

Thermal and Dynamic Mechanical Characterization of Polyurethane–Urea–Imide Coatings

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Received 14 July 2005; accepted 26 February 2006

DOI 10.1002/app.24343

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of NCO terminated polyurethane (PU)–imide copolymers were synthesized by a systematic three-step process and were chain extended with different diol/diamine chain extenders. In the first step, isocyanate terminated PU prepolymers were prepared by reacting soft segments such as polyester (PE) polyols and polyether polyols such as polypropylene glycol (PPG-1000) with hard segments like 2,4-tolylene-diisocyanate (TDI) or isophorone-diisocyanate (IPDI) with NCO/OH ratio 2:1. In the second step, thermally stable heterocyclic imide ring was incorporated using isocyanate terminated PU prepolymers by reacting with pyromellitic dianhydride (PMDA) in a excess-NCO:anhydride ratio of 1:0.5. The surplus NCO content after imidization was both moisture cured or partially reacted with chain extender and moisture cured. The films

were characterized by thermogravimetric (TG), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) instruments. The adhesion strength of these coatings on mild steel (MS), copper (Cu), and aluminum (Al) is dependent on the nature of the substrate. The TGA analysis show good thermal stability. The DMTA results show the microphase separation between the different hard and soft segments. Finally, a structure to property correlation was drawn based on the structure of the soft, hard, and chain extender and the observed properties are useful for understanding and design of intelligent coatings. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3158–3167, 2006

Key words: polyurethane–imide; coatings; TGA; DSC; DMTA; adhesion

INTRODUCTION

Polyurethanes (PUs) are widely used as binder in coatings because of their excellent mechanical properties like good hardness, high abrasion, and chemical resistance.¹ The properties of the PU coatings can be tailor made by properly selecting the constituents such as soft and hard segments and the appropriate amount of crosslinker. Accordingly, the resultant bulk properties are derived from the two-phase structure, i.e., the hard phase composed of aromatic (or aliphatic) urethane or urea segments, and the soft phase composed of polyester polyol or polyether segments. Factors that control the phase separation include composition, symmetry of diisocyanate, the type and number of carbon atoms in the chain extender,^{2–5} the type and the chain lengths of soft segments,^{5–7} crystallizability of either segments,⁷ the thermal history of the PUs,^{8,9} and the method of synthesis.^{10,11}

In spite of the ability to customize the properties of the PU elastomeric coatings as per the requirement, the serious disadvantage lies on their thermal stability.

It was found that the acceptable mechanical properties of the PU elastomers disappear above 80–90°C and thermal degradation takes place above 200°C.¹² Hence considerable amount of research is going on to obtain a synergistic well-balanced property profile of the PU elastomers for various coating applications.

Various attempts were made to improve the thermal and mechanical properties of the PU elastomers. Some of the methods used are (a) by using a rigid-structure diisocyanate and trimers of isocyanate or polyether-ol containing a thermostable heterocyclic ring such as an s-triazine ring,^{13–19} (b) chemically modifying its structure and making PU–epoxy IPN, poly(urethane-urea), poly(urethane-epoxy), PU–diacetylene, and PU–polysiloxane crosslinked polymer networks,^{20,21} (c) addition of appropriate amount of crosslinker such as a triol or triisocyanate,³ (d) incorporation of appropriate amount of aromatic rings into the PU backbone, (e) partial replacement of urethane segment with urea functions to improve the interchain association,^{2–4} and (f) chemical modification of the backbone or by introducing stable heterocyclic groups like imide, oxazolidone, triazine and phosphazene.^{22–33}

Recently, lot of interest has been paid to improve the thermomechanical properties of PUs by chemical modification of its structure containing various hard and soft segments with stable aromatic heterocyclic rings. It was hypothesized that one way to improve

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the thermal stability of PUs without much sacrificing the mechanical properties was to utilize dianhydrides as a reactive material for incorporation of imide rings into the PU backbone, since imide rings are heterocyclic in nature and possess excellent heat resistance and mechanical properties, and they can retain their applicability for long time at high temperature.³⁴

In the present work, we have synthesized different PU-urea-imide copolymers from polyester polyol (PE) and polyether diol (PPG). NCO terminated PU prepolymers (NCO-PU) of PPG and PE were prepared from IPDI or TDI with NCO:OH ratio of 2:1. Then, NCO-terminated PU-imide copolymers were synthesized from NCO-PU by reacting with PMDA in a excess-NCO:anhydride ratio of 1:0.5. The synthesized PU-imide copolymers were partially chain extended with diols, diamines and partially moisture cured. The obtained films were used for thermal degradation and dynamic mechanical property evaluation.

EXPERIMENTAL

Materials

Polypropylene glycol-1000 (PPG), trimethylol propane (TMP), isophorone diisocyanate (IPDI: mixture of *Z* and *E* isomer in 3:1 ratio) neopentyl glycol (NPG) and dibutyl tin dilaurate (DBTL) from Aldrich (Milwaukee, WI); 4,4'-diamino-diphenyl sulfone (DDS), 4, 4'-diamino-diphenyl ether (DDE), toluene diisocyanate (TDI: mixture of 2,4- and 2,6-isomer in 9:1 ratio), 1,4-butane diol (BD) from Fluka Chemical Corp. (Ronkonkoma, NY); 1,2-propane diol (PD), adipic acid (AA), triethylamine, dimethyl formamide and sulfur free toluene from S. D. Fine chemicals (Mumbai, India); 1-methyl-2-pyrrolidinone (NMP) from Merck India (Mumbai, India), isophthalic acid (IPA) from Sisco Chemicals (Mumbai, India); methyl isobutyl ketone (MIBK) from Ranbaxy (Mumbai, India) and pyromellitic dianhydride (PMDA) from Spectrochem (Mumbai, India) were used. PMDA was purified by recrystallization from acetic anhydride, followed by sublimation. The used solvents were freed from moisture by the addition of 4 Å molecular sieves.

Synthesis of polyester polyol

Polyester polyol (PE) was synthesized by charging 2.2 mol NPG, 0.825 mol AA, 0.825 mol IPA, and 0.35 mol TMP into a four-necked flask, equipped with mechanical stirrer, thermometer, nitrogen inlet, and deanstark apparatus. The reactant mixture was slowly heated upto 160°C. After complete melting of the reactants, the temperature of the flask was increased to 180–190°C with constant nitrogen flow and maintained at that temperature for about 6 h and gradually

TABLE I
Chemical Composition, Equivalent Ratio and Sample Abbreviations of the Synthesized PU-Urea-Imide Copolymers

Sample name	Chemical composition	Equivalent ratio
PUI-2	PE/IPDI/PMDA	1:2:0.5
PUI-3	PE/IPDI/PMDA/PD	1:2:0.5:0.25
PUI-6	PE/IPDI/PMDA/DDS	1:2:0.5:0.25
PUI-7	PE/TDI/PMDA/DDS	1:2:0.5:0.25
PUI-8	PE/TDI/PMDA	1:2:0.5
PUI-12	PPG/TDI/PMDA	1:2:0.5
PUI-13	PPG/TDI/PMDA/DDS	1:2:0.5:0.25
PUI-16	PPG/TDI/PMDA/PD	1:2:0.5:0.25

increased upto 210°C and the esterification reaction was continued for another 6 h. The reaction was monitored periodically by checking the acid value and continued the reaction till the acid value reached below five. The hydroxyl value of the synthesized PE was determined by acetic acid/pyridine titration method and was found to be 280.

Synthesis of the PU-urea-imide resin

The NCO terminated PU prepolymer of PPG and the synthesized polyester were prepared by carrying out the reaction in a 250 mL four-necked round bottomed flask as reported earlier.³⁴ In brief, 50 g PE in 80 g of MIBK was reacted with 37.2 g TDI with NCO/OH ratio of 2:1 at 50°C for 2 h with stirring and then the reaction was continued for another 3 h at 70–75°C. The same process was repeated by reacting 50 g of PE with 47.5 g IPDI and 50 g PPG with 17.4 g TDI, respectively. The synthesized resins were named as PE/TDI, PE/IPDI, and PPG/TDI, respectively. Then reaction kettle was cooled to room temperature and the required amount of PMDA (excess NCO:anhydride ratio was 1:0.5) was dissolved in a minimum amount of DMF was added at 40–45°C. After complete addition, the imidization reaction was continued for additional 1 h. To control the viscosity of PU-imide during imidization reaction, appropriate amount of NMP was added in the reaction mixture.

Preparation of PU-urea-imide films

The synthesized PU-imide polymers were divided into three parts. The excess NCO groups of the first part were allowed to react completely with atmospheric moisture and named as PUI-2. 50% of the available NCO groups from the second and third part were chain extended with DDS and PD and were named as PUI-6 and PUI-3 respectively. Similarly PU-urea-imide films were also obtained from PE/IPDI and PPG/TDI. Table I shows the details of the reactant and equivalent ratio used, to prepare different PU-

urea–imide coatings along with their abbreviations. The coated films were kept at 30 °C for 20 days.

FTIR spectroscopy

PU–urea–imide thin films coated on the KBr disc were subjected to FTIR study for the structural elucidation. Samples were scanned 128 times with 4 cm^{-1} resolution on a Thermo Nicolet Nexus 670 spectrometer under the range of 400–4000 cm^{-1} .

Thermal properties

The thermal stability of PU–urea–imide coatings was studied using Mettler Toledo TGA/SDTA 851^e thermal system (Switzerland). For TGA analysis, films were cut into small pieces and about 15 mg of sample was taken and heated at a constant rate of 20°C min^{-1} in nitrogen atmosphere from 25 to 500°C with N_2 gas flow rate 30 mL min^{-1} . To know the thermal stability with heating rate, a representative sample PUI-8 was subjected to different heating rates in nitrogen atmosphere. DSC thermograms were recorded on a Mettler-Toledo DSC 821^e thermal system (Switzerland). For DSC analysis, the samples were placed in sealed aluminum pans and initially heated at a heating rate of 10°C min^{-1} from –60 to 170°C in nitrogen atmosphere; then the samples were quenched immediately from 170 to –60°C at a cooling rate of 30°C min^{-1} to remove the previous thermal history. Then the samples were subsequently rescanned at a heating rate of 10°C min^{-1} from –60 to 200°C. The instrument was calibrated with indium standards before the measurements. The average sample size was 10 mg, and the nitrogen flow rate was 30 mL min^{-1} . From these thermograms, the glass-transition temperatures (T_g 's) were determined.

Dynamic mechanical analysis

The viscoelastic behavior of the synthesized PU–urea–imide films in nitrogen atmosphere was analyzed with DMTA IV instrument (Rheometric Scientific, United States) in shear mode at a frequency of 1Hz and a heating rate of 3°C min^{-1} . The scan temperature used was from 30 to 200°C for PE based materials, whereas PPG based samples it was from –90 to 150°C. T_g was taken from the peak temperature of G'' versus temperature curve.

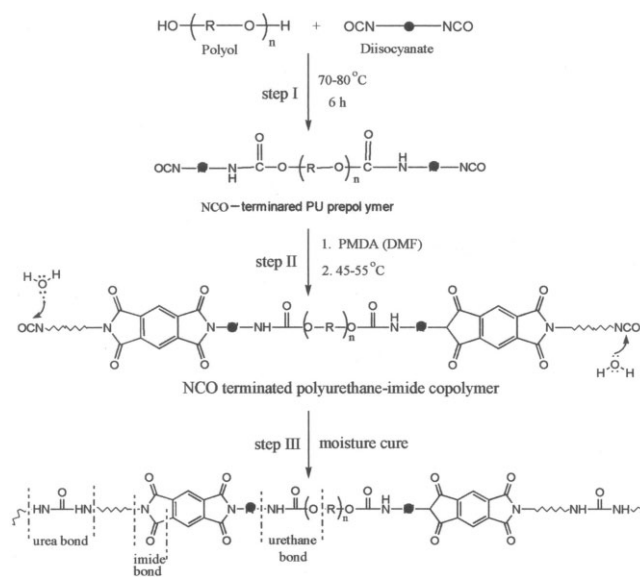
Adhesion testing

Mild steel (MS), aluminum (Al) and copper (Cu) discs were pretreated with dilute HCl (acid cleaning: chemical pickling), washed several times with distilled water and finally with acetone. The pretreated discs were spin coated uniformly and dried at controlled temper-

ature and humidity room for 20 days. The adhesion strength was determined by pull-off test (Microtech Tensiometer, UK).

RESULTS AND DISCUSSION

Several methods are available to incorporate thermally stable heterocyclic imide rings into the PU coatings. However, introduction of imide groups via chain extender has some advantages such as the possibility of using commercially available NCO-terminated PU prepolymers and enhancing the phase separation due to strong dipole–dipole interaction of imide groups present in the hard segment. As the imide structures have high rigidity, these groups decrease the flexibility and extensibility of PUs. So, an optimum concentration should be used to tailor properties without sacrificing much of the flexibility.³⁵ On the other hand, as urea groups produce additional interchain stiffness when compared to urethane functions, therefore the experimental design in this study includes the presence of both urethane, urea and imide groups in optimum level. Consequently, the reason behind the incorporation of urethane, urea and imide groups in a polymer is to combine the properties of these individual identities and generate synergistic well-balanced property profile. For that, NCO terminated PU prepolymers were prepared (Step I: Scheme 1), which was then partially reacted with PMDA (Step II) and the remaining excess NCO groups were both moisture cured (Step III) or partially chain extended and moisture cured. Based on this strategy, different PU–urea–imide coatings were prepared either from PPG or polyester polyol (PE). Scheme 1 shows the basic reac-



Scheme 1. Synthesis of PU–urea–imide coatings.

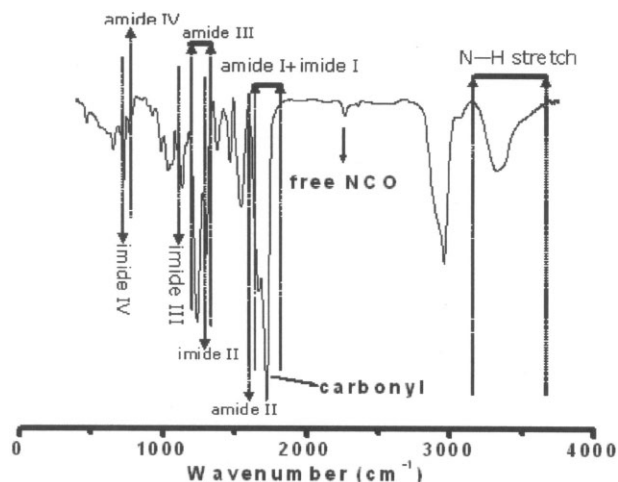


Figure 1 FTIR spectrum of the sample PUI-3 in the range of 400–4000 cm^{-1} .

tions involved in the preparation of PU-urea-imide coatings.

FTIR analysis

The FTIR spectra of a representative sample, PUI-3 is shown in Figure 1. The presence of characteristic bands such as N—H stretching, amide I, amide II, amide III, amide IV, imide I, imide II, imide III, imide IV vibrations at 3150–3650, 1600–1800, 1540, 1190–1310, 766, 1730–1780, 1320–1380, 1120, and 720 cm^{-1} , respectively, suggests the presence of urethane, urea and imide functions in the sample and confirms that the imide group was introduced into the PU backbone. A detailed analysis of the structure of the synthesized samples through FTIR spectroscopy is presented in our earlier publication.³⁴

Thermal properties of PU-urea-imide coatings

The study of the thermal decomposition of polymers constitutes an important feature from both fundamen-

tal and technological perspective; since it determines a number of parameters including the upper limit of temperature at which the coatings can work for a long time without appreciable degradation. Thermogravimetric analysis (TGA) is a technique used to measure changes in the mass of a sample as a function of temperature and/or time. In TGA, typical weight loss profiles are analyzed for the amount or percent of weight loss at any given temperature, the amount or percent of noncombusted residue at some final temperature, and the onset/endset temperature of various degradation steps. The mass loss of PU-urea-imide coatings at different temperatures and the initial and peak decomposition temperatures were evaluated from the respective TG and DTG thermograms. Three and one-step decomposition profile was obtained for PE and PPG based PU-urea-imide coatings, respectively. The characteristic thermal degradation temperatures for the first step (onset: $T_{1\text{ON}}$; endset: $T_{1\text{EN}}$; for PE based coatings this is second step) and last step (endset: $T_{2\text{EN}}$), the temperature of maximum rate of weight loss for the first ($T_{1\text{MAX}}$) and second step ($T_{2\text{MAX}}$), percent weight loss at 280 and 470°C of different PU-urea-imide coatings were compared. The results of TG analysis are summarized in Table II and Figures 2–4 show the TG profiles of the different samples analyzed.

Figure 2 shows a three-step decomposition profile of PU-urea-imide coatings prepared from PE with the onset of the first step was around 180°C and corresponds to the decomposition of the urethane segment. The percentage of wt. loss in this step corresponds to 8.3, 10.0, and 8.0 for PUI-2, PUI-3, and PUI-6 respectively. The second stage of degradation corresponds to the decomposition of soft PE segment, which stated above 297°C and the endset is at about 348°C. The third step corresponds to the degradation of advanced fragments produced after the second decomposition step as well as the decomposition of imide rings. This third step of thermal decomposition started above 350°C and ends above 440°C with char residues. A

TABLE II
Thermal Stability Data of PU-Urea-Imide Coatings with Different Soft Segment and Chain Extender

Sample	$T_{1\text{ON}}$	$T_{1\text{MAX}}$	$T_{1\text{END}}$	$T_{2\text{MAX}}$	$T_{2\text{END}}$	wt % remaining at	
						280°C	470°C
PUI-2 (20°C min^{-1})	307.1	348.5	359.0	428.9	446.4	83.4	21.1
PUI-3 (20°C min^{-1})	297.2	341.0	348.6	420.7	438.6	82.8	19.8
PUI-6 (20°C min^{-1})	321.6	349.0	370.0	436.4	464.7	86.3	33.9
PUI-7 (5°C min^{-1})	279.0	326.0	373.7	431.3	468.0	86.7	32.5
PUI-8 (5°C min^{-1})	260.5	315.0	371.2	339.0	457.6	83.3	22.0
PUI-8 (10°C min^{-1})	266.2	323.0	376.5	342.6	459.8	87.5	34.5
PUI-8 (15°C min^{-1})	279.1	327.0	376.9	316.0	458.1	84.3	24.3
PUI-8 (20°C min^{-1})	282.3	330.6	380.0	353.0	467.4	89.4	34.6
PUI-12 (20°C min^{-1})	278.2	366.2	390.7	—	—	95.9	15.9
PUI-13 (20°C min^{-1})	286.4	371.7	394.8	—	—	97.5	17.9
PUI-16 (20°C min^{-1})	281.1	362.1	382.9	—	—	96.5	18.7

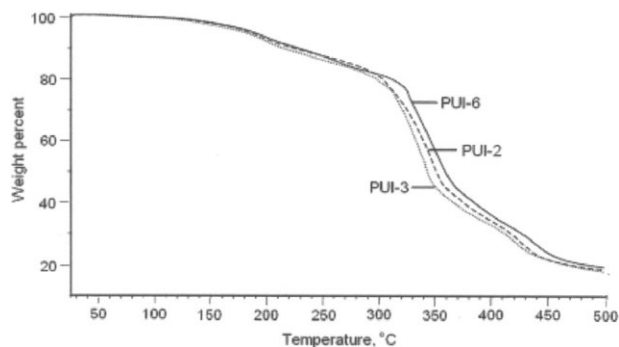


Figure 2 Thermogravimetric curves of polyester based PU-urea-imide coatings.

comparison of the characteristic thermal decomposition data from Table II and decomposition profile from Figure 2 shows that the stability order follows: PUI-6 > PUI-2 > PUI-3.

Similarly, Figure 3 shows the three step-decomposition profile of PUI-8 at different heating rates along with the decomposition profile of PUI-7. The first step of decomposition corresponds to 8–10% wt loss of the sample, which again depends on the heating rate used. A comparison of characteristic thermal decomposition data from Table II suggests that the stability increased with increasing heating rate with few exceptions. For instance, the decomposition onset temperature for the second step (T_{1ON}) of PUI-8 with 5, 10, 15, and 20°C min⁻¹ corresponds to 260.5, 266.2, 279.1 and 282.3°C, respectively. Similarly, T_{1MAX} and T_{1EN} also increased with increasing heating rate. However the outcome of TGA curve and the corresponding data of PUI-8 sample at 15°C min⁻¹ to the other heating rate shows some deviation in the third decomposition step. This may be due to the complicity involved during decomposition because of the formation of degradable intermediates at that heating rate or may be an experimental error. A comparison of the thermal stability between the samples PUI-7 and PUI-8 (Fig. 3) analyzed at a heating rate of 5°C min⁻¹ suggests that the

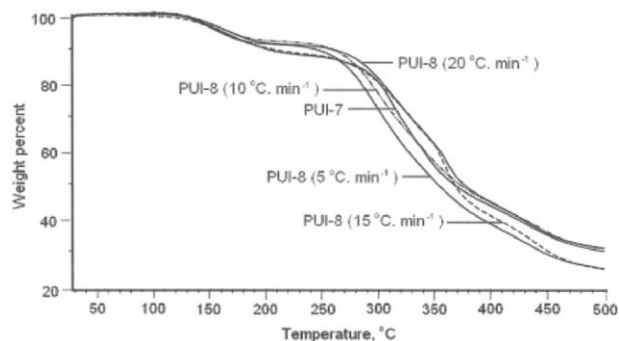


Figure 3 Thermogravimetric curves of polyester based PU-urea-imide coatings in different heating rate.

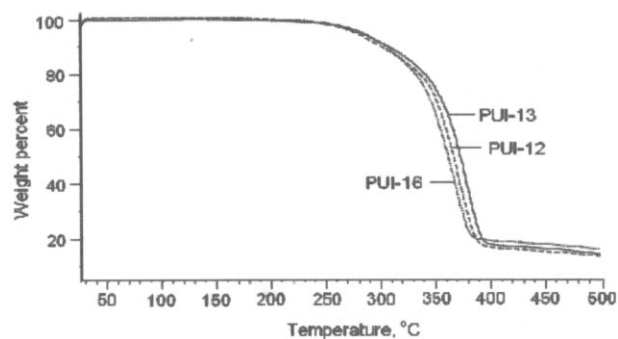


Figure 4 Thermogravimetric curves of PPG based PU-urea-imide coatings.

thermal stability of PUI-7 was higher when compared to PUI-8. On the contrary, the thermal decomposition profile of the samples prepared from PPG soft segment as can be seen in Figure 4 shows predominantly single step degradation. Here the stability order follows the trend: PUI-13 > PUI-12 > PUI-16 except the char yield value at 470°C. For instance, the T_{1MAX} and T_{1EN} values of PUI-12, PUI-13, and PUI-16 were 366.2, 391.0; 371.7, 394.8; and 362.1, 382.9°C respectively. The above observed values suggest that (a) the PU-urea-imide copolymers prepared from DDS are more stable and the ones prepared by PD are least stable when a comparison was made between DDS and PD chain extended polymers along with the moisture cured systems prepared from both the PE as well as PPG soft segments. This phenomenon is attributed to the more polar nature of DDS, which enhances the interchain association between the macromolecular chains due to the presence of polar sulfone groups and thereby is more phase separation. PD chain extended polymer contains more urethane bond concentration; whereas DDS and moisture cured formulations have more urea functionality. Since urea bonds are more polar in nature when compared to urethane bonds, thereby, we can expect that the degree of phase separation will follow an order of DDS > moisture cured > PD containing polymers. Again as the degree of phase separation is a measure of intermolecular association through hydrogen bonds and other polar forces, the thermal stability should also follow the same trend, and similar phenomenon was observed, (b) thermal stability increased with increasing heating rate and this observation is in agreement with the earlier studies,³ and (c) at lower temperature PPG soft segment containing polymers were more stable than PE soft segment containing PU-urea-imide coatings. This is because the first decomposition steps of PE based PU-urea-imide coatings correspond to 8–10% weight loss, which is absent in PPG based PU-urea-imide coatings Hence, wt % remaining at 280°C were higher for PPG soft segment containing polymers. On the other hand at high temperature, the stability order

follows the reverse trend. For instance, the wt % remaining at 470°C was higher for PE soft segment containing polymers in comparison to PPG soft segmented PU-urea-imide copolymers. Now, let us analyze the thermal stability in terms of decomposition kinetic parameters derived from Broido³⁶ and Coats-Redfern³⁷ methods. The derivation of kinetic parameters in the study of the polymer decomposition by exploiting TG data is useful in the determination of rate constants, activation energies (E ; kJ mol^{-1}), reaction orders (n), and pre-exponential factors (Z ; min^{-1}). Though the values of kinetic triplet (E , n and Z) depend on several factors such as the flow rate and the nature of gas flowing, heating rate, sample mass, as well as the mathematical models used to evaluate the data and have wide controversy about their use and abuse, still researchers³⁸⁻⁴⁶ claim a physical meaning to these parameters, and have shown that a dynamic TG curve may be correctly described by various kinetic models.

The reaction rate in TGA can be defined as the derivation of the conversion with respect to time. The conversion at time t , $[\alpha(t)]$ is defined as the ratio of the final mass loss to the total mass loss corresponding to a particular stage of decomposition:¹¹

$$\alpha(t) = \frac{w_0 - w_t}{(w_0 - w_\infty)} \quad (1)$$

where, w_t is the mass at any degradation time, w_0 is the initial mass and w_∞ is the final mass at the end of the degradation process.

All the kinetic studies assume that the rate of conversion, $d\alpha/dt$, is a linear function of temperature dependent rate constant, k , and a temperature-independent function of conversion, α . The mathematical form of $d\alpha/dt$ is as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where, $f(\alpha)$ depends on the particular decomposition mechanism.

The temperature dependence of the kinetic constant can be expressed according to the following Arrhenius equation:

$$k(T) = Ze^{-E/RT} \quad (3)$$

where Z is assumed to be independent of temperature, T is the absolute temperature, and R is the Universal gas constant.

Combination of eqs. (2) and (3) gives:

$$\frac{d\alpha}{dt} = Zf(\alpha)e^{-E/RT} \quad (4)$$

The rate of conversion in a dynamic TGA experiment at a constant heating rate ($\beta = dT/dt$) can be expressed as follows:

$$\frac{d\alpha}{dt} = \beta \left(\frac{d\alpha}{dT} \right) = k(T)f(\alpha) \quad (5)$$

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

The integral form of rate equation in a dynamic heating experiment may be expressed as follows:

$$g(\alpha) = (ZE/\beta R)p(x) \quad (6)$$

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

Broido³⁶ has developed a model and the equation has the form:

$$\ln[\ln(I/Y)] = E/R(I/T) + \text{Constant} \quad (7)$$

where, $Y = (w_0 - w_t)/(w_0 - w_\infty)$ is the fraction of the number of initial molecules not yet decomposed, w_0 , w_t , and w_∞ are the weight of the sample at the beginning of TGA evaluation, at time t and at infinite time ($=0$), respectively. Thus a plot of $\ln[\ln(I/Y)]$ versus $1/T$ is related to E .

Coats-redfern equation³⁷

Coats and Redfern provided an approximation to the integral of eq. (6) and thus obtained the following expressions:

$$\begin{aligned} \ln[-\ln(1-\alpha)/T^2] &= \ln[ZR/\beta E(1-2RT/E)] \\ &= E/RT \quad \text{for } n = 1 \end{aligned} \quad (8)$$

The plot of $\ln[-\ln(1-\alpha)/T^2]$ verses $1/T$ gives the value of activation energy in the regression analysis. The slope of this plot gives the value of E/RT . Therefore E value can be obtained by multiplying slope of the curve with the value of Universal gas constant. From which we get the value of the activation energy.

when, n is not equal to 1, the equation takes the form:

$$\begin{aligned} \ln[1 - (1-\alpha)^{1-n}/(1-n)T^2] \\ = \ln[ZR/\beta E(1-2RT/E)] - E/RT \end{aligned} \quad (9)$$

Thus a plot of $\ln[1 - (1-\alpha)^{1-n}/(1-n)T^2]$ verses $1/T$ gives the value of E for the correct chosen value of n .

Now let us analyze the kinetic parameters derived from the above-mentioned methods and are listed in Table III. The activation energies (E_1) for the first step

TABLE III
Kinetic Parameters of Different PU-Urea-Imide Coatings Derived from TG Thermograms

Sample	Broido		Coats-Redfern	
	E_1, E_2 (kJ/mol)	E_1, E_2 (kJ/mol)	n_1, n_2	
PUI-2 (20°C/min)	50.1, 48.6	52.9, 48.8	2.9, 1.8	
PUI-3 (20°C/min)	48.2, 48.4	45.4, 48.5	2.9, 1.8	
PUI-6 (20°C/min)	53.1, 74.2	55.3, 74.4	3.1, 1.9	
PUI-7 (5°C/min)	47.8, 46.0	47.3, 46.8	3.2, 2.0	
PUI-8 (5°C/min)	46.7, 41.3	41.4, 45.4	3.0, 2.0	
PUI-8 (10°C/min)	47.6, 45.3	43.6, 46.7	3.0, 2.2	
PUI-8 (15°C/min)	48.5, 44.8	49.9, 46.2	3.0, 2.1	
PUI-8 (20°C/min)	48.8, 47.0	50.9, 47.2	3.0, 1.9	
PUI-12 (20°C/min)	103.8	106.4	1.1	
PUI-13 (20°C/min)	113.1	113.4	1.1	
PUI-16 (20°C/min)	91.9	95.0	1.1	

decomposition for PUI-2, PUI-3, and PUI-6 calculated using Broido model were 50.1, 48.2, and 53.1 kJ/mol, respectively. The corresponding E_1 values calculated from the Coats-Redfern method shows 52.9, 45.4, and 55.3 kJ/mol., respectively. The correlation coefficients in the linear regression analysis were more than 0.983 in all the activation energy calculations derived from Broido equation. These values clearly suggest that the PU-urea-imide coatings chain extended with polar DDS are more stable. A similar trend in E_1 values was also observed from the PU-urea-imide coatings prepared from PPG soft segment. The PPG based system showed a single step decomposition profile; therefore we have calculated a single activation energy value by fitting into Broido and Coats-Redfern models. A comparison of activation energy of PE and PPG based PU-urea-imide coatings suggests that PPG based systems are more stable when compared to PE based coatings. Now on a look of the activation energy values of PUI-8 with different heating rate suggests an increasing E_1 values calculated by both the Broido and Coats-Redfern methods, whereas an irregular trend is observed in the E_2 values. Since the second step of decomposition is very complex as the overall decomposition arises not only from the decomposition of urethane/urea and the soft segment but also from the decomposition of imide segments, therefore it is rather difficult to draw a structure-thermal stability correlation based on E_2 values. The order of decomposition for the first step (n_1) of PE based coatings are in between 2.9 and 3.1 as calculated from the Coats-Redfern models, whereas the second step (n_2) decomposition profile shows a nearly second order kinetics. The correlation coefficient values were more than 0.980 in different analyzed samples derived from Coats-Redfern equation. A nearly first order decomposition was observed for PPG based PU-urea-imide coatings during their thermal decomposition.

In summary, the TGA result implies: (a) when the soft and hard phases are more separated, the PU-

urea-imide samples possess greater thermal stability, (b) PU-urea-imide coatings derived from PPG and PE soft segment showed different thermal degradation profile, and (c) rate of heating played significant role in the thermal decomposition behavior.

Also the thermal behavior of different PU-urea-imide samples was studied with DSC instrument and the obtained thermograms are shown in Figure 5. The T_g value of the pure polyester (PE) was -23°C . The soft segment T_g values of PE based PU-urea-imide coatings were -20.1 , -19.5 , and -7.2°C for PUI-6, PUI-2, and PUI-3, respectively. Similarly, the soft segment T_g values of PPG based PU-urea-imide coatings were -18.8 , -12.1 , and -10.4°C for PUI-13, PUI-12, and PUI-16 respectively. Therefore, the observed soft segment T_g values suggests that the use of highly polar DDS chain extender favors a better phase separation in the PU-urea-imide coatings. The DSC thermograms of PD chain extended PU-urea-imide coatings showed a prominent mixed phase glass transition temperature, which was rather weak and could not be observed when DDS was used as a chain extender.⁴⁷

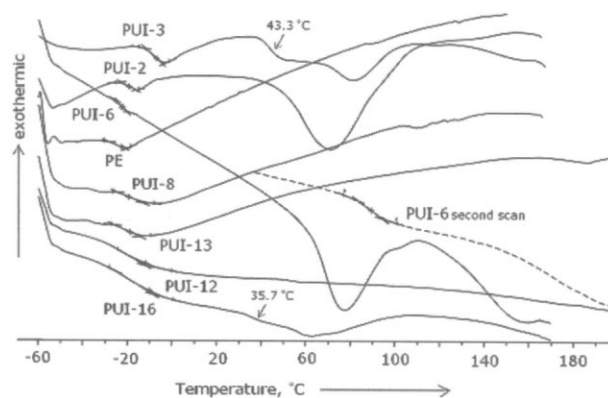


Figure 5 DSC thermograms of different PU-urea-imide coatings.

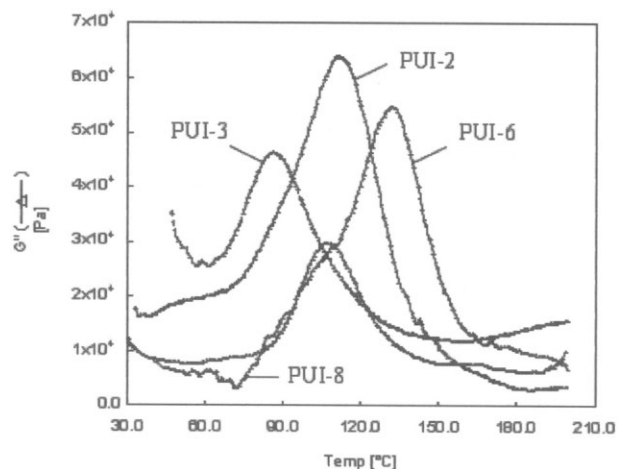


Figure 6 G'' versus temperature profile of different PU-urea-imide coatings prepared from PE.

Viscoelastic properties of PU-urea-imide coatings

Dynamic mechanical thermal analysis (DMTA) is a good method to study the relaxation behavior and to detect the glass transition temperature as well as the change in loss and storage modulus with temperature. This provides information on the phase separation and the mechanical behavior of a polymer. Figure 6 shows the G'' versus T curve of PE soft-segmented PU-urea-imide coatings. The T_g values of PUI-2 (MC), PUI-3 (PD), PUI-6 (DDS), and PUI-7 (TDI/DDS) coatings were determined from the peak temperature in the G'' versus T curve and are 110.2, 87.5, 131.2, and 107.7 °C, respectively, (Table IV). The DMTA spectrum of PUI-8 coating is shown in Figure 7. PUI-8 coatings showed a T_g value of 106.5°C. The steep fall of G' curve started at 95°C with a value of 1.75×10^5 Pa. and ends above 130°C with a value of 9.7×10^4 Pa. The G' value of PUI-7 coatings at 95 and 130°C were 1.93×10^5 and 9.9×10^4 Pa., respectively. The above-mentioned T_g and G' data suggests that the incorporation of polar DDS has improved the interchain as-

TABLE IV
Glass Transition Temperatures and Adhesion Strength in kg/cm² of Different PU-Urea-Imide Coatings

Sample name	T_g (°C) (from G''_{max})	Adhesive strength (kg/cm ²)		
		MS	Al	Cu
PUI-2	110.2	80.7	73.6	63.1
PUI-3	87.5	59.6	24.5	59.6
PUI-6	131.2	122.8	91.2	91.2
PUI-7	107.7	91.2	80.7	80.7
PUI-8	106.5	50.7	23.8	63.1
PUI-12	21.4	175.4	112.2	87.7
PUI-13	31.1	263.1	112.2	140.3
PUI-16	21.2	175.4	87.7	77.1

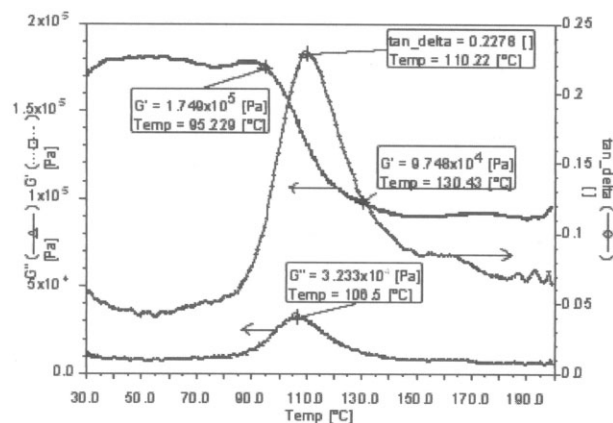


Figure 7 DMTA spectra of PUI-8 coatings.

sociation and stiffness considerably and IPDI based coatings (PUI-2) showed higher T_g value in comparison to TDI based coatings (PUI-8). PD is a diol chain extender and forms urethane bonds during reaction with —NCO, whereas moisture curing and DDS diamine chain extender formed urea bond on reaction with —NCO end groups. Again, urea bond presents two nitrogen atoms suitable to form hydrogen bonding, whereas urethane groups have only one nitrogen in this position. Consequently, the presence of urea groups produces an increase in the hard segment cohesion and more phase separated structure of the material and, thus, increase the rigidity. Furthermore, the presence of aromatic ring in diamine chain extenders increases the stiffness to the polymer. Therefore, the substitution of a diamine chain extender in place of the diol created a larger soft/hard segment polarity difference and thereby an enhanced physical crosslinking and/or filler effect. Figure 8 shows the DMTA spectra of PUI-12 coatings. The steep fall of G' has started at -16.5°C with a modulus of 1.82×10^5 Pa, and ends above 40.0°C with a modulus of 2.0×10^4 Pa. Figure 9 shows the G'' versus temperature spectra

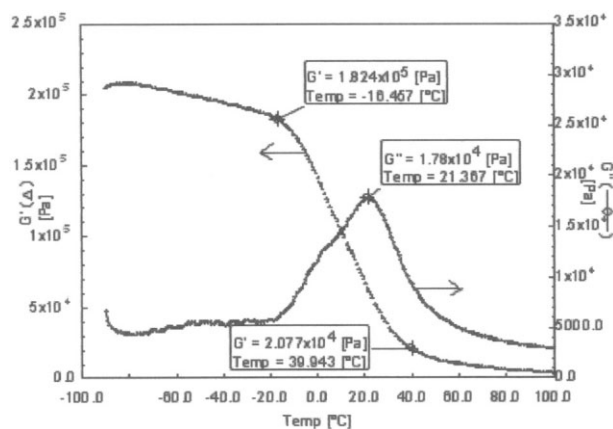


Figure 8 DMTA spectra of PUI-12 coatings.

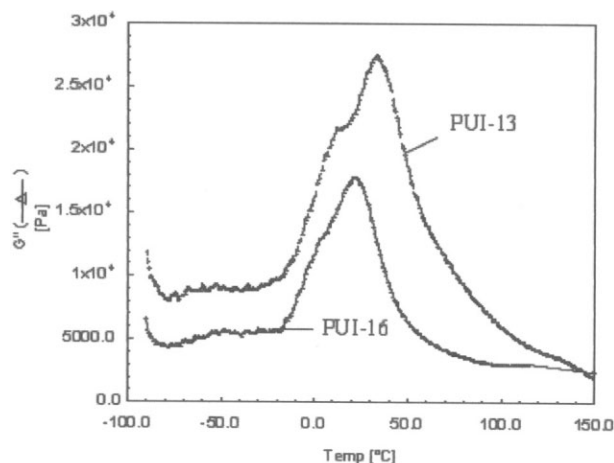


Figure 9 G'' versus temperature profile of PUI-13 and PUI-16 coatings.

of PUI-13 and PUI-16 coatings. The T_g value of PUI-12, PUI-13, and PUI-16 are 21.4, 31.1, and 21.2°C, respectively, (Table IV). This T_g could be due to the mixed phase glass transition temperature, which was rather prominent than the individual soft and hard segment T_g 's in DMTA experiments for PPG based PU-urea-imide coatings. Therefore, the trend in mixed phase T_g observed with PPG based systems closely resembles with that of PE based PU-urea-imide coatings. A comparison of G' values at the beginning and end of glass transition of PUI-8 and PUI-12 suggests that PE based coatings were hard and PPG based PU-urea-imide coatings were soft and flexible at a constant temperature (say, 25°C).

In summary, the DMTA study shows that (a) the DDS chain extended PU-urea-imide coatings were more stiff than PD chain extended coatings, (b) IPDI based coatings showed higher T_g values than the corresponding TDI based PU-urea-imide coatings, and (c) coatings prepared from PE soft segment were harder than that of PPG soft segmented PU-urea-imide coatings.

Adhesion

Interfacial adhesion plays an important role from the application point of view of the coatings since good adhesion resists delamination and protects the substrate in a better way. Therefore, it is crucial to ensure adequate adhesion between the substrate and coatings for product performance in the intended operating environment. Typically, adhesion depends on chemical interaction and mechanical interlocking at the interface. Unlike the bulk properties of the polymer that corresponds to the cohesion of polymer and are mainly determined by the coating material and its crosslink density, the interfacial features determines

by several features not directly related to the coatings involved such as the substrate nature, surface roughness, surface energy, and other specific morphology associated with the surface. Therefore, understanding the surface and interfacial properties of polymeric materials is of vital importance for predicting adequate performance in various applications. For example, the surface energies of polymeric materials determine their adhesion properties to substrates, which in turn can affect the mechanical properties and performance of composite materials. During the mechanical deformation, the possible bonding failures are: interfacial failure, which occurs along the metal:polymer interface, and the cohesive failure which occurs inside of the polymer near the metal:polymer interface.²

Now, let us analyze the obtained adhesive strength on different metals with the structural variation in the studied PU-urea-imide coatings, which is shown in Table IV. In our earlier article,³⁴ we have shown that the surface segregation behavior of PU-urea-imide coatings is due to the phase separation behavior of hard and soft segment. Because of this segregation behavior of PU-urea-imide coatings, after application on a metal, the soft segment migrate towards the polymer:air interface, whereas the more polar hard segment moves towards the metal:polymer interface. As the metal contains positive charged ions and free electron cloud, therefore the polar components easily binds with the metal ions at the interface thorough coordination bond and is partly responsible for good adhesion. Therefore, any structural components that favor a faster migration of hard segment towards the metal interface results in better adhesion. Our results show a similar kind of observations. For instance, the adhesive strength of PUI-2, PUI-3, and PUI-6 on MS disc was 59.6, 80.7, and 91.2 kg/cm², respectively. Similarly, PUI-12, PUI-13, and PUI-16 possess the adhesive strength on MS disc of 112.2, 112.2, and 87.7 kg/cm², respectively. The polar nature of DDS increases both the cohesive energy because of the increased interchain association through hydrogen bonding as well as adhesive energy due to better phase separation phenomenon, whereas PD chain extended PU-urea-imide coatings showed worse phase separation characteristic due to the presence of increased concentration of less polar urethane groups as well as methyl group in the side chain, which due to butane-gauch interaction hinder the hard segment interaction. The other observations from this study were the dependence of adhesive strength on (a) the substrate, (b) the soft segment e.g., PE and PPG, and (c) the diisocyanate used to prepare PU-urea-imide coatings. In summary, the adhesive strength values showed that (a) when the soft and hard phases are more separated, the coatings showed superior adhesive strength, (b) PU-urea-imide coatings derived from PPG (e.g., polyether based coatings) showed bet-

ter adhesive strength in comparison to PE soft segmented coatings, (c) IPDI as diisocyanate showed superior adhesive strength than TDI, and (d) adhesive strength depends on the substrate: a better adhesive strength results with MS disc. The surface sensitive nature of MS towards corrosion makes its surface with more imperfection, and hence a better adhesion. Here corrosion enhances the number of active sites for bonding with MS disc.²

CONCLUSIONS

In this work, different PU-urea-imide coatings have been synthesized by using two different methods. In one method, polyester polyol (PE) was used as soft segment, whereas the other method contains a polyether soft segment (PPG). A systematic investigation of thermal, viscoelastic and adhesive strength on various metal surfaces enables us to conclude the following observations.

- DDS chain extended PU-urea-imide coatings showed better thermal stability, high T_g and superior adhesive strength on MS, CU and Al metal substrates.
- PPG soft-segmented PU-urea-imide coatings showed single step thermal decomposition profile and possess better thermal stability upto 300°C, whereas PE containing coatings showed three-step thermal decomposition profile with an initial weight loss of around 8–10 wt % before 300°C.
- Thermal stability and the activation parameters are sensitive to the method used to analyze the sample characteristics and evaluate the thermograms.
- Adhesive strength depends on the nature of the chain extender, diisocyanate, soft segment and the substrate; say metal like MS, Cu and Al in this investigation.
- These results open up new possibilities from both practical and fundamental point of view, for the paint formulator to improve the performance and durability and to understand the important role of phase separation and morphology on the coating properties.

References

1. Keiji, I.; Handbook of Polyurethane Resins; The Nikkan Kogyo Shimmbun: Japan, 1987; Chapter 1.
2. Chattopadhyay, D. K.; Sreedhar, B.; Raju, K. V. S. N. *Ind Eng Chem Res* 2005, 44, 1772.
3. Chattopadhyay, D. K.; Sreedhar, B.; Raju, K. V. S. N. *J Appl Polym Sci* 2005, 95, 1509.
4. Chattopadhyay, D. K.; Sreedhar, B.; Raju, K. V. S. N. *J Polym Sci Part B: Polym Phys* 2006, 44, 102.
5. Sung, C. S. P.; Smith, T. W.; Sung, N. H. *Macromolecules* 1980, 13, 117.
6. Adhikari, R.; Gunatillake, P. A.; McCarthy, S. J.; Meijs, G. F. *J Appl Polym Sci* 2000, 78, 1071.
7. Wang, C. B.; Cooper, S. L. *Macromolecules* 1983, 16, 775.
8. Martin, D. J.; Meijs, G. F.; Gunatillake, P. A.; McCarthy, S. J.; Renwick, G. M. *J Appl Polym Sci* 1997, 64, 803.
9. Leung, L. M.; Koberstein, J. T. *Macromolecules* 1986, 19, 706.
10. Seymour, R. W.; Cooper, S. L. *Macromolecules* 1973, 6, 48.
11. Miller, J. A.; Lin, S. B.; Kirk, K. S.; Hwang, K. K. S.; Wu, K. S.; Gibson, P.E.; Cooper, S. L. *Macromolecules* 1985, 18, 32.
12. Fabris, H. J. *Advances in Urethane Science and Technology*; Technomic Publishing Co: Westport, 1976; p 89.
13. Kazmierczak, M. E.; Fornes, R. E.; Buchanan, D. R.; Gilbert, R. D. *J Polym Sci Part B: Polym Phys* 1989, 27, 2189.
14. Kazmierczak, M. E.; Fornes, R. E.; Buchanan, D. R.; Gilbert, R. D. *J Polym Sci Part B: Polym Phys* 1989, 27, 2173.
15. Irimina, C. C.; Jacek, L. *Macromol Mater Eng* 2002, 287, 665.
16. Moss, E. W.; Skinner, D. L. *J Cell Plast* 1978, 14, 243.
17. Zimmerman, L. R.; Austin, H. T. U. S. Pat. 4026 837 (1977).
18. Glinka, Z.; Majewska, F. *Polimery (Warsaw)* 1966, 11, 167.
19. Lubczak, J.; Chmiel, E. *Polimery (Warsaw)* 1990, 35, 194.
20. Mahesh, K. P. O.; Alagar, M.; Ananda Kumar, S. *Polym Adv Technol* 2003, 14, 137.
21. Zhu, Q. Z.; Feng, S. Y.; Zhang, C. *J Appl Polym Sci* 2003, 90, 310.
22. Smith, T. L.; Magnusson, A. B. *J Appl Polym Sci* 1961, 5, 218.
23. Consaga, J. P.; French, D. M. *J Appl Polym Sci* 1971, 15, 2941.
24. Kothandaraman, H.; Venkatarao, K.; Thanoo, B. C. *Polym J* 1989, 21, 829.
25. Kothandaraman, H.; Venkatarao, K.; Thanoo, B. C. *J Appl Polym Sci* 1990, 39, 943.
26. Kontou, E.; Spathis, G.; Niaounakis, M.; Kefalas, V. *Colloid Polym Sci* 1990, 268, 636.
27. Petrovic, Z. S.; Ilavsky, M.; Dusek, K.; Vidakovic, M.; Javni, I.; Banjanin, B. *J Appl Polym Sci* 1991, 42, 391.
28. Chang, W.; Baranowski, T.; Karalis, T. *J Appl Polym Sci* 1994, 51, 1077.
29. Krakovsky, I.; Bubennykova, Z.; Urakawa, H.; Kajiwara, K. *Polymer* 1997, 38, 3637.
30. Krakovsky, I.; Urakawa, H.; Kajiwara, K. *Polymer* 1997, 38, 3645.
31. Haska, S. B.; Bayramli, E.; Pekel, F.; Ozkar, S. *J Appl Polym Sci* 1997, 64, 2347.
32. Petrovic, Z. S.; Javni, I.; Divjakovic, V. *J Polym Sci Part B: Polym Phys* 1998, 36, 221.
33. Spirikova, M.; Matejka, L.; Hlavata, D.; Meissner, B.; Pytela, J. *J Appl Polym Sci* 2000, 77, 381.
34. Mishra, A. K.; Chattopadhyay, D. K.; Sreedhar, B.; Raju, K. V. S. N. *Prog Org Coat* 2006, 55, 231.
35. Yeganeh, H.; Shamekhi, M. A. *Polymer* 2004, 45, 359.
36. Broido, A. *J Polym Sci Part A-2: Polym Phys* 1969, 7, 1761.
37. Coats, A. W.; Redfern, J. P. *Nature* 1964, 68, 201.
38. Budrugaec, P.; Segal, E. *J Therm Anal* 1998, 53, 269.
39. Koga, N.; Tanaka, H. *J Therm Anal* 1991, 37, 347.
40. Bourbigot, S.; Delobel, R.; Le Bras, M.; Normand, D. *J Chim Phys* 1993, 90, 1909.
41. Criado, J. M.; Ortega, A. *J Therm Anal* 1984, 29, 1225.
42. Criado, J. M.; Morales, J.; Rives, V. *J Therm Anal* 1978, 14, 221.
43. Adonyi, Z.; Korosi, G. *Thermochim Acta* 1983, 60, 23.
44. Campisi, L. R.; Bourbigot, S.; Le Bras, M.; Delobel, R. *Thermochim Acta* 1996, 275, 37.
45. Rose, N.; Le Bras, M.; Bourbigot, S.; Delobel, R. *Polym Degrad Stab* 1994, 45, 45.
46. Park, J. W.; Oh, S. C.; Lee, H. P.; Yoo, K. O. *Polym Degrad Stab* 2000, 67, 535.
47. Lui, J.; Ma, D. *J Appl Polym Sci* 2002, 84, 2206.