Thermal Stability of Chemically Crosslinked Moisture-Cured Polyurethane Coatings

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ABSTRACT: Polyurethane prepolymers are widely used in reactive hot melt adhesives and moisture-cured coatings. The segmented moisture-cured formulations, based on polytetramethylene glycol (PTMG-1000)/trimethylol propane (TMP)/isophorone diisocyanate (IPDI) and PTMG/TMP/ toluene diisocyanate (TDI), were prepared with NCO/OH ratio of 1.6 : 1.0. The excess isocyanate groups of the prepolymers were chain extended in the ratio of 2 : 1 (NCO/ OH) with different aliphatic diols and 4 : 1 with different aromatic diamines. The surplus isocyanate groups of the formulations were completely reacted with atmospheric moisture, and the thermal stability of the postcured materials obtained as cast films were evaluated by thermogravimetric (TG) analysis. It was observed that initial degradation temperatures were above 270°C, with two- or three-step degradation profiles. The degradation parameters were evaluated using the Broido and Coats–Redfern methods.

The thermal resistance of moisture-cured formulations using diisocyanates with the cycloaliphatic structures (IPDI) and the aromatic TDI, at the same NCO/OH ratio (1.6), and TMP content were compared from the isothermal TG experiments at different temperatures and dynamic TG experiments at different heating rates in nitrogen and oxygen environments. The observation suggests that polyurethane-containing sulfone groups and straight-chain diol chain extenders were more stable. It was also observed that at lower temperature polyurethane, prepared from aliphatic diisocyanates (IPDI), was more stable than the aromatic diisocyanate (TDI) containing polyurethanes. At high temperature, the stability order follows the reverse trend. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1509–1518, 2005

Key words: moisture curing; polyurethanes; chain; thermal properties; stability

INTRODUCTION

Moisture-curable thermosetting polyurethanes are widely known as protective and decorative coatings or films in a broad range applications because of the wide range of physical properties and performance characteristics. They are formed by urethane groups originating from diisocyanates and also contain urea groups originating from the reaction of atmospheric moisture and/or a low molecular weight diamine chain extender used in the synthesis. The soft or flexible segments, which are in a viscous or rubbery state, provide the elastomeric character to the polyurethane chain. The hard or rigid segments, which are in a glassy or semicrystalline state, provide dimensional stability by acting as thermally reversible and multifunctional pseudo or physical crosslinks and also as reinforcing fillers. Incorporation of chemical crosslinks and the presence of side products strongly influence the material properties. Determination of the thermal stability is an important aspect of the technological application of polymeric materials such as polyure-

thane (PU). The thermal degradation investigation of polymers allows determination of the optimum conditions for manipulating and processing them, and for obtaining high-performance products that are stable and free of undesirable byproducts.[1–6]

The broadness in chemical structure and functionality of these materials poses a complex problem to a coating technologist with respect to determination of its stability and definite degradation profile. In addition, network structure of the polymer is an important factor, which must be taken into account to study the extent of thermal degradation of the urethane segments. Coatings degrade in the presence of thermal stress, and thermogravimetric analysis (TGA) is a widely used technique to monitor the stability of polymeric coatings. TG curves provide information about the decomposition behavior, the temperature up to which the coating can work without appreciable degradation of the coating. In reports of recent studies dynamic thermogravimetry has been used to determine the activation energy and other kinetic parameters of polymer and coating degradation, which can be used to predict the stability of materials. The thermal stability of polyurethane was studied extensively and it was proposed that thermal degradation is primarily a depolycondensation process, which starts at about

250°C, and is related with the type of isocyanate and polyol used.[7,8] The complexity of the degradation increases if more complex soft segments, such as polyester or polyether polyol, are involved. The thermal degradation kinetics in polymers is more complicated than that of other materials because of the nature of polydispersity of polymer chains. Upon thermal excitation, the covalent bonds in polymer chains undergo complex vibration and rotation within their local space. With further excitation these bonds can break to form a variety of fragment radicals or small molecules, which may further mutually recombine or break. Ultimately, the resulting fragments may be vaporized, diffused out, or carbonized. The process ends with the loss of all volatile material and with char residue that changes only negligibly above the char temperature.[9–17]

The chain-extender structures have a substantial effect on the thermostability, and the understanding of their structure to stability behavior is of immense importance. A number of investigations corroborated that sulfone-containing polymers display good thermal, physicomechanical, and high barrier properties. A polymer containing polar sulfone groups has greater intermolecular force between chains and also has the advantage of resisting thermal deformation.[18] In this study, the kinetics of the thermal decomposition of moisture-cured and chemically crosslinked polyurethanes, with different chain extenders in nitrogen from ambient temperature to 500°C, were investigated using the Broido[19] and Coats–Redfern methods.[20]

EXPERIMENTAL

Materials

The following reagents were used as received: dibutyltin dilaurate (DBTL), PTMG-1000, TMP, IPDI (Z and E isomer in 3 : 1 ratio), 2-methyl-1,3-propanediol (MPD), 2,2-diethyl-1,3-propanediol (DIE), 2-butyl 2-ethyl-1,3-propanediol (BUE), neopentyl glycol (NPG), bisphenol-A (BIS), 4-aminophenyl disulfide (DIS), and 4,4'-diamino-diphenyl methane (MET) were obtained from Aldrich (Milwaukee, WI); TDI (9 : 1 ratio of 2,4- and 2,6-isomer) and 4,4'-diamino-diphenyl sulfone (SUL) were from Fluka Chemical Corp. (Ronkonkoma, NY); 1,4-butanediol (BD) was from Spectrochem Pvt. Ltd. (Mumbai, India); propane 1,2 diol (PD), 2-ethoxyethyl acetate, and sulfur-free toluene were obtained from S.D. Fine Chemicals (Mumbai, India). Solvents were stored over activated 3- to 4-Å molecular sieves.

Method

The resin kettle was equipped with a dropping funnel, stirrer, thermometer, reflux condenser, and a nitrogen inlet. An excess amount of IPDI was taken to obtain a 1.6 : 1 ratio of NCO : OH. A mixture of PTMG (50 g) and TMP (9 g) was added to the kettle at 60–70°C and the reaction was continued at 75–85°C for 6 h in the absence of catalyst. The synthesized isocyanate terminated prepolymers (ITPs) were then chain extended in the ratio of 2 : 1 (NCO/OH) with different aliphatic diols, and 4 : 1 with different aromatic diamines in the presence of 0.05 wt % dibutyltin diluarate and 0.05 wt % triethylamine catalyst. The polymers were cast onto tin foil by using a power-driven automatic applicator and cured at room temperature and 40% humidity for more than 2 months, after which time the films were amalgamated in mercury. Similarly, moisture-cured formulation with TDI was prepared and chain extended with diols and diamines under identical environments and NCO/OH ratios. The free films were completely cured in the presence of atmospheric moisture for more than 2 months and the postcured samples were used for thermal stability evaluation. The complete moisture-cured formulations, without any chain extenders, were designated as PUIT-15 for PTMG/TMP/IPDI and PUIT-16 for PTMG/TMP/TDI systems, respectively. The corresponding chain-extended PUs was designated as PUBD-15 for PTMG/TMP/IPDI/1,4-butanediol, PUSUL-16 for PTMG/TMP/TDI/4,4'-diamino-diphenyl sulfone systems, and so forth, respectively.

TGA analysis

Thermogravimetric experiments were performed on TGA/SDTA 851e thermal system (Mettler Toledo, Zurich, Switzerland). Film samples, ranging from 10 to 12 mg, were placed in the sample pan and heated from 25 to 500°C under N_2, at heating rates of 10 and 5°C/min. During the heating period, the weight loss and temperature difference were recorded as a function of temperature. PUIT-15 and PUIT-16 were subjected to TG evolution at different heating rates in nitrogen and oxygen environments. The isothermal experiments of the moisture-cured formulations without any chain extenders were carried out at 200, 230, 280, 300 and 330°C for different periods of time. The dynamic heating rate used to attend the isothermal temperature was 5°C/min.

Kinetic methods for thermal degradation

The derivation of kinetic data in the study of polymer decomposition using TGA has received increasing attention in the last decade; along with much criticism regarding its use in the determination of rate constants, activation energies, reaction orders, and preexponential factor. Values obtained depend on atmosphere, sample mass, sample shape, flow rate, heating
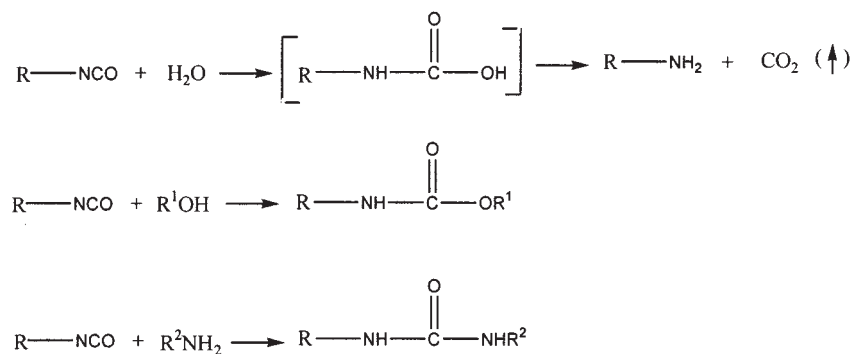
Scheme 1 Reaction of excess isocyanate in the prepolymers with moisture and chain extenders.

rate, and the mathematical treatment used to evaluate the data.[21]

A reaction rate is defined as the derivative of conversion with respect to time. The normalized TG curves were used for the percentage conversion evaluation. In TGA, conversion is defined as the ratio of percentage mass loss of the sample after a certain period of time (t) to the total mass in percentage at the beginning of the experiment (100), that is, $\alpha = (100 - w_t)/100$, where w_t is the percentage sample mass at time t.

The rate of conversion in a dynamic TGA experiment at a constant heating rate can be expressed as

$$d\alpha/dt = Q(d\alpha/dT) = k(T)f(\alpha) \quad (1)$$

where Q is the heating rate, $k(T)$ is the rate constant, and $f(\alpha)$ is the conversion functional relationship.

An Arrhenius expression, which describes the temperature dependency of the rate constant, may be expressed as

$$k(T) = Z \exp(-E/RT) \quad (2)$$

where Z is the preexponential factor, E is the activation energy, and R is the universal gas constant.

The integral form of the rate equation in a dynamic heating expression experiment may be expressed as

$$g(\alpha) = (ZE/QR)p(x) \quad (3)$$

where $p(x) = \int_\infty^x [\exp(-x)/x^2]\, dx$, and $x = E/RT$; $g(\alpha)$ is the integral form of the conversion dependency function.[22,23]

To solve the function $p(x)$ several methods have been developed. Broido, Coats–Redfern, and other researchers have solved this function. The equations used herein are as follows:

Broido equation[19]

$$\ln \ln(1/Y) = E/R(1/T) + \text{Constant} \quad (4)$$

where $Y = (w_0 - w_t)/(w_0 - w_\infty)$ is the fraction of the number of initial molecules not yet decomposed; and w_t, w_∞ (=0), and w_0 are the weight at time t, the weight at infinite time, and the initial weight, respectively. The slope of the respective plot of $\ln \ln(1/Y)$ versus $1/T$ leads to the activation energy, as is clear from eq. (4).

Coats–Redfern equation [20]

Coats and Redfern provided an approximation to the integral of eq. (3), thus obtaining the following expression:

TABLE I
Thermal Stability Data of Polyurethane (PU-15) with Different Chain Extenders (heating rate, 10°C/min)

Sample	T_{1ON}	T_{1MAX}	T_{2ON}	T_{2MAX}	T_F	Weight percentage at 300°C	450°C
PUBD-15	325.2	388.4	417.0	428.6	465.5	98.3	16.7
PUBUE-15	314.1	351.9	395.8	413.2	434.8	90.2	3.4
PUDIE-15	320.3	370.5	409.5	427.4	449.6	96.7	7.64
PUPD-15	327.1	393.9	421.8	439.8	468.3	98.5	18.2
PUMPD-15	321.5	376.0	415.8	431.7	457.1	98.1	13.1
PUMET-15	328.35	366.1	413.8	427.4	444.1	98.5	6.8
PUSUL-15	359.3	382.2	429.3	444.1	464.6	99.3	24.0
PUDIS-15	316.6	356.2	414.4	428.0	439.7	96.0	4.2

TABLE II
Thermal Stability Data of Polyurethane (PU-16) with Different Chain Extenders (heating rate, 10°C/min)

Sample	T_{1ON}	T_{1MAX}	T_{2ON}	T_{2MAX}	T_F	Weight percentage at	
						300°C	450°C
PUBD-16	310.7	317.8	426.2	465.2	487.0	97.3	43.3
PUPD-16	312.3	350.0	430.0	468.9	494.3	95.7	47.9
PUDIE-16	302.1	316.0	418.1	450.3	477.5	95.9	31.9
PUBUE-16	301.1	324.3	421.2	454.0	472.6	97.6	30.8
PUNPG-16	306.0	346.3	418.5	463.9	489.3	97.3	42.0

$$\log_{10}[g(\alpha)/T^2] = \log_{10}(ZR/QE)[1 - 2RT/E]$$
$$- E/2.3RT \quad (5)$$

Thus a plot of $\log_{10}[g(\alpha)/T^2]$ versus $1/T$ should result in a straight line with slope equals to $-E/2.3R$ for the correct chosen value of n, the order of degradation. The above equations are used extensively for calculating the activation energies and other parameters to supplement the qualitative thermostability data in spite of the controversy. The controversy arises from different assumptions and approaches used for solving the function $p(x)$ by different workers. Budrugeac[24] showed that the evaluation of the kinetic parameters of thermal and thermooxidative degradation of a polymeric material, by using a single TG curve recorded at a certain heating rate, does not lead to reliable results. Vyazovkin and Wight[25] critically analyzed different methods for the evaluation of the kinetic triplet (E, Z, and n). These authors noted that these methods ignore the fact that the correlation coefficient and other statistical measures are subject to random fluctuations. However, some authors[26–33] claim a physical meaning for these parameters, showing that a TG curve may be correctly described by several various kinetic models.

RESULTS AND DISCUSSION

High solids isocyanate terminated polyether–urethane prepolymers were prepared from IPDI (Z and E isomer in a 3 : 1 ratio) and TDI (9 : 1 ratio of 2,4- and 2,6-isomer) in 2-ethoxyethyl acetate. The secondary isocyanate group of IPDI was more reactive than the primary isocyanate group in the absence of catalyst

because of the steric and stereo-electronic factors, as observed earlier.[34] The synthesized polymers were chain extended and cured in the presence of a mixture of catalyst as reported in the experimental section. Because synthesis of the mother polymers "PU-15" and "PU-16" was carried out for 6 h in the absence of any added catalyst, where both the NCO groups of IPDI/TDI may not react with the macrodiols or crosslinker, as a result the product mixture contains primary monourethane, secondary monourethane, diurethane, and unreacted IPDI/TDI. In addition, the reactivity of two different NCO groups of asymmetric IPDI (*primary* and *secondary*-NCO) as well as TDI (*ortho*- and *para*-NCO) are different and depend on the type and concentration of catalyst used during solid-state curing. Therefore, in the final postcured polymers, the concentration of urethane and urea groups, overall geometry/orientation, and the quality of the polymer depend on the ratio of the amine to the metal catalyst. In the present investigation equal weight percentages of the mixture of catalyst were used. The reaction of the excess isocyanate with atmospheric moisture and with chain extenders is often described by a very simplified reaction Scheme 1.

During reaction of excess NCO with moisture the other side reactions, such as dimerization of isocyanate group, appearance of the allophanate, and/or biuret linkages, are also possible at room temperature. Formations of side products greatly influences the thermal stability of the material because of the higher stability of allophanate and biuret.[35,36] However, Dusek et al.[37] reported that formation of biuret is much faster than that of allophanate and at low temperature (≤60°C) formation of biuret and allophanate

TABLE III
Thermal Stability Data of Polyurethane (PU-16) with Different Chain Extenders (heating rate, 5°C/min)

Sample	T_{1ON}	T_{1MAX}	T_{2ON}	T_{2MAX}	T_F	Weight percentage at	
						300°C	450°C
PUSUL-16	307.9	342.0	418.1	452.8	486.2	96.0	34.2
PUMET-16	282.3	311.0	398.9	426.2	456.5	87.6	12.8
PUDIS-16	273.9	319.7	382.2	407.6	441.6	87.1	11.3
PUBIS-16	282.0	304.8	386.5	420.6	454.0	87.0	12.2

Sample (heating rate °C/min)	T_{1ON}	T_{1MAX}	T_{2ON}	T_{2MAX}	T_F	Weight percentage at	
						300°C	450°C
IT-15 (5)	282.0	338.9	371.1	402.7	427.4	90.1	2.5
IT-15 (10)	302.4	356.3	382.4	410.1	438.6	93.3	3.5
IT-15 (15)	311.0	368.0	391.6	415.7	442.9	94.6	4.2
IT-15 (20)	311.7	369.9	393.1	421.9	447.9	96.0	4.7
IT-16 (5)	267.7	304.9	374.8	410.1	433.6	83.1	8.9
IT-16 (10)	277.6	319.1	386.0	417.6	449.7	90.0	11.3
IT-16 (15)	280.4	325.3	392.8	430.6	457.1	91.0	12.6
IT-16 (20)	293.2	329.6	403.3	436.8	464.0	94.6	18.0

is very slow. Duff and Maciel[38] showed that the predominant postcure process could be the result of the reaction of isocyanate group with atmospheric moisture, to form an amine that further condenses with an additional isocyanate group from the immediate vicinity to form an urea linkage. While developing moisture-cured polyurethane coatings we used the same amount of polyether diol (PTMG-1000) and TMP, and maintained the same ratio of NCO/OH, so the difference in thermograms is attributed to the variation in chain-extender structure and the combined effect of isocyanate and polyol. For a comparison of thermal stabilities, the chain-extended polymers were stored under identical environmental conditions.

The main aim of this article was to understand with reasonable precision how the chain-extender structure governs the thermal stability of the moisture-cured polyurethane. TMP was introduced as a crosslinking agent to increase the mechanical integrity, stiffness, hardness, and thermal stability. The thermal stability of polyurethane plays an important role in determining the final film properties and is greatly influenced by the structure, chemical composition, segment lengths and their concentration, ratio of soft to hard segments, and different interaction parameters.[39–41] The infrared spectrum of the samples (not shown) after 2 months showed the complete disappearance of NCO peaks, and therefore these samples were subjected to TG analysis.

The characteristic temperatures obtained from TG and differential thermogravimetric (DTG) curves are tabulated in Tables I–III for the chain-extended poly-

urethanes. The values of T_{1ON} (initial decomposition temperature for the first step of decomposition), T_{2ON} (initial decomposition temperature for the second step of decomposition), T_{1MAX} (temperature of maximum rate of weight loss for the first step), T_{2MAX} (temperature of maximum rate of weight loss for the second step), T_F (final decomposition temperature), percentage weight loss at 330°C, and char yield at 450°C are shown. Table IV shows the thermal stability data of polyurethane PUIT-15 and PUIT-16 with different heating rates in nitrogen, whereas Table V represents thermal stability data of polyurethane PUIT-15 and PUIT-16 with different heating rates in the presence of oxygen. The activation energies, order of degradation, and preexponential factors, as obtained from the Broido and Coats–Redfern methods, are summarized in Tables VI–X.

The T_{1ON} values of the diol and diamine chain-extended polyurethane prepared from IPDI lie between 314 and 327 and 316 and 359°C, respectively. It is clear that the thermal stability of PUSUL-15 was greater than that of PUMET-15 and PUDIS-15, and in fact the char yield value of PUSUL-15 was 24.0% at 450°C, much higher than that of the other polymers reported in Table I. Table I also shows the least stability of PUBUE-15 on the basis of the value reported in the characteristic TG temperatures, that is, the value of percentage weight remaining at 300 and 450°C, which were 90.2 and 3.4%, respectively. On the basis of T_{1ON}, T_F values, and percentage weight at 300 and 450°C, the stability order of the diol chain-extended polyurethane prepared from IPDI is as follows: PUPD-15

Sample (heating rate °C/min)	T_{1ON}	T_{1MAX}	T_{2ON}	T_{2MAX}	T_F	Weight percentage at	
						300°C	450°C
IT-15 (10)	258.3	319.7	351.8	362.4	407.6	91.6	28.7
IT-15 (20)	311.0	366.1	406.7	415.0	468.8	96.7	30.2
IT-16 (10)	260.3	335.8	383.5	400.8	442.9	85.9	23.1
IT-16 (20)	273.3	339.5	389.6	419.4	446.6	92.9	31.7

TABLE VI
Kinetic Parameters of Polyurethane (PU-15) with Different Chain Extenders (heating rate, 10°C/min)

Sample	Broido		Coats–Redfern	
	E_1, E_2 (kJ/mol)		E_1, E_2 (kJ/mol)	n_1, n_2
PUBD-15	122.6, 110.3		123.5, 98.4	3.3, 0.9
PUBUE-15	86.5, 100.1		85.5, 93.2	1.6, 0.5
PUDIE-15	111.4, 97.4		110.5, 91.3	2.1, 0.5
PUPD-15	126.9, 112.5		136.2, 111.4	2.7, 1.3
PUMPD-15	117.7, 108.0		115.8, 104.7	2.4, 1.1
PUMET-15	122.3, 106.7		123.6, 95.7	4.3, 0.2
PUSUL-15	163.8, 101.2		170.8, 94.7	4.0, 0.8
PUDIS-15	111.8, 118.3		110.7, 113.7	3.4, 0.5

> PUBD-15 > PUMPD-15 > PUDIE-15 > PUBUE-15. The T_{1ON} values of diol chain-extended polyurethanes derived from TDI (Table II) were between 301 and 312°C, showing the lower stability of these materials compared to that of PU-15 diol chain-extended series. However, char yield values at 450°C for the diol chain-extended PU-16s were considerably higher than those of the corresponding PU-15 series. These results demonstrate that TDI-based polyurethanes were more stable at high temperature than PUs prepared from IPDI; for further confirmation we compared the thermostabilities of PUIT-15 and PUIT-16 by isothermal experiments at different temperatures (discussed later).

On the basis of T_{1ON} and char yield values at 450°C, the stability order is as follows: PUPD-16 > PUBD-16 > PUNPG-16 > PUDIE-16 > PUBUE-16. Table III represents the thermal stability data of diamine chain-extended PU-16s, where the TG evaluations were carried out at a heating rate of 5°C/min, showing that polyurethanes with sulfone groups were more stable than other diamine chain-extended PUs. It is in the hard segment, composed of urethane and urea linkages, where the initial thermal decomposition occurs. When urea linkages are present, the thermal stability should be higher because of the greater hydrogen-bonding capacity of this group compared with that of urethane.[42] The thermal stability data of PUIT-15 and PUIT-16, with different heating rates in nitrogen, are tabulated in Table IV. It is generally believed that the best result of stability can be acquired if the minimum heating rate is achieved. The result shows that the stability of PUIT-15 and PUIT-16 decreases with decreasing heating rate. The value of T_{1ON} and percentage weight at 300°C shows that PUIT-15 was more stable at lower temperature, whereas the char yield at 450°C and T_F values of PUIT-16 and PUIT-15 at different heating rates showed that PUIT-16 was more stable at higher temperature. Table V represents the thermal stability data of PUIT-15 and PUIT-16, at 10 and 20°C/min heating rates in an oxygen environment, illustrating substantial stability of the synthesized polymers.
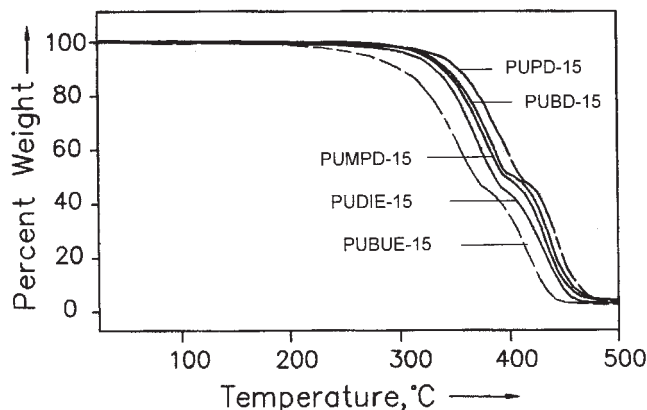

Figure 1 Thermogravimetric curves of diol chain-extended polyurethanes prepared from isophorone diisocyanate.

Figures 1 to 4 represent the degradation behavior of polyurethane films (PU-15 and PU-16) with different chain extenders. The TGA curve displays two distinct regions of weight loss that are reflected in two peaks in the DTGA curve. In some samples, the first or the second stage of the degradation was split into two peaks, illustrating the complexity of the process (DTGA curves are not shown). After the initial degradation in the hard segments, the second stage of degradation was related to the soft segments and started above 270°C, for both PUIT-15 and PUIT-16 chain-extended polyurethane series. The decomposition temperature of PU is mostly influenced by the chemical structure of the components having the lowest bond energy, and in such a complex thermoset system, thermal stability is governed not necessarily by the weakest link in the chain but by the environment
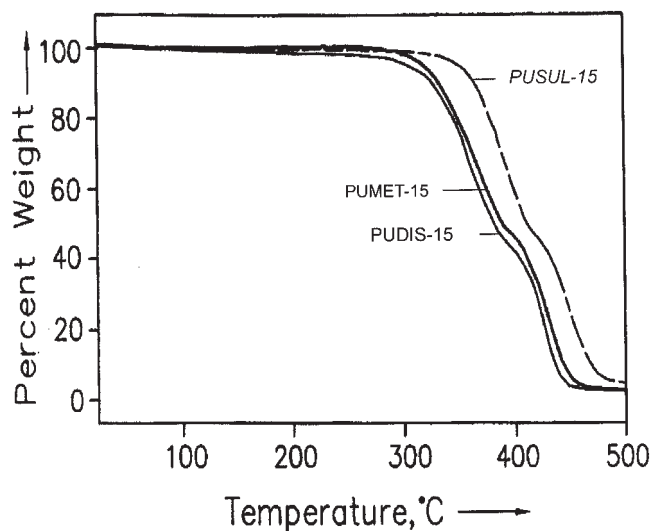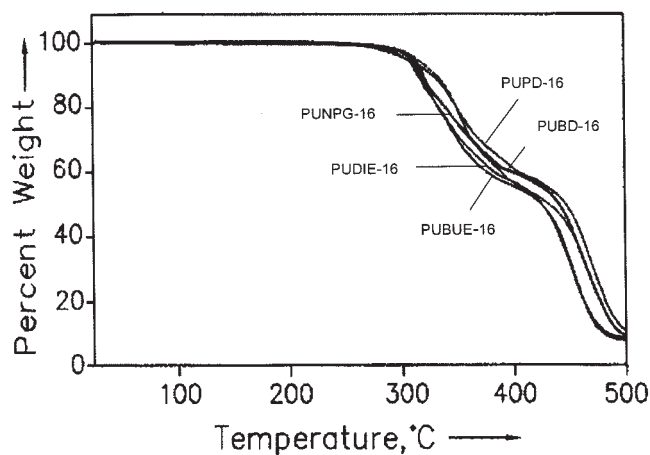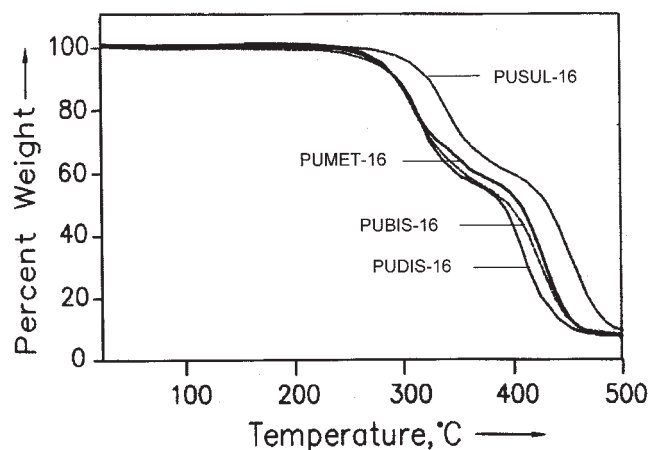

Figure 2 Thermogravimetric curves of diamine chain-extended polyurethanes prepared from isophorone diisocyanate.

Figure 3 Thermogravimetric curves of diol chain-extended polyurethanes prepared from toluene diisocyanate.

of the given groups, and a number of other parameters, such as phase separation attributed to the immiscibility of hard and soft segments and ionic forces inside the domains, for example.

The activation energy values of the thermal decomposition of various samples are reported in Tables VI–X. The correlation coefficients of both the Broido and Coats–Redfern methods were found to be >0.99. The higher E and n values clearly indicate the higher thermostability and slower degradation rate. The difference of E values of the two applied methods might be attributable to the different mathematical approaches used to calculate the kinetic parameters. The order of degradation observed by use of Coats–Redfern method for the first stage (n_1) of the diol chain-extended PU-15 series lies between 1.6 and 3.3 (Table VI), whereas for the second stage (n_2) it was 0.5–1.3. With increasing degradation order the complexity of

Figure 4 Thermogravimetric curves of diamine chain-extended polyurethanes prepared from toluene diisocyanate (heating rate 5°C/min).

TABLE VII
Kinetic Parameters of Polyurethane (PU-16) with Different Chain Extenders (heating rate, 10°C/min)

Sample	Broido E_1, E_2 (kJ/mol)	Coats–Redfern E_1, E_2 (kJ/mol)	n_1, n_2
PUBD-16	71.5, 102.4	78.5, 109.3	4.0, 1.5
PUPD-16	75.9, 110.6	79.4, 110.8	3.5, 1.4
PUDIE-16	57.0, 100.0	60.7, 102.9	3.5, 0.8
PUNPG-16	62.0, 89.8	60.2, 86.1	4.0, 0.6
PUBUE-16	53.3, 96.5	59.8, 97.5	3.0, 0.5

degradation increases and thus it is proposed that the second stage of decomposition was much easier than the first stage. The lower activation energy values of the second stage (E_2) of decomposition, as calculated by both methods, further supports the assumption for these systems. The only deviation was observed for PUBUE-15, where the activation energy of the second stage of decomposition (E_2), calculated by the Broido method, shows more than that for the first step (E_1) of decomposition. Table VI showed the equivalent stability order, as observed earlier from the analysis of the characteristic TG temperatures reported in Table I. The order of decomposition for diamine chain-extended PUs was 3.4–4.3 for the first stage (n_1), much higher than that of diol chain-extended PUs.

Table VII represents the kinetic parameters of polyurethane (PU-16) with different diol chain extenders. The activation energy values (E_1 and E_2) of diol chain-extended PUs showed that PUPD-16 was most stable and PUBUE-16 was least stable. The lower stability of PUBUE-16 was associated with steric crowding, resulting from the presence of two bulky substituents in the chain-extender structure. The thermal stability decreases with increasing branching on the side chain of the diol chain extenders (i.e., in the series PD, BD, MPD, DIE, and BUE). The degradation order for the first stage (n_1) was between 3.0 and 4.0, whereas for the second stage (n_2) the value was 0.5–1.5. On a comparison of the activation energy values (E_1), as calculated by the Broido method (Table V and VI), it was observed that PU-15 series diols were more stable

TABLE VIII
Kinetic Parameters of Polyurethane (PU-16) with Different Chain Extenders (heating rate, 5°C/min)

Sample	Broido E_1, E_2 (kJ/mol)	Coats–Redfern E_1, E_2 (kJ/mol)	n_1, n_2
PUSUL-16	102.4, 95.7	102.1, 90.0	4.0, 1.5
PUMET-16	97.8, 96.5	96.0, 88.6	4.0, 0.9
PUBIS-16	36.2, 82.0	40.8, 81.0	2.8, 2.0
PUDIS-16	77.2, 89.1	81.5, 87.5	3.0, 1.9

TABLE IX
Kinetic Parameters of Polyurethane PUIT-15 and PUIT-16 with Different Heating Rates (in nitrogen)

| Sample (heating rate °C/min)	Broido E_1, E_2 (kJ/mol)	Coats–Redfern E_1, E_2 (kJ/mol)	n_1, n_2
PUIT-15 (5)	105.8, 81.9	98.5, 80.2	1.7, 0.7
PUIT-15 (10)	106.0, 99.6	107.2, 98.0	1.5, 1.0
PUIT-15 (15)	117.3, 98.8	117.3, 102.9	1.8, 1.2
PUIT-15 (20)	129.7, 103.7	131.9, 105.9	1.7, 1.2
PUIT-16 (5)	83.7, 73.9	82.9, 77.3	3.7, 1.1
PUIT-16 (10)	86.0, 92.3	85.7, 88.0	4.0, 1.1
PUIT-16 (15)	87.1, 91.1	90.0, 89.3	3.5, 1.0
PUIT-16 (20)	93.5, 101.0	94.3, 99.1	4.0, 1.0

than the PU-16 series of diols. The E values obtained for the first stage of decomposition by the Broido and Coats–Redfern methods for PUSUL-16 and PUMET-16 were substantially higher than those for PUDIS-16 and PUBIS-16 (Table VIII).

Although PUDIS-15/PUDIS-16 contains an aromatic ring in the chain extender, there is lower stability compared to that of PUSUL-15/PUSUL-16 and PUMET-15/PUMET-15, which may be attributable to the presence of weak sulfur–sulfur (S—S) bond or divalent sulfur (S^{11}). The larger size of 3p orbital than that of 2p orbital causes poor sp^3 hybridization and overlapping, thus promoting a weaker S—S σ-bond formation than that of sp^3–sp^3 (2p–2p) overlap as in the C—C bond. The excellent stability of PUSUL-15/PUSUL-16 was explained by the presence of strong resonant aryl sulfone groups, and by the hexavalent sulfur.[43] In addition, the C—S^{VI} bond is stronger than the C—S^{11} bond, attributed to the higher electron affinity of S^{VI}, and greater σ-bonding orbital overlap. Additionally, PU chain extended with 4,4'-diaminodiphenyl sulfone is expected to have more phase-separated structure because of the polarity difference between soft and hard segments that favor higher thermal stability. On a closer examination of the thermal stability data of the coatings systems (Tables V and VI) it was found that stability order is as follows: PUSUL-15/16 > PUMET-15/16 > PUDIS-15/16.

Tables IX and X compare the activation energy val-

TABLE X
**Kinetic Parameters of Polyurethane PUIT-15 and PUIT-16 with Different Heating Rates (in oxygen)**

Sample (heating rate °C/min)	Broido E_1, E_2 (kJ/mol)	Coats–Redfern E_1, E_2 (kJ/mol)	n_1, n_2
PUIT-15 (10)	110.8, 24.1	111.7, 23.8	4.0, 0.6
PUIT-15 (20)	150.1, 43.3	152.6, 41.0	3.4, 0.8
PUIT-16 (10)	131.7, 34.1	131.3, 25.7	4.0, 1.2
PUIT-16 (20)	72.7, 50.3	72.8, 40.3	3.0, 1.7
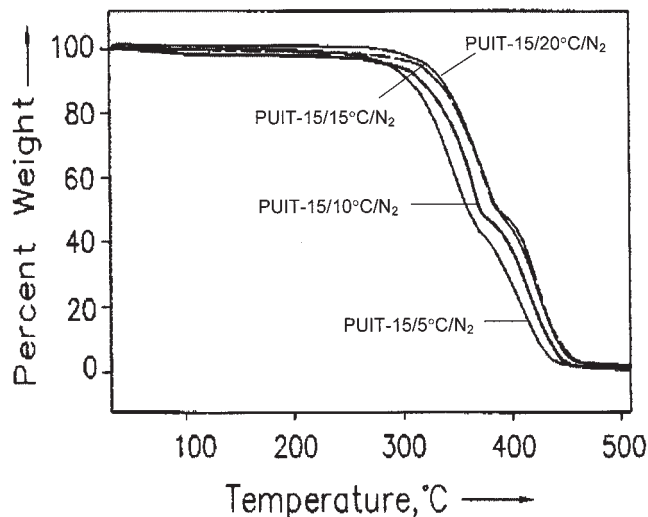
Figure 5 Thermogravimetric curves of PUIT-15 at different heating rates under nitrogen environment.
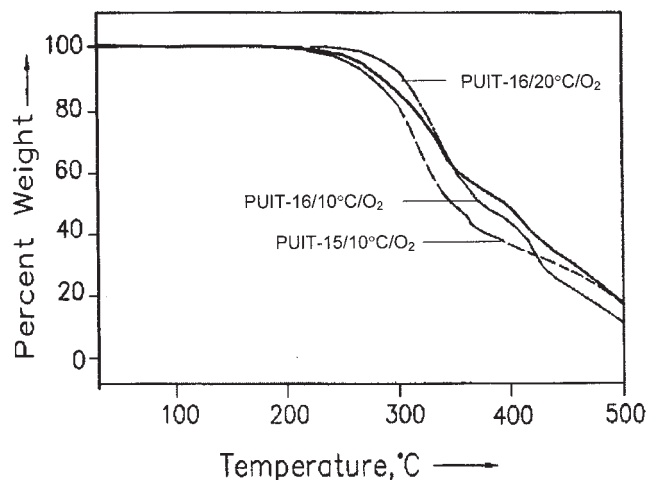
ues of PUIT-15 and PUIT-16 with different heating rates in the presence of nitrogen and oxygen gas, respectively, and the corresponding TG curves are shown in Figures 5, 6, and 7. Tables IX and X showed that activation energy increases with increasing heating rate.

The thermal resistance of PUIT-15 and PUIT-16 formulations using diisocyanates with aliphatic structures (IPDI) and the aromatic TDI, at the same NCO/OH ratio (1.6) and TMP content, were compared. The isothermal TG curves of PUIT-15 and PUIT-16 at 200 and 230°C are shown in Figure 8, whereas Figure 9 represents the isothermal TG curves at 280, 300, and 330°C in a nitrogen environment. Figure 8 shows that at a particulate temperature PU-15 was more stable than PU-16, whereas Figure 9 shows that, initially, PUIT-15 was more stable and after a
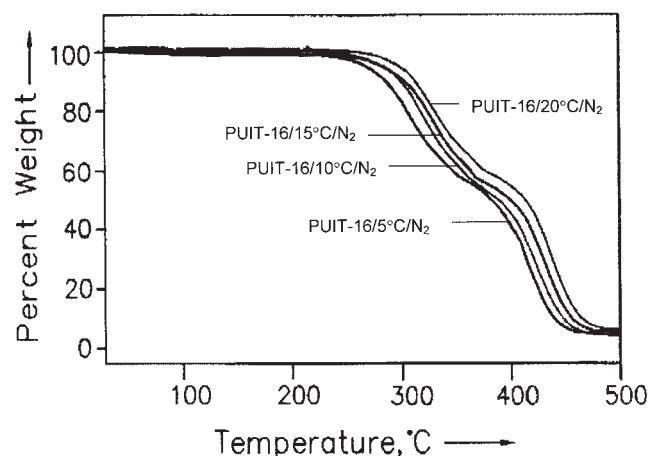

Figure 6 Thermogravimetric curves of PUIT-16 at different heating rates under nitrogen environment.

Figure 7 Thermogravimetric curves of PUIT-15 and PUIT-16 at different heating rates under oxygen environment.

certain period of time (say 100 min at 280°C) the stability order follows the reverse trend. These observations confirm that, at lower temperature, PUIT-15 was more stable. The aromatic rings, with 2,4- and 2,6-isocyanate groups, formed more rigid and asymmetrical chains, which seems to hinder the interactions between the hard segments, thus reducing their thermal resistance at lower temperature. However, the presence of TDI seemed to impart higher thermal stability to the flexible segments, compared with that of the cycloaliphatic IPDI at higher temperature. In addition, high reactivity of TDI, compared to that of IPDI, makes PU-16 with a higher concentration of urethane groups compared to that of PU-15, given that the reaction was carried out in the absence of catalyst. Urea groups are more stable than urethane groups at lower temperature, whereas the presence of an aromatic ring in PU-16 explained the difference in stability order at high temperature.
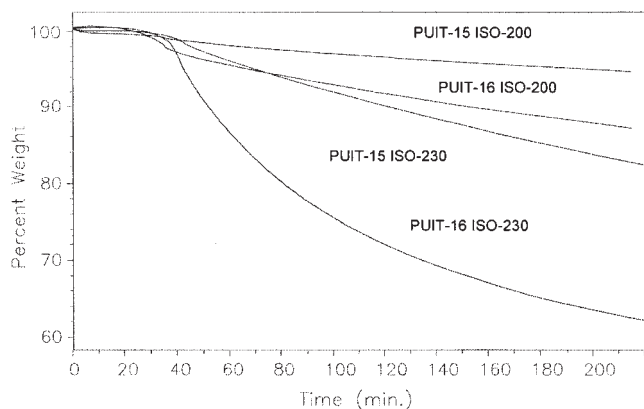
Figure 8 Isothermal TG curves of PUIT-15 and PUIT-16 at 200 and 230°C.
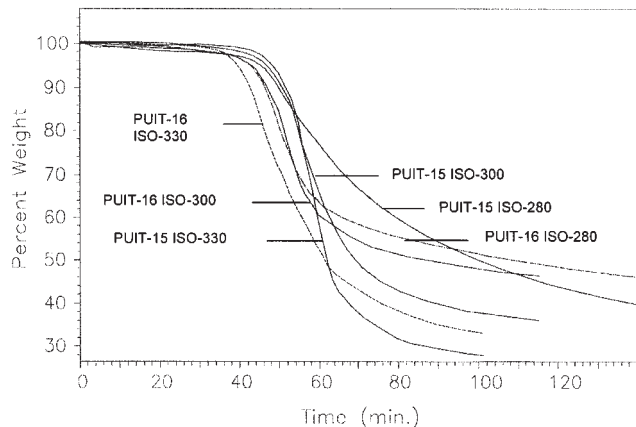
Figure 9 Isothermal TG curves of PUIT-15 and PUIT-16 at 280, 300, and 330°C.

CONCLUSIONS

An experimental investigation was undertaken to study the thermal degradation behavior of moisture-cured polyurethane in the presence of different chain extenders. The degradation parameters were evaluated using the Broido and Coats–Redfern methods. Thermal stabilities of PUIT-15 and PUIT-16 were evaluated at different heating rates in nitrogen and oxygen environments. Isothermal experiments of the mother formulations were carried out at different temperatures. During this study we observed the following points:

- Sulfone groups containing polyurethanes were more stable than 4-aminophenyl-disulfide chain-extended polyurethane in a comparison of the thermostability data for polyurethanes prepared from aromatic diamine chain extenders.
- Propane 1,2 diol containing polyurethane showed better stability than that of other aliphatic diol chain-extended polyurethanes. Increasing branching in the diol chain-extender structure resulted in a decrease in stability. Polyurethane derived from 2-butyl-2-ethyl-1,3-propanediol chain extender was the least stable.
- Polyurethanes derived from aromatic diamine chain extenders (PUSUL) showed superior stability to that of aliphatic diol chain-extended (PUBD) polyurethanes.
- Polyurethanes prepared from TDI showed better stability at high temperatures than that of those prepared from IPDI. The thermal stability of the polyurethane changes with the change of heating rate and environment. The thermal stability of the samples in an oxygenated environment was modest.

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