Degradation Profiles of Polyester-Urethane (HP-MDI) and Polyester-Melamine (HP-HMMM) Coatings: A Thermal Study

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ABSTRACT: This article investigates the effect of diol structure and acetoacetylation of the hydroxylated polyesters (HPs) on thermal stability and degradation profiles of HPs/hexamethoxymethylmelamine (HMMM) as well as HPs/diphenylmethane diisocyanate (MDI) high solids coatings (HSCs) by thermogravimetry. Thermal stability of HP-MDI and HP-HMMM coatings constitute the main focus of this investigation. It is found that variations in the constituent groups to synthesize HPs and acetoacetylation of HPs are important to achieve superior performance. Results of this study indicated a good thermal stability of coatings. However, not much variation in thermal stability was observed with the structural variations in HPs. Mathematical equations of Broido, Coats-Redfern, and Chang were used to evaluate the kinetic parameters. Activation energy was found to be dependent on the kinetic methods used. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 518–526, 2005

Key words: polyesters; structure; polyester-melamine; polyurethane; coatings

INTRODUCTION

Hydroxylated polyesters (HPs) are one of the most important oligomeric precursors that are widely used to develop ecofriendly high solids coatings (HSCs). These can be crosslinked with diisocyanates and melamine, respectively, to obtain two-pack polyurethane and one-pack baking thermoset coatings. It is well known that coatings made from polyester resins provide greater durability and resistance to UV radiation than other coatings. However, the growing need to develop high performance coatings with application solids has been a challenge to coatings industries. Thus, variation of constituents during the synthesis of HP and acetoacetylation of HP are important to increase application solids. Oligomers formed can further react with the added crosslinker to meet their high performance criteria. To develop efficient HSCs, optimum degrees of cure and crosslink density are important.[1] However, crosslinking and side product formation during the curing process present a complex picture to determine their performance. Thus, the most important criterion to assess the coating performance is to study its degradation behavior. Coatings degrade due to various types of stresses, including thermal, environmental, and corrosion effects, during their service life. Studies on thermodegradative behavior of the coatings at high temperatures could provide a valuable information on the original product, its processing, and the final quality of the material formed.[2]

Considerable efforts have been made to study the thermal degradation of coatings using thermogravimetric analysis (TGA), since it analyzes the degradation response and determines the upper temperature limit of use and durability. The onset of mass loss defines the upper limit of stability, above which coatings degrade appreciably. Primarily, HSCs are thermosets and involve complex chemical structures. Thus, their thermal degradation is quite complex, involving successive and/or parallel steps, where a number of products will form, thereby affecting the degradation kinetics along with other structural, physicochemical, and instrumental parameters as well as the method of calculation.[3–8] Bourbigot et al.[9] studied the thermal degradation of fire-retarded polypropylene and found that activation energy depends on the kinetic model used. The dynamic method pro-

posed by Park et al.[10] for the nonoxidative degradation of polyethylene gave apparent activation energies and the overall reaction orders were quite different than those reported in the literature for a similar type of materials.[11–13] With polyurethanes, the type of isocyanate/polyol has a profound influence on thermal stability, because its degradation mechanism is very complicated, involving the disruption of the urethane bond at about 210°C with the formation of isocyanate and alcohol groups.[14] Comparatively, not much has been studied on melamine-based systems.[15,16] In the melamine-based systems, the initial degradation temperature of 150–200°C has been associated with the loss of alkyl chain and ether linkage. At higher temperatures, the oxidation of activated methylene of the $-N-CH_2-O-$ group could occur most likely through the formation of hydroperoxide.[17] At still higher temperatures, the crosslink scission takes place, resulting in the formation of melamine–melamine crosslinks.

In continuation of our ongoing studies[1,16,18,19] to synthesize new coatings and to study their durability, we report here the thermal stability data on diphenylmethane diisocyanate (MDI) and hexamethoxymethylmelamine (HPMMM) coatings. The effect of structural variations using diol and β-ketoester on thermal stability was investigated. TGA results on thermal degradation were used to compute the kinetic parameters using Broido,[20] Coats-Redfern,[21] and Chang[22] equations.

EXPERIMENTAL

Materials

Neopentyl glycol (NPG) and 1,4-cyclohexane dimethanol (CHDM) were purchased from Eastman Chemical Company (USA). Trimethylolpropane (TMP) was procured from Aldrich (USA), while 1,3-propane diol (PD) was purchased from Lancaster (USA); adipic acid (AA) and cellosolve acetate (CA) were obtained from s d Fine Chemicals (Mumbai). Iso-phthalic acid (IA) was procured from SISCO (Mumbai), while ethyl acetoacetate (EAA) and methyl isobutyl ketone (MIBK) were obtained from Ranbaxy (Mumbai). Hexamethoxymethylmelamine (HMMM) was supplied from ONWARD Chemicals (Mumbai), while diphenylmethane diisocyanate (polymeric MDI) was procured from ICI, Mumbai. All the chemicals were used as received; wherever necessary, they were purified and dried as per standard procedures.

Synthesis and characterization of HPs and acetoacetylated HPs

Three hydroxylated polyesters viz., HP100, HP200, and HP300 with the hydroxyl value of 240 and differ-ent diol structures were prepared by the conventional melt condensation technique. To create branching, a fixed amount of TMP was incorporated in all of the HPs and the reaction was continued until the acid value of all of the HPs was less than 5. These HPs were *trans*-esterified with EAA for acetoacetylation. The stoichiometry of HP and EAA was adjusted to acetoacetylate 30% of the available hydroxyl groups. Resultant acetoacetylated HPs were coded as HP103, HP203, and HP303.

Characterization of HPs and acetoacetylated HPs was done by gel permeation chromatography (GPC: C-R4A Chrotopac; Shimadzu, Kyoto, Japan), differential scanning calorimetry (DSC: Mettler Toledo DSC 821^e Switzerland), and Haake rotational viscometer (Germany). Polyols were dissolved in THF by taking 0.1 g/10 mL and experiments were carried out at a flow rate of 1.0 mL/min using THF as the mobile phase. Columns were calibrated with Aldrich polystyrene standards crosslinked with divinyl benzene. DSC thermograms were recorded in the temperature range of $-40°$ to 200°C with a heating rate of 10°C/min under nitrogen atmosphere at a flow rate of 30 mL/min to determine the glass transition temperatures (T_g) of the polyols.

Detailed synthetic methods and coatings properties have been reported elsewhere.[1,16,18,19] To confirm the acetoacetylation of HPs, Fourier transform infrared (FTIR: Nicolet spectrometer FTIR-740 with a wavelength resolution of 4 cm^{-1} and 64 scans) and ^{1}H, ^{13}C, and DEPT NMR (Varian-Inova-500 MHz) spectra were recorded. The recycle delay of 2 s was used for 1D NMR experiments.

Formulation of HP-MDI polyurethane coatings

The two pack clear coats of base and acetoacetylated HPs were formulated by mixing them in a stoichiometric amount of MDI with a required amount of MIBK : CA mixture (5 : 3) to get the desired application viscosity. Coatings were coded by adding MDI to their parent HP code viz., HP100-MDI. Crosslinking reaction of the active methylene group in acetoacetylated HPs with diisocyanate and melamine resin is shown in Scheme 1.

HP-HMMM melamine polyester coatings

HPs and acetoacetylated HPs were taken separately in a mixture of 7 : 3 MIBK and butyl cellosolve and mixed with HMMM (98% NV, DP 1.75, clear viscous liquid, King Industries) crosslinker in the presence of 0.5% *p*-TSA catalyst (King Industries) and viscosity was adjusted to the application level. The weight ratio of resin to HMMM was 70 : 30. Coatings formed were coded by adding M to their parent HP code viz., HP100*M*.
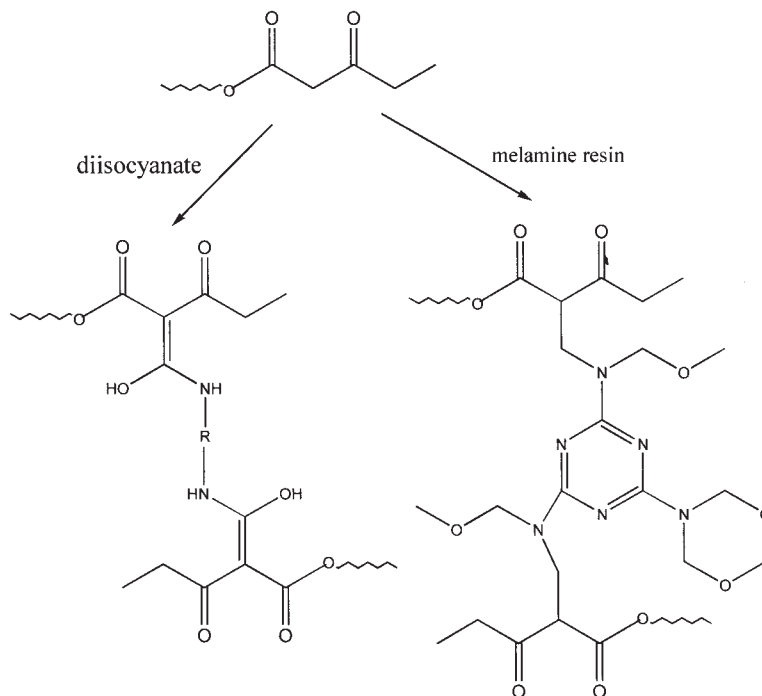
Scheme 1 Crosslinking reaction of the acetoacetate group with diisocyanates and melamine.

Preparation of free films of coatings

The HP-MDI coatings were cast on the smooth surface of a tin foil by using a power-driven automatic applicator and cured at 40°C for 48 h. Similarly, HP-HMMM coatings were cast and cured for 35 min at 140°C in an air-circulated oven. The supported coatings were placed in a clean mercury bath to amalgamate the tin substrate. The bottom of the unsupported coating was cleaned of mercury or amalgam adhering to it. Free films of thickness 60–140 μm were used for thermal stability evaluation.

Thermogravimetric analysis

Dynamic thermogravimetric analyses of all the coating films were carried out by using a Mettler Toledo TGA/SDTA 851^e thermal system controlled by a computer at a heating rate of 20°C/min under nitrogen atmosphere in the temperature range of 50–600°C. Sample weights were in the range of 9–10 mg at the nitrogen flow rate of 30 mL/min.

Kinetic analysis of thermogravimetric data

Evaluation of activation energy, E_a, from TGA data has reached increasing importance in the literature.[23,24] The normalized TG curves were used to calculate the % conversion. To study the polymer degradation, kinetic analysis of TG data from the weight loss curve is based on the kinetic equation

$$d\alpha/dt = k(1 - \alpha)^n \qquad (1)$$

where α is the fraction of the material decomposed at time t, n is the reaction order, and k is the rate constant. In TGA, the conversion is defined as the ratio of mass % loss of the sample after a certain period of time, t, to the total mass % at the beginning of the experiment such that $\alpha = (100 - w_t)/100$, where w_t is the mass % of sample at time, t. Combing eq. (1) with the Arrhenius relationship, we get

$$d\alpha/dt = Z\exp(-E_a/RT)(1 - \alpha)^n \qquad (2)$$

where Z is a preexponential factor, E_a is the activation energy of thermal decomposition, R is the molar gas constant, and T is the temperature in Kelvin. Introducing the heating rate, β, we get

$$d\alpha/dt = (Z/\beta)\exp(-E_a/RT)(1 - \alpha)^n \qquad (3)$$

Equation (3) is a fundamental expression of the analytical methods to calculate kinetic parameters using the TGA data.[25] Based on eq. (3), many methods have been developed to derive the kinetic parameters from the TG curves.

In the present work, we have used Broido,[20] Coats-Redfern,[21] and Chang[22] equations to calculate the kinetic parameters. Of these, the Briodo equation[20] has the form

TABLE I
Resin Properties of HPs and Acetoacetylated HPs

Sample code	HP100	HP200	HP300	HP103	HP203	HP303
Components	NPG, AA, IA, TMP	CHDM, AA, IA, TMP	PD, AA, IA, TMP	30% acac[a] of HP100	30% acac of HP200	30% acac of HP300
Mole ratio	4.4 : 1.65 : 1.65 : 0.7	4.4 : 1.65 : 1.65 : 0.7	4.4 : 1.65 : 1.65 : 0.7			
$\bar{M}_n$	1242	1309	1079	766	1257	585
$\bar{M}_w/\bar{M}_n$	1.54	1.18	1.69	2.21	1.26	2.05
T_g (DSC) (K)	269	239	226	246	238	232
Viscosity (η) (Pa.s) at 30°C	229.1	149.5	30.23	133.5	55.36	11.19

[a] acac*, acetoacetylation.

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

Here, $Y = (w_o - w_t)/(w_o - w_\infty)$ is the fraction of number of initial molecules not yet decomposed; w_t, w_∞, and w_o are, respectively, weights of the sample at time t, at infinite time, and the initial time. The slope of the plot of $\ln \ln(1/Y)$ versus $1/T$ gives the activation energy, E_a. The Coats-Redfern[21] equation has the form:

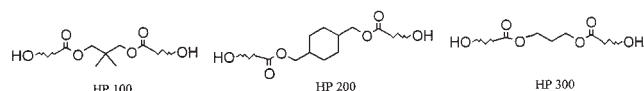$$\ln[g(\alpha)/T^2] = \ln(ZR/QE_a)[1 - 2RT/E_a] - E_a/RT \qquad (5)$$

Thus, the plot of $\ln [g(\alpha)/T^2]$ versus $1/T$ yields a straight line with a slope $= E_a/R$ for the appropriately chosen value of n. The Chang[22] equation has the form:

$$\ln[(d\alpha/dt)/(1 - \alpha)^n] = \ln Z - E_a/RT \qquad (6)$$

Thus, by plotting of $\ln[(d\alpha /dt)/(1 - \alpha)^n]$ versus $1/T$, a straight line was obtained for using accurate values of n in the linear regression analysis. The values of E_a and $\ln Z$ were obtained from the slope and intercept of the straight line, respectively.

RESULTS AND DISCUSSION

Table I compiles the results of molecular weight, polydispersity, and T_g of HPs and the corresponding acetoacetylated products. The representative structure of hydroxylated polyesters used in the present study is shown in Structure 1. Solid contents of the coatings were determined and results are reported in Table II. Higher molecular weight of HP200 compared to HP100 is attributed to higher esterification rate of CHDM than NPG. Thus, the difference in polyesterification is due to greater steric crowding of the NPG molecule. Low molecular weight of HP300 is due to concurrent sluggishness of the very low molecular weight oligomers to build up large polymer chains. Upon acetoacetylation, there is a gradual decrease in the molecular weight of HPs, probably due to breakdown and/or scrambling of polyester backbone. This type of reduction might be accompanied by the capping of polyester with ethyl alcohol coproduct from ethyl acetoacetate as reported earlier.[25] However, the polydispersity increases with increasing acetoacetylation of HPs. The effect of accetoacetylation on the coatings characteristics is shown in Scheme 2.

The FTIR spectrum of the acetoacetylated HPs showed a significant decrease in intensity between 3200 and 3600 cm^{-1} (see Fig. 1) due to the replacement of the –OH groups with an acetoacetate group as well as due to a reduction of hydrogen bonding in HPs. The ^{13}C-NMR of HPs and the corresponding acetoacetylated HPs are shown in Figure 2. In the ^{1}H-NMR spectra of HPs, the appearance of new resonance peaks at 2.3 and 3.4–3.5 δ are due to the respective methyl and methylene protons of acetoacetate moities in the acetoacetylated HPs. The splitting of resonance peak at 2.3 δ is due to the presence of methylene protons (from AA) in acetoacetylated HPs. In the acetoacetylated HPs, three new peaks appeared at 30, 50, and 200 ppm. The peak at 200 ppm indicates ketoester carbonyl, while the peaks at 50 and 30 ppm are due to ketoester methylene carbons and methyl carbons, respectively. The % application of solids (see Table II) increased with increasing acetoacetylation.

From the TG tracings, we observed (1) initial decomposition temperature (T_{id}), i.e., the temperature at which samples started decomposing, which was determined by extrapolating the steep portion of the weight loss curve and the initial base line; (2) temperature at maximum rate of weight loss (T_{max}), i.e., the temperature at which rate of degradation is maximum, which was obtained from the intersection line of the maximum peak intensity of DTG and TG curves;

Structure 1 Structure of hydroxylated polyesters used in the present study (diol variation was only shown).

TABLE II
Percent Application Solids of Coatings

Coatings	HP100-MDI	HP200-MDI	HP300-MDI	HP103-MDI	HP203-MDI	HP303-MDI	HP100-M	HP200-M	HP300-M	HP103-M	HP203-M	HP300-M
% Solids	72.0	75.7	81.0	78.2	80.5	84.6	75.2	77.1	82.5	78.5	81.3	83.3
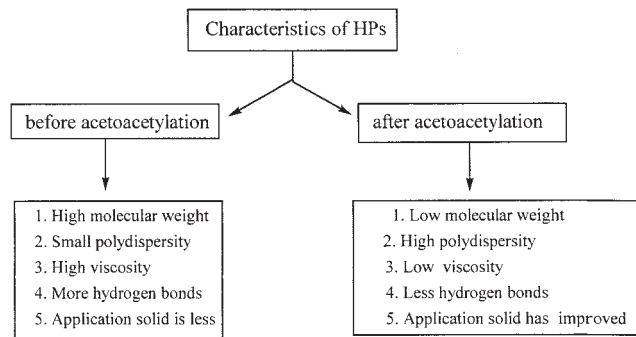
Scheme 2 Effect of accetoacetylation on the coating characteristics.

and (3) final decomposition temperature (T_{df}), i.e., the temperature at which weight loss is completed, which was obtained by the extrapolation method. The char yield values (i.e., % conversion) at 300 and 450°C are evaluated and reported in Table III for both HP-MDI and HP-HMMM coatings.

HP-MDI polyurethane coatings

Figure 3(a and b) shows TG and DTG (derivative thermogravimetry) thermograms of HP-MDI polyurethane coatings. The first thermal event occurred in the temperature interval of 120–200°C, where all of the samples showed negligible degradation as observed by weight loss due to the decomposition of urethane linkages as well as the entrapped solvent evolution in addition to volatilization of the unreacted oligomers.[14] The DTG curve shown in Figure 3(b) follows a two-step decomposition. The first stage of decomposition starts above 270°C and ends around 350–380°C, while the second step of decomposition ends above 470°C with a less carbonaceous mass. Polyurethane followed a two-step degradation profile, which depends on the type of polyols used, type of isocyanate, NCO/OH ratio, etc.[26,27] While developing polyurethane coatings, we have used the same amount of diisocyanate (MDI) by maintaining the same ratio of NCO/OH. Thus, the difference in thermogram could be attributed only due to the difference in polyol structure resulting from the structural variation of diol, acetoacetylation as well as the cooperative effect of isocyanate and polyol.

As seen in Figure 3(b), the first step of decomposition of HP200-MDI was slower while that of HP100-MDI was faster compared to HP300. The T_{id} and T_{max} values of HP200MDI are 333 and 397°C, respectively, while the corresponding values for HP100MDI and HP300MDI suggest that HP200-MDI is more stable. The slow decomposition of HP200-MDI is due to the presence of a cycloaliphatic ring in the oligoester backbone due to diol CHDM. Higher molecular weight of
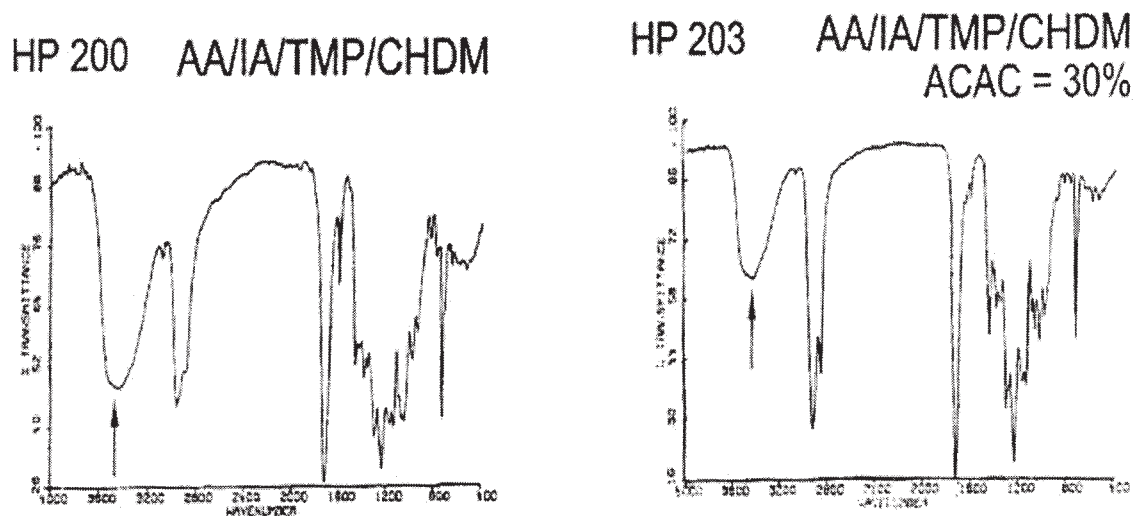
Figure 1 Representative FTIR spectra of HP-200 and the corresponding acetoacetylated HP (HP-203) showing decrease in intensity of –O–H band on acetoacetylation.
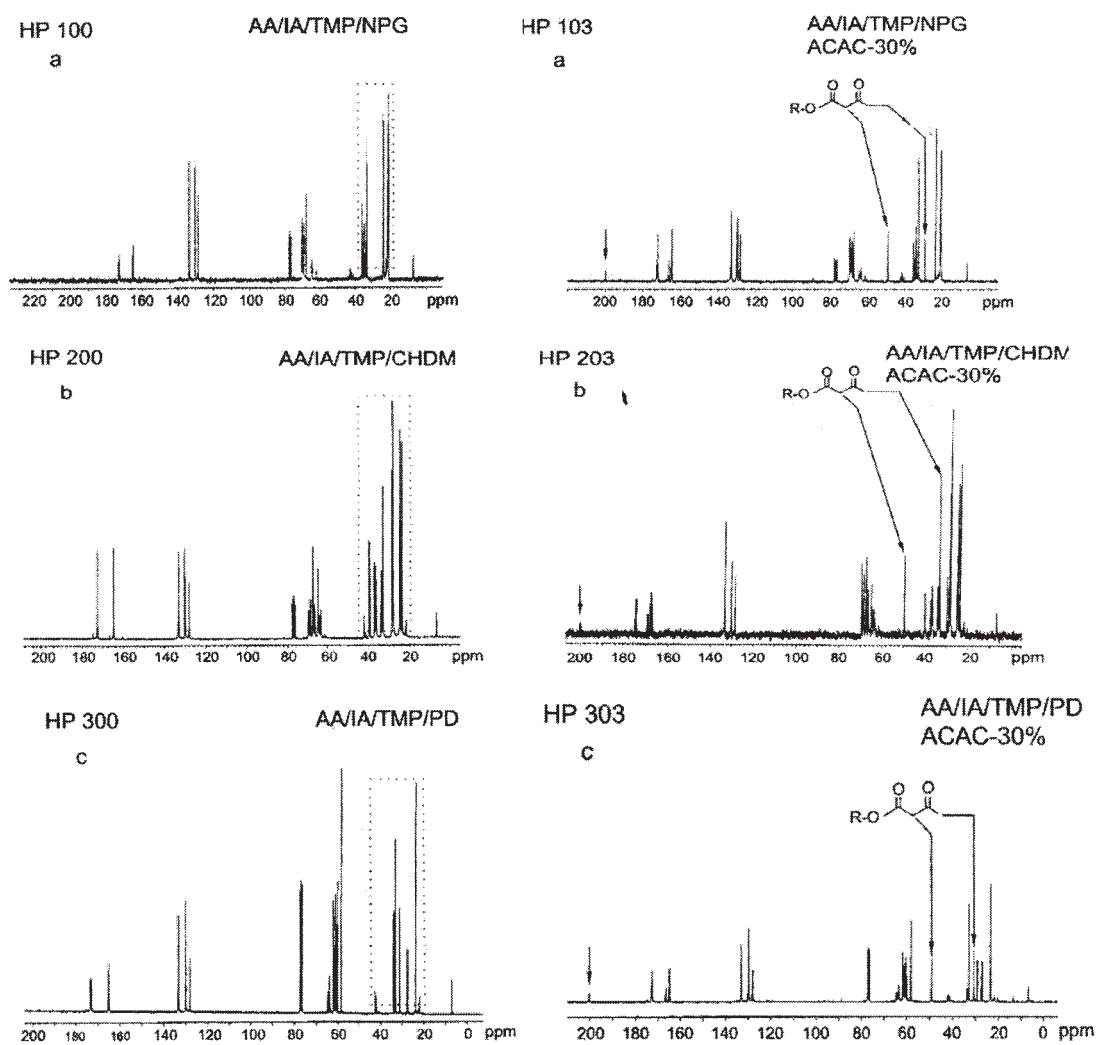

Figure 2 ^{13}C-NMR spectra of HPs and the corresponding acetoacetylated HPs.

TABLE III
Thermal Decomposition Data of HP-MDI Polyurethane and HP-HMMM Polyester-Melamine Coatings

Sample code	T_{id}	T_{max}	T_{df}	% Conversion at	
				300°C	450°C
HP100	307	367	489	9.0	70.4
HP200	333	397	469	6.8	69.5
HP300	314	359	513	6.0	64.4
HP103	337	386	542	5.2	60.0
HP203	310	394	446	8.1	69.8
HP303	327	365	520	4.4	61.4
HP100M	315	412	453	13.5	83.7
HP200M	305	415	445	13.4	85.6
HP300M	322	392	452	11.8	85.2
HP103M	321	396	472	9.4	83.6
HP203M	319	422	443	11.2	84.9
HP303M	333	379	436	9.0	82.3

HP200 could also be the reason for its greater stability. The low values of T_{id} (307°C) and T_{max} (367°C) for HP100MDI suggest its lower stability and faster decomposition due to the presence of a greater amount of methyl branching in oligoester backbone from the diol NPG, and, therefore, HP100MDI is quite susceptible to chain scission to relieve the structural crowding.

Based on the T_{id} value, thermal stability exhibits the sequence HP100 < HP300 < HP200. The % conversion values at 300°C further support that HP100MDI is the least stable among the three systems studied. While comparing acetoacetylated coatings and the corresponding unacetoacetylated coatings, the observed thermal data, T_{id}, T_{max}, T_{df}, and % conversion values at 300°C suggest that HP103 (acetoacetylated) MDI coating is more stable than HP100 (unacetoacetylated) MDI coating (see Table III). Similar trends were observed for HP300MDI and the corresponding acetoacetylated coatings. This may be due to increased crosslink density of the acetoacetylated coatings due to the presence of two active methylene protons in place of a single hydroxyl group for the crosslinking reaction to take place in HPs. Lower thermal stability of HP203MDI compared to HP200MDI may be due to the increase in polydispersity as well as a decrease in molecular weight of the corresponding polyol HP203.[16]

We have chosen the temperature range of 310 to 530°C for calculating the kinetic parameters because the maximum decomposition takes place in this zone. The activation energy, E_a, and order of degradation, n, calculated from their respective best fits (with regression coefficients > 0.99), are presented in Table IV. Lower values of E_a are associated with less stability, which signifies easy decomposition. The Broida method gave E_a values of 45.1, 58.8, and 53.7 kJ/mol, respectively, for HP100MDI, HP200MDI, and HP300MDI coatings, which suggests the stability order to follow the sequence: HP100 < HP300 < HP200. Similar observations in E_a values

were seen with the Coats-Redfern and Chang methods. However, the order of decomposition was between 2.2 to 2.8 by the Coats-Redfern method. Acetoacetylated series exhibited a higher E_a than the corresponding unacetoacetylated systems, which is due to the higher crosslink density of these coatings. The HP203MDI-based system is less stable than the HP200-MDI systems, which further supports the thermal stability patterns based on polydispersity and molecular weight of HP203. However, the differences in E_a as computed by the Broido, Coats-Redfern, and Chang equations arise because different assumptions were used to solve eq. (3). However, the preexponential factor, ln Z, calculated from Chang's equation showed very small variation, which is within the range reported for such polymers.[28]

HP-HMMM coatings

TGA and DTG thermograms of HP-HMMM coatings are shown in Figure 3(c and d). Thermal decomposition data are included in Table III. Based on the DTG thermogram, HP-HMMM melamine coatings present a complex decomposition pattern below 300°C. However, the major decomposition is one step except for the HP100M and HP103M systems. The major decomposition starts above 300°C and ends below 470°C. Several reasons could be attributed to the complex small steps observed in the DTG curves before the start of the major degradation. These could be (i) due to loss of entrapped water and solvents around 100°C, (ii) extra crosslinking with methanol evolution, (iii) melamine-melamine bond formation, (iv) unreacted oligomer evaporation around 150–180°C, and (v) formation of the volatile byproducts due to random scission of some of the bulky constituents above 180°C, but below the major step of degradation.[1]

The most pronounced effect of the use of different diol structures in HP backbone can be seen from the difference in degradation steps of HP-HMMM coatings. The two-step decomposition of HP100M and HP103M in comparison to other melamine crosslinked systems could be due to the use of NPG diol in the HP backbone. This may be attributed to the side or branch chain scissioning of the bulky methyl groups and the steric factors associated with the corresponding HP-HMMM structure. From an interpretation of T_{id}, T_{max}, T_{df}, and % conversion results at 300 and 450°C of melamine-based systems, it is difficult to identify the most and least stable systems to infer about the stability order in conjunction with the structure–property relationship in the original coatings films. The extra crosslinking beyond 140°C (i.e., cure temperature for developing HP-HMMM coatings) will result in a more complex and complicated degradation mechanism of these systems than the isocyanate-based systems. However, we have compared the effect of structural variations on the thermal stability of these systems by
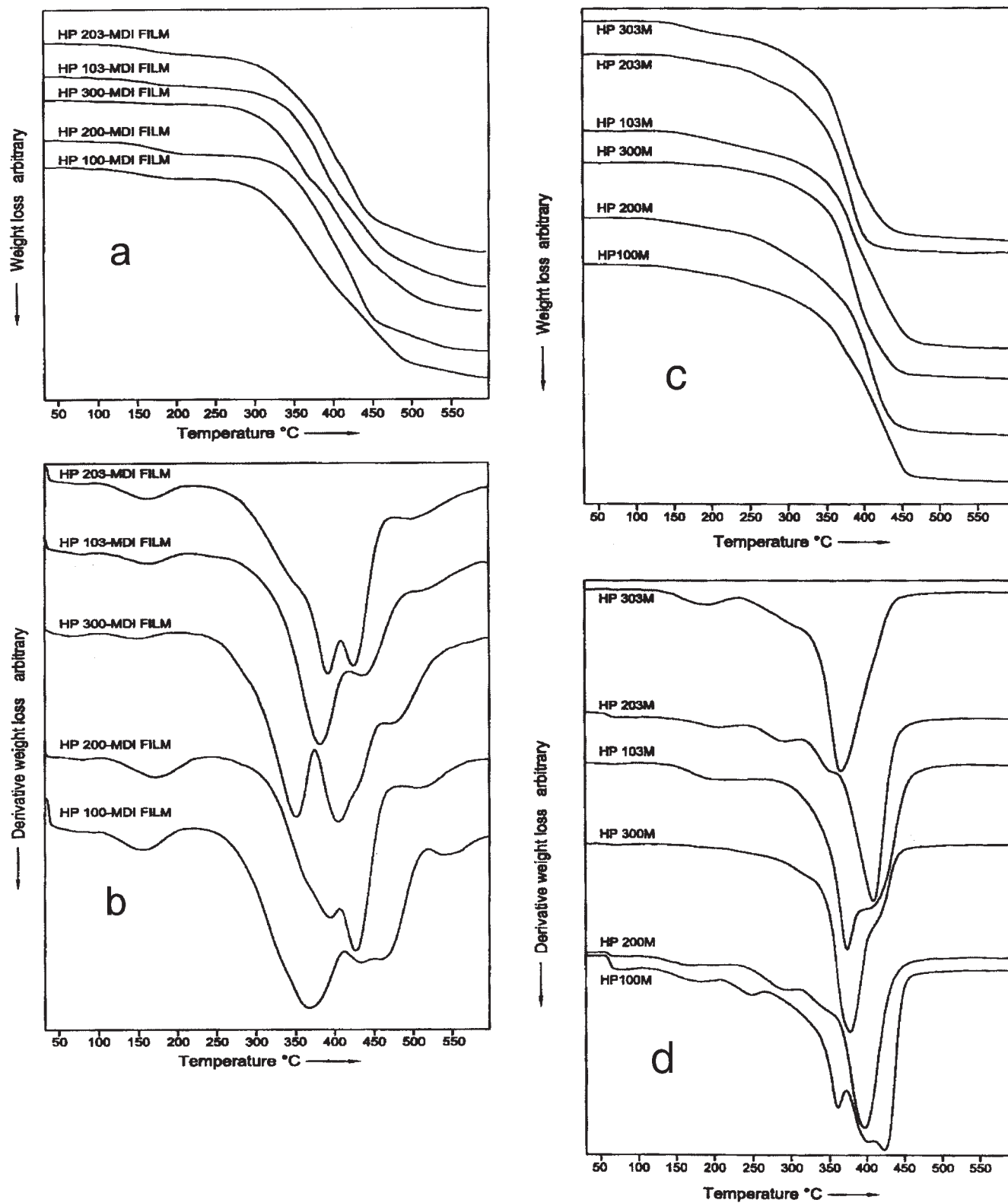
Figure 3 Representative TG and DTG thermograms of HP-MDI polyurethane coatings (a and b) and HP-HMMM coating films (c and d).

comparing their % conversion at 300 and 450°C. Based on the combined analysis, thermal stability has the sequence: HP103M > HP100M, HP203M > HP200M and HP303M > HP300M. From the onset decomposition temperature, T_{id}, we conclude that these coatings can be used up to 300°C.

TABLE IV
Kinetic Parameters for Thermal Degradation of HP-MDI Polyurethane and HP-HMMM Polyester Melamine Coatings

Sample code	Broida	Coats-Redfern		Chang		
	E_a (kJ/mol)	E_a (kJ/mol)	n	E_a (kJ/mol)	$\ln Z$ (min^{-1})	n
HP100	45.1	91.7	2.5	101.6	33.4	2.2
HP200	58.8	95.4	2.5	110.6	29.77	3.0
HP300	53.7	94.7	2.2	105.9	25.55	2.0
HP103	56.0	103.5	2.3	105.8	30.44	2.0
HP203	51.3	88.1	2.7	94.9	27.21	2.3
HP303	57.0	106.3	2.8	109.0	27.95	2.6
HP100M	61.3	62.8	2.2	83.7	22.7	2.1
HP200M	83.3	74.8	2.1	101.1	32.2	2.6
HP300M	64.5	65.4	2.0	93.6	28.8	2.7
HP103M	67.2	63.4	2.1	105.6	22.6	1.9
HP203M	88.7	79.4	2.5	113.4	33.7	3.0
HP303M	69.5	68.8	2.0	107.6	23.4	2.7

Kinetic parameters calculated from different equations are given in Table IV. It is obvious that HP300M is more stable, while HP100M is the least stable. The order of degradation by Coats-Redfern equation is around 2.0 to 2.8, whereas Chang's method gave the value in the range 2.0 to 3.0. The range of ln Z values given in Table IV are in good agreement with the reported data[28] for other polymers studied in the same temperature range. The % conversion (at 300 and at 450°C) data of HP-MDI coatings (see Table III) and HP-HMMM coatings suggests that HP-MDI coatings are more stable than HP-HMMM coatings.

CONCLUSIONS

Hydroxylated polyesters with varying diol structures were prepared, partially acetoacetylated, and characterized by FTIR, 1D NMR spectroscopy, viscosity, and solid contents to study the effect of diol structure and acetoacetylation. Considerable improvement in the solids content was achieved after acetoacetylation of HPs. Corresponding isocyanate and melamine coatings were formulated and their thermal degradation patterns were investigated. Thermal decomposition and kinetic parameters indicated higher thermal stability of HP200, if a comparison is made on the basis of diol structure. Upon acetoacetylation, thermal stability was found to increase further.

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