decrease in overall crystallinity after heating at 200 °C. We know that crystallinity is developed in polyurethane due to the ordering of hard segments in polyurethanes. It is evident from the quantitative TGA analysis that the hard segments are destroyed continuously at this temperature during depolycondensation reactions. Hence such degradation of hard segments causes loss in crystallinity. Moreover, PPUD showed an overall decrease in the peak intensity as well as a shift in peak position from $2\theta = 19.85^\circ$ to 19.25° on heat treatment (Fig. 8). The intensities and positions of other crystalline peaks remained almost unchanged for both PPUD and PUUSD20 on heat treatment.

4. Conclusion

The thermal degradation of PPUD and polyurethaneureas starts in hard segments through depolycondensation reaction at the temperature range 200–350 °C as observed in TGA and FTIR spectroscopy. This involves dissociation of urethane and urea bonds as well as breakdown of allophanate and biurate cross-links.

Increase in cross-link density in polyurethaneureas was associated with lower weight loss in depolycondensation step. A lower weight loss is also evident in thermo-oxidative degradation of polyurethaneurea (PUUSD20) due to build up of cross-links in soft segments during heating in the presence of air. Above 350 °C the fragmentation and cyclic ring formation in soft butadiene segments take place followed by chain scission at higher temperature. The activation energies associated with thermal degradation at different temperature ranges were calculated following Coats–Redfern and Chatterjee–Conrad methods. The simultaneous degradation of soft and hard segments at high temperature unique for polyurethanes [37] is also evident for HTPB-based polyurethane and polyurethaneureas under investigation.

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