JOURNAL OF MATERIALS SCIENCE **37** (2002) 4911–4918

# Cure, viscoelastic and mechanical properties of hydroxylated polyester melamine high solids coatings

RAMANUJ NARAYAN*, D. K. CHATTOPADHYAY*,
B. SREEDHAR‡, K. V. S. N. RAJU*, §
**Organic Coatings and Polymers Division and ‡Inorganic Chemistry Division,*
*Indian Institute of Chemical Technology, Hyderabad-500 007, India*
*E-mail: kvsnraju@iict.ap.nic.in*

This paper presents the effects of diol structure and acetoacetylation on cure, viscoelastic and mechanical properties of hydroxylated polyesters (HPS)/ hexamethoxymethylmelamine (HMMM) clear coatings. Acetoacetylation of HPs is a potential tool for researchers to get the equivalent or superior performance at higher application solids than their base counterpart. Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analyzer (DMTA) and Thermo Gravimetric Analysis (TGA) have been utilized to study the cure, cure and viscoelastic behavior and thermal stability of the coatings respectively. The crosslink density (XLD) and elastically effective chain length between crosslinks ($M_c$) of the coating films has also been determined. Furthermore, the mechanical film properties such as tensile properties, adhesion strength and hardness were measured and related to chemical composition. The results indicate that the combined analysis helps in correlating the structure property relationship with end use properties. © *2002 Kluwer Academic Publishers*

## 1. Introduction

Considerable effort has been made in recent years to understand the network structure and viscoelastic behavior of coatings and their relationship to conventional empirical paint tests. The understanding of viscoelastic properties of coatings enables coating performance to be more readily interpreted in structural and molecular terms. Molecular properties such as monomer types, copolymer character, composition, sequence length and sequence distribution, crosslink density and network arrangement are among the features that can influence the viscoelastic behavior of coatings. The various physical and mechanical coating properties such as hardness, flexibility, tensile strength, elongation, impact and abrasion resistance are interrelated and dependent upon the basic material properties, the visco-elastic behavior [1–4].

Billmeyer [5] and Blank [6] have explained the importance of structure property relationship in coatings and shown how structural variations in polymeric parts can affect the properties of coatings. Study of cure behavior i.e., transformation of a liquid coating to viscoelastic material and the evaluation of viscoelastic properties of crosslinked films are the two approaches generally adopted for determining the structure property relationships of coatings. The importance of cure characterization and structure property relationships of coatings has been explained by Provder [7] and Hill [8] respectively in their pioneering J. Mattiello Memorial Lectures.

Determination of cure conditions is the prime prerequisite for developing successful baked coatings because the ultimate properties of coatings depend on it. Over the years the assessment of cure has been done by using coating tests such as flexibility, hardness and solvent resistance and by using various instrumental techniques such as attenuated total reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) to study the conversion of functional groups, Differential Scanning Calorimetry (DSC) to study the cure kinetics and also conversion of reactive groups, and Dynamic Mechanical Analyzer (DMA) to study the changes in physical properties [7–9]. To understand the viscoelastic behavior the determination of dynamic mechanical properties is essential. Several techniques [10] have been used to determine the dynamic mechanical properties of coating films of which DMTA is one. The interpretations and application of dynamic data provide an insight on network structure, which can be utilized to calculate crosslink density (XLD), elastically effective chain length between crosslinks ($M_c$) and the glass transition temperature ($T_g$) of the crosslinked resin.

### 1.1. High solids coatings (HSCs)

HSCs currently in use in the eco-friendly protective coating sector are typically thermosets. HSCs contain

---

[§] Author to whom all correspondence should be addressed.

a mixture of resins or oligomers and crosslinkers that have mutually reactive functional groups and derive most of their physical and chemical properties from the formation of a highly crosslinked three-dimensional networks [11]. Hydroxylated polyesters (HPs) [12–14] form one of the most widely used oligomer types for HSCs. The extensive use of HPs is basically due to potentially wide variations in compositions, which results in quite different properties and performance. This is partially accomplished by incorporating a mixture of di-, tri- or multifunctional alcohols (polyols) into HPs in combination with different dibasic acids. One of the problems associated with HPs is their high initial viscosity due to hydrogen bonding or auto-associative effect. Several workers [15–18] have explained the application of acetoacetyl chemistry for coating formulators. The replacement of the hydroxyl group with the less polar acetoacetate groups leads to an increase in solid content at the application viscosity as well as increase in adhesion due to chelate effect. To get the ultimate coating properties the selection of crosslinker is also very important. Among the different melamine crosslinkers, hexamethoxymethylmelamine (HMMM) is widespread in HSCs due to its monomeric nature which will give more solid content at the application viscosity, good compatibility, faster cure, better hardness and film properties. Film properties of the coatings using acetoacetylated resins with melamine crosslinker are reported to be comparable or superior to those made from hydroxy functional resins with improved adhesion and also the presence of both hydroxy-melamine and acetoacetyl melamine crosslinks provides better chemical resistance [19]. However, there is no detailed report on its cure and viscoelastic behaviour.

The aim of the present work is to study and compare the viscoelastic and mechanical behaviour of HP/HMMM and acetoacetylated HP/HMMM clear coatings. The effect of diol structure variation in HPs backbone and acetoacetylation of pendant hydroxyl group on the coating properties has been reported.

## 2. Experimental

### 2.1. Materials

Neopentyl glycol (NPG) and 1,4 cyclohexane dimethanol (CHDM) from Eastman Chemical Company (USA), trimethylolpropane (TMP) from Aldrich (USA), 1,3 propane diol (PD) from Lancaster (USA), adipic acid (AA) from SD Fine Chemicals (Mumbai), iso-phthalic acid (IA) from SISCO (Mumbai) and ethylacetoacetate (EAA) from Ranbaxy (Mumbai) and hexamethoxy methylmelamine (HMMM) from ONWARD Chemicals (Mumbai) were used.

### 2.2. Synthesis of HPs and acetoacetylated HPs

Three hydroxylated Polyesters HP100, HP200 and HP300 of theoretical hydroxyl value of 240 and with different diol structures were synthesized by conventional melt condensation technique [20]. In order to make branching small fixed amount of TMP was incorporated in all HPs. The reaction was continued until the acid value of all HPs became less than 5. These HPs were transacetoacetylated [16] with stoichiometric amount of ethyl acetoacetate (EAA) to acetoacetylate 30% of available hydroxyl groups and the resultant acetoacetylated HPs were coded as HP103, HP203 and HP303. The characterizations of HPs were performed by gel permeation chromatography (GPC), DSC, Haake rotational viscometer and Infrared Spectrophotometer as reported in our earlier publication [13, 21, 22]. The components and some of the resin properties are reported in Table I.

### 2.3. Formulation of coatings

HPs and acetoacetylated HPs were taken individually in a blend of 7 : 3 methyl ethyl ketone, butyl cellosolve and mixed with HMMM (98% NV, DP 1.75, clear viscous liquid) crosslinker in presence of 0.5% p-TSA catalyst and the viscosity was adjusted to the application viscosity. The weight ratio of resin vs. HMMM used was 70:30. This material was used for DMTA and DSC to determine the cure conditions. The coatings were named by adding letter M in the HPs code e.g., HP100M etc.

### *2.3.1. Preparation of free film of coatings*

The coatings were cast on smooth surface of tin foil by using a power driven automatic applicator and cured for 35 minutes at 140°C in an air-circulated oven. The supported coatings were placed in a clean mercury bath to amalgamate the tin substrate. The underside of the unsupported coating was cleaned of mercury or amalgam adhering to it [23]. The free films were used for thermal, tensile and dynamic mechanical measurements.

### *2.3.2. Preparation of test specimen*

The methods used for the surface preparation and application of coatings on mild steel tin panels (150 × 100 × 2 mm) was done according to standard procedure [24] and they were used for evaluation of scratch hardness and MEK rub resistance properties. For conducting adhesion strength analysis, mild steel discs (25 mm diameter, 2 mm thick) were coated by

TABLE I Resin properties of HPs and acetoacetylated HPs

| Code | HP100 | HP200 | HP300 | HP103 | HP203 | HP303 |
|---|---|---|---|---|---|---|
| Component | AA, IA, TMP | AA, IA, TMP | AA, IA, TMP | 30% acac[a] of HP100 | 30% acac[a] of HP200 | 30% acac[a] of HP300 |
| Diol | NPG | CHDM | PD | | | |
| $T_g$(°K) (DSC) | 269 | 239 | 226 | 246 | 238 | 232 |
| Viscosity (Pa.s) 30°C | 229.1 | 149.5 | 30.23 | 133.5 | 55.36 | 11.19 |

[a] acac - Acetoacetylation.

using a spin coater. All these panels were cured at 140°C for 35 min in an air-circulating oven.

## 2.4. Test procedures

### 2.4.1. Adhesion, scratch hardness and flexibility

The adhesion strength of coatings was determined by the pull-off test (Microtech Tensiometer). The scratch hardness of coatings was determined by using a powered automatic scratch tester (Erichson 601, Germany) and flexibility was assessed by the conical mandrel bend test (Sheen Instruments, UK).

### 2.4.2. Tensile properties

Tensile properties of the free films of coatings were measured by Universal Testing Machine (UTM) AGS-10k NG (Shimadzu, Japan). The test specimens were in the form of dumbbells according to ASTM D-638. The gauge length was 50 mm and crosshead speed of 10 mm/min. The data reported are the average of five measurements.

### 2.4.3. Determination of cure conditions

*2.4.3.1. DMTA.* The use of filter paper as inert support for studying the cure conditions has been described by Skrovanek [25]. The paper serves as an excellent substrate for the wet coating because it supports the liquid coating well, is inert, inexpensive and does not undergo any physical changes at temperatures up to 250°C. A thin layer of uncured coatings was applied on desiccated ashless filter paper and was allowed to air dry at ambient temperature to tackiness. The coated paper was then placed horizontally in a dual cantilever-bending beam clamping geometry of the DMTA-IV (Rheometric Scientific, UK). The modulus ($E'$) and energy dissipation (tan $\delta$) of all samples were measured at a frequency of 1 Hz, 0.9 percent minimum strain and heating rate of 3°C per minute. Samples were scanned from 30°C to 180°C and isothermally at 140°C for 1 hour. The minimum strain has been fixed corresponding to a deformation equal to the sample thickness by running the dynamic strain sweep experiment of DMTA. The storage modulus, $E'$, is utilized to assess the cure of coatings.

*2.4.3.2. DSC.* About 10 mg of samples were placed in the aluminium pan, sealed properly and were scanned from room temperature to 200°C at a heating rate of 10°C per minute and isothermally at 140°C under nitrogen atmosphere.

### 2.4.4. Viscoelastic properties

The viscoelastic or dynamic mechanical properties of cured coating films ($15 \times 10 \times 0.5$ mm) were determined by using DMTA IV. DMTA instrument measures the deformation of a material in response to vibrational forces. In principle, DMTA techniques detect the viscoelastic behaviour of polymeric materials and yield quantitative results for the tensile storage moduli $E'$ and the corresponding loss moduli $E''$, the loss factor tan $\delta$ as the quotient of loss and storage, $E''/E'$. $E'$ and $E''$ characterise the elastic and viscous components of a viscoelastic material under deformation.

The DMTA spectra of films were recorded in tensile mode in the temperature range of 30°C to 200°C at a frequency of 1 Hz, 0.2 percent strain and with heating rate of 3°C/min. The frequency of 1 Hz and strain of 0.2 percent has been selected by running frequency and strain sweep experiments of DMTA on the free films of coatings.

### 2.4.5. Thermal stability

The thermal stability of coating films was studied using METTLER TOLEDO STAR SYSTEM thermal analyzer. The films were cut into small pieces and about 4–10 mg of sample was taken and heated at a constant rate of 20°C/min in nitrogen from 25°C to 600°C.

## 3. Results and discussion

The main aim of this paper is to understand with reasonable precision how the resin structure governs the film properties of baked coatings. Several workers have reported on this aspect to correlate the chemical structure with performance of higher solids coatings despite the limitation caused by the complexity of resin structure used in the coating formulations. Generally monomer mixtures containing more than two monomers are in use for polymerization to elicit desired coating properties, which is the cause for complexity of understanding resin structure and the nature of linkages present. Jones and co-workers [26] have described the film properties of polyester/melamine enamels made by using symmetric and asymmetric diols in a nearly mono-dispersed oligoester and shown that the oligoester structure is a sensitive indicator for both basic and empirical film properties along with bake conditions and formulation. Researchers such as Golob [27], Duncan [28], Shoemaker [29], and Hood [30] and their co-workers have also carried out similar types of studies. The structure of the diols used for comparing the film properties in the present study are shown in Fig. 1. We tried to maintain the same mole ratio and reaction condition for comparison purposes.

The other aspect of our study is to study the effect of acetoacetylation on the HPs backbone and their coating properties. The effect of diol structure variation and acetoacetylation on the molecular weight, glass transition temperature and viscosity was reported in our earlier publications [13, 21, 22] and, encouraged with the results of the overall superior performance of isocyanate coatings based on 30% acetoacetylation at higher application solids, we have chosen this study for evaluation. We have maintained the same ratio of HMMM

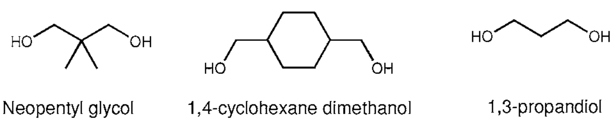


*Figure 1* Structure of diols used in the present study.

crosslinker with all the HPs and acetoacetylated HPs resin and the same catalyst concentration so as to compare its performance.

## 3.1. Determination of cure conditions

Curing of thermosetting materials generally involves the transformation of low molecular weight amorphous solid by chemical reactions. The cure process involving melamine crosslinker is a complex process, so to assess the cure and optimizing the cure conditions is necessary for attaining good coating properties. Melamines are used in thermoset coatings to chemically link the molecules of the primary film former into a three dimensional network which is accomplished through reacting the melamine with functional groups on the film former and simultaneous self condensation with other melamine [6]. With increasing crosslink density, hardness, toughness and solvent resistance increase. Blank has explained the reactions of —OH functional resins with melamine [31]. Two of the major cure reactions involving hydroxyl group and acetoacetyl group in the presence of an acid catalyst of the present system under study are shown in Fig. 2.

We have used both DSC and DMTA to optimize the cure conditions of coatings. Fig. 3 is a representative DSC cure thermogram of coating formulation of HP100M and HP103M and the isothermal thermogram at 140°C of one of the HP100M coatings is shown as inset. Usually cure reactions result in a sharp exothermic peak in the DSC temperature scan and we have also experienced sharp exothermic peaks while working on isocyanate polyester coatings [32] but as shown in Fig. 3 this is not the case with the present system under study. This is attributed to the complexity of reactions involved during cure as well as to the presence of solvents, partially volatile oligomer etc. In this type of complex coating mixture, endothermic processes compete with exothermic cure reactions, resulting in ambiguous DSC information [33] but still it can be used as an advantage in determining the cure conditions. Solvents and other volatile matter present consume the heat of cure reaction at low temperature for their evaporation. As shown in Fig. 3 the exothermic zone appears at around 100°C for HP100M while at 115°C for HP103M, which may be regarded as an onset of cure for these coatings. The maximum is attained in the range of 130–160°C and any temperature in this range may be taken as a satisfactory cure temperature based on the isothermal DSC thermogram in this temperature range. Indeed we have carried out several isothermal experiments and found that 140°C is the ideal temperature for cure. The acetoacetylated HP based coatings takes 5 minutes more time to cure as compared to HP based coatings. Similar experiments were carried out on all the other coating systems.

As mentioned in Section 2.4.3 we have carried out cure experiments on paper supported coating specimens. The cure studies were carried out from 30°C to 180°C and isothermally at selected temperatures. The representative DMTA cure spectrums are shown in Fig. 4a and b. The storage modulus, $E'$, which in this case is essentially a measure of the rigidity of coating/substrate composite is utilized to assess the cure of coatings for desired properties. As shown in Fig. 4a there was little effect on the value of $E'$ up to the temperature of 100°C and the modulus starts to increase sharply at this temperature, and at temperatures of around 140°C $E'$ entered into a plateau region. The increase in modulus is indicative of molecular weight build up of coatings due to crosslinking and this result suggests that the curing starts at around 100°C. Skrovanek [25] and Provder and coworkers [7] have

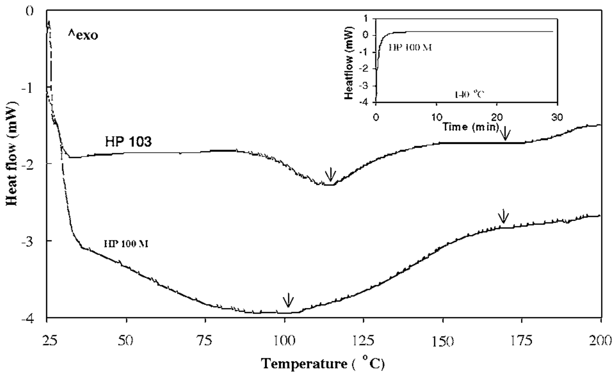
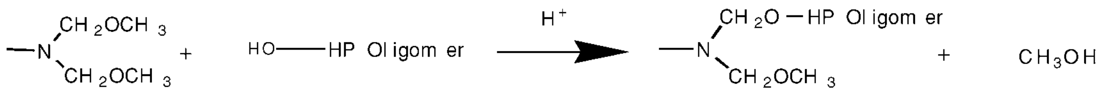


*Figure 3* DSC cure thermogram of HP 100 M and HP 103 M coatings.

**Hydroxyl Reaction :**



**Acetoacetyl Reaction :**

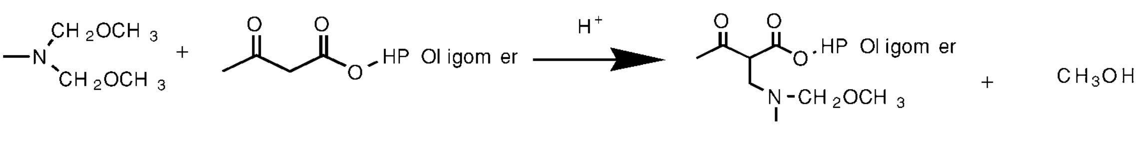
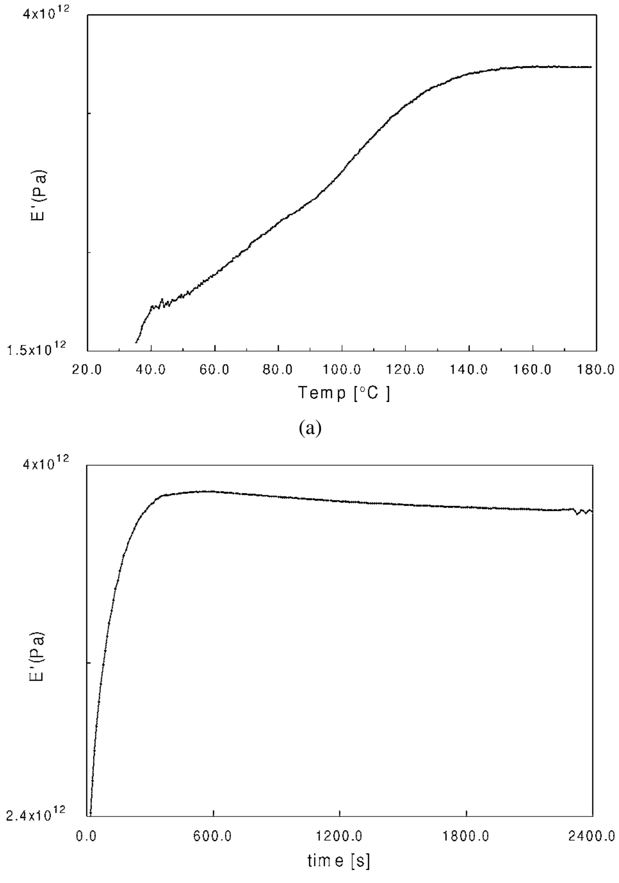


*Figure 2* Hydroxyl and acetoacetyl group reaction with melamine.



(a)

(b)

*Figure 4* (a) DMTA cure spectrum of HP200M coatings. (b) DMTA isothermal cure spectrum at 140°C of HP200M coatimgs.

obtained similar results for various coating systems by following the modulus as a function of temperature with dynamic mechanical analysis (DMA).

After this we have carried out several isothermal experiments to assess the time of cure of coatings and found that 140°C is the ideal temperature of cure and coatings attain the plateau region within 10 minutes and take a maximum of 30 minutes to attain maximum $E'$. As can be seen in Fig. 4b initially there was only a slight increase in the value of $E'$, suggesting that at these early stages of cure the molecular weight increase was rather modest as would be expected when relatively low molecular weights are joined together. The $E'$ increase reached a nearly terminal value as the cure reactions were essentially completed. The selection of 140°C as cure temperature was reconfirmed by performing MEK double rub test ($>180$) on coating film cast at different temperatures and times.

On the combined analysis of DMTA and DSC results and also with MEK double rub test we have optimized the cure conditions as 140°C and 30 minutes for all the coating systems under study.

## 3.2. Viscoelastic properties

As our aim was to evaluate the influence of the structural variation on the dynamic mechanical properties, we have maintained the same conditions (140°C, 30 min) of cure for all the coatings and also maintained the same resin and HMMM ratio.

### 3.2.1. Effect of diol structure and acetoacetylation on $E'$

The tensile storage modulus $E'$ is a measure of the stiffness of a material and the value of $E'$ at room temperature is regarded as a measure of hardness for coating materials [34]. The room temperature $E'$ values taken from the spread sheet of DMTA spectra are reported in Table II and one of the representative log $E'$ vs. temperature plots is shown in Fig. 5a. The $E'$ values as reported in Table II are found to be well within the range of $E'$ values ($10^4$ to $10^{10}$ Pa.) generally encountered for the films in coating research [8]. Usually hard materials have modulus of $10^9$ to $10^{10}$ Pa. and rubbery materials of $10^6$ Pa. This comparison indicates the good mechanical integrity of the coating films under study. The diol structure variation has resulted in different modulus values for coating films as shown in Fig. 5a and surprisingly the room temperature modulus value of the HP 300M coating was found to be higher than other coatings under study while on acetoacetylation HP103 the coating based on NPG diol was found to have a higher modulus value. This signifies the anomalous behaviour of thermoset coating films.

### 3.2.2. Effect of diol structure and acetoacetylation on $T_g$

Roller [35] has explained the use of dynamic mechanical properties of coatings for the determination of $T_g$. The glass transition temperature ($T_g$) taken at tan $\delta_{max}$ is reported in Table II [1]. The tan $\delta$ vs. $T$ plot is useful not only for determining the $T_g$ but the nature, shape, height and breadth of curve provides valuable information to the coating formulators. The breadth and height of the tan $\delta$ curve can be used to interpret the crosslink density and flexibility of coatings qualitatively. As reported in Table II and shown in Fig. 5b the variation in diol structure has resulted in different $T_g$ values of coatings and follows the order HP300M<HP100M<HP200M and again on acetoacetylation there is a slight increase in $T_g$ of coatings with the exception of HP303M. Based on tan $\delta_{max}$ values (Table II) or the height of the tan $\delta$ peak, HP200M coatings are expected to have higher crosslink density based on diol structure while HP203M and HP303M on the basis of acetoacetylation. The breadth of the tan $\delta$ peak shows uniform crosslinking

TABLE II $E'$ and $T_g$ of cured coatings films

| Coating | HP100M | HP200M | HP300M | HP103M | HP203M | HP303M |
|---|---|---|---|---|---|---|
| $10^{-8} \times E'_{max}$, (Pa.), 30°C | 2.788 | 2.014 | 5.246 | 6.476 | 1.381 | 1.37 |
| $T_g$ (K) | 335 | 353 | 327 | 336 | 358 | 320 |
| tan $\delta_{max}$ | 0.379 | 0.329 | 0.355 | 0.327 | 0.280 | 0.254 |

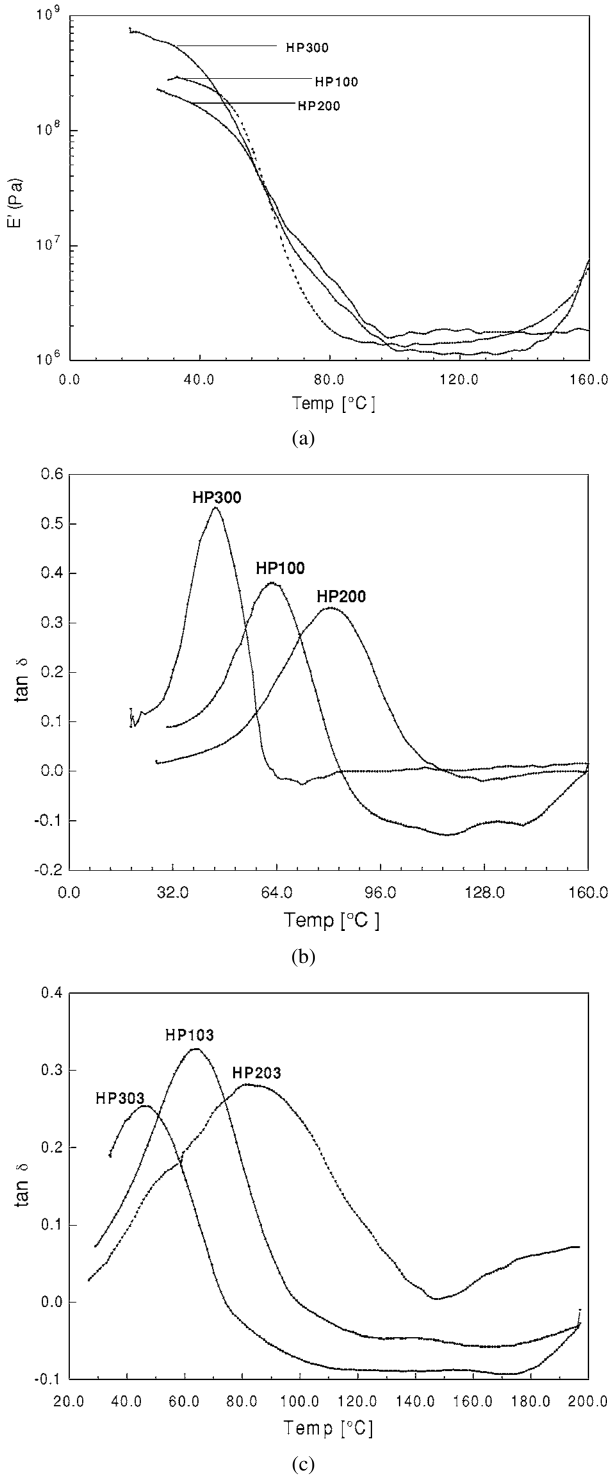


*Figure 5* (a) log $E'$ vs temperature DMTA spectrum of coating films. (b) and (c) tan $\delta$ vs. temperature plot of coating films.

in HP300M and HP303M coatings, which may be due to use of straight chain diol PD in these coatings.

The explanation for the $T_g$ variation is a difficult task because the $T_g$ of crosslinked polymers depends on the structure of the segments between crosslinks, the crosslink density and network defects, free volume as well as on the composition of the coatings [35, 36]. An approximate explanation for the present study may be that the inter-chain stiffness caused by the rigid structure of CHDM helps raise the value of $T_g$ along with other intermolecular forces. The anomalous behaviour indicates that the self-condensation of the melamine resin may be the cause for enhancement in the properties of HP300M and HP303M coatings.

### *3.2.3. Determination of XLD and $M_c$*

The methods for the determination or estimation of crosslink density of thermoset coatings include MEK double rub tests, swelling and determination of the modulus at temperatures well above the $T_g$ of coatings [37]. The modulus measurements provide the most direct relationship to crosslink density, provided that the cure temperature lies well above the $T_g$ for complete conversion of functional groups, $T_{g\infty}$ [38]. The modulus value from DMTA measurements can be utilized for the calculation of crosslink density (XLD), $v_e$, the number of moles of elastically effective network chains per cubic meter of sample and $M_c$, the elastically effective chain length between crosslinks by using the kinetic theory of rubber elasticity [8] and by utilising Equations 1 and 2:

$$v_e = E'/3RT \tag{1}$$

where, $R$ is the universal gas constant and $T$ is temperature ($T > T_g$).

$$M_c = \rho/v_e \tag{2}$$

where, $\rho$ is the density (kg/m$^3$) of coating films.

The values of $v_e$ and $M_c$ of the coating films under study were calculated by using Equations 1 and 2 and reported in Table III. For calculation the $E'$ values at temperature above the glass transition (Table III) were taken from the spreadsheet view of the DMTA spectrum and $\rho$ values were determined experimentally by displacement (found to be in the range of 1010–1110 kg/m$^3$ for all of the coating films).

The data as shown in Table III indicate that the coatings HP200M and HP203M have more tighter and tougher networks than the other coatings while HP300 is more flexible. Based on diol structure, the order of crosslink density is HP300<HP100<HP200 while on acetoacetylation there is a uniform increase in crosslink density as compared to unacetoacetylated counterparts. Generally, the higher the crosslink density, the lower the elastically effective chain length ($M_c$) and the harder the film, whereas flexibility is best in non-crosslinked resins.

## 3.3. Adhesion, tensile, hardness, flexibility and MEK rub of coatings

The results of adhesion, tensile, hardness flexibility, MEK double rub resistance are reported in Table IV.

The adhesion strength values of coatings follow the order HP300<HP200<HP100 while tensile strength values follow the order HP300<HP100<HP200. The scratch hardness of the coatings followed the same order as that of the tensile data. All these properties were found to increase on acetoacetylation as shown in Table IV. All the clear coats were found to pass the mandrel test of flexibility. The MEK rub test and determination of crosslink density are usually implied to

TABLE III Crosslink density and $M_c$ values of coating films

| Coating/Property | HP100M | HP200M | HP300M | HP103M | HP203M | HP303M |
|---|---|---|---|---|---|---|
| $10^{-7} \times E'_{\text{min}}$ (Pa.), $>T_g$ | 1.628 | 1.642 | 1.209 | 1.713 | 1.925 | 1.237 |
| $10^{-3} \times \upsilon_e$ (mol/m$^3$) | 1.94 | 1.95 | 1.43 | 2.02 | 2.32 | 1.53 |
| $10^3 \times M_c$ (kg/mol) | 562 | 564 | 722 | 514 | 470 | 660 |

TABLE IV Adhesion, tensile, hardness, flexibility and MEK rub of coatings

| Coating/Properties | HP100M | HP200M | HP300M | HP103M | HP203M | HP303M |
|---|---|---|---|---|---|---|
| $10^{-5} \times$ Adhesion strength (N/m$^2$) | 137.6 | 128.5 | 118.2 | 183 | 171 | 154.9 |
| $10^{-5} \times$ Tensile strength (N/m$^2$) | 105 | 122.8 | 60.4 | 139.1 | 159.6 | 47.2 |
| Scratch hardness (kg) | 0.82 | 0.94 | 0.50 | 1.03 | 1.12 | 0.55 |
| Flexibility (1.6 mm) Con. mandrel | Pass | Pass | Pass | Pass | Pass | Pass |
| MEK rub | >180 | >180 | >180 | >180 | >180 | >180 |

TABLE V Thermal stability of coatings

| Coating/Properties | HP100M | HP200M | HP300M | HP103M | HP203M | HP303M |
|---|---|---|---|---|---|---|
| Initial degration temp. ($T_i$,°C) | 368 | 383 | 362 | 349 | 349 | 351 |
| Final degration temp. ($T_f$,°C) | 467 | 438 | 447 | 453 | 441 | 433 |

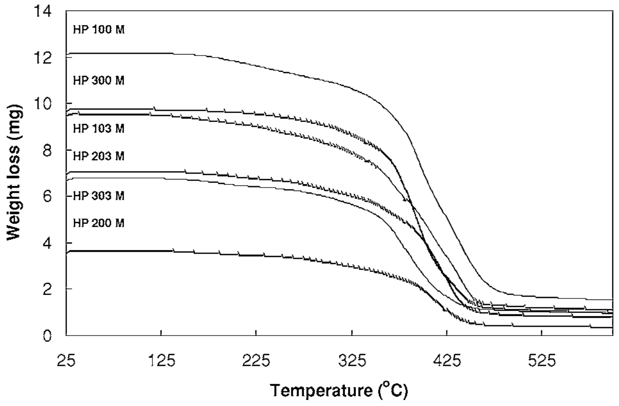


*Figure 6* TGA curve of crosslinked coating films.

check the film integrity. All the coatings under study were found to pass >180 MEK rubs, which indicate good film properties.

## 3.4. Thermal stability

The results of thermo gravimetric analyses are summarized in Table V and shown in Fig. 6. The initial degradation temperature ($T_i$) of all the coating films are found to be in the range of 349°C to 383°C while the final degradation temperatures ($T_f$) are in the 432°C to 468°C range which indicates their good thermal stability. The thermal stability data [39] of coating films also supports good crosslinking ability of coating systems under study because thermal stability depends on the XLD of coatings.

## 4. Summary and conclusions

A combined approach to yield quantitative results on coating properties and its relation to chemical composition has been demonstrated by studying the HPs/HMMM clear coatings. The effects of variation of diol structure in HPs backbone and acetoacetylation of pendant hydroxyl group of HPs have been used as a parameter to change the chemical composition of HPs/HMMM clear coats by maintaining the same ratio of HMMM. The following inferences besides the anomalous behaviour can be drawn from the study:

- The diol structure has affected the coating properties but it has almost negligible effect on determining the cure conditions. The coating based on CHDM diol (HP200M) is found to be better and equivalent to NPG diol (HP100M) at higher application solids based on overall performance. The PD diol based coating (HP300M) is found to be more flexible than HP100M and HP200M.
- The acetoacetylation of HPs has resulted in substantial reduction of viscosity, which is translated to higher application solids and improved the adhesion properties of all the coating systems studied and it is also reflected in higher tensile strength of the coating coupled with more flexibility. Almost the same trend is observed in the coating properties as obtained on their unacetoacetylated counterpart.

Based on the above observations and information obtained one can conclude that the structural variation in HPs backbone and a combined approach of study leads us towards rational design criteria for coating formulations for desired end use properties.

## References

1. L. W. HILL., "Dynamic Mechanical and Tensile Properties," Paint and Coatings Testing Manual, 14th. ed. (ASTM, Philadelphia, 1995) ch 46, 534p.
2. M. AKAY, S. J. BRYAN and E. F. T. WHITE, *J. Oil Col. Chem. Assoc.* **56** (1973) 86.
3. K. DUSEK and M. D. SMREKOVA, *Prog. Polym. Sci.* **25** (2000) 1215.
4. P. J. TORDELLA, *Official Digest* **4** (1965) 357.
5. F. W. BILLMEYER JR., *J. Paint Technol.* **41**(528) (1969) 1.
6. W. BLANK, *J. Coat. Technol.* **54**(687) (1982) 6.

7. T. PROVDER, *ibid.* **61**(770) (1989) 32.
8. L. W. HILL, *ibid.* **64**(808) (1992) 29.
9. D. R. BAUER and R. A. DICKIE, *ibid.* **54**(685) (1982) 57.
10. A. ZOSEL, *Prog. Org. Coat.* **8** (1980) 47.
11. L. W. HILL and Z. W. WICKS JR., *ibid.* **10** (1982) 55.
12. Z. W. WICKS JR., F. N. JONES and S. P., PAPPAS, "Organic Coatings Science & Technology," Vol. 1 (John Wiley & Sons, 1992) 122.
13. R. NARAYAN and K. V. S. N. RAJU, *Euro. Coat. J.* **78** (2001) 40.
14. W. FRIETAGAND and D. STOYE, "Resins for Coatings," (Hanser, New York, 1996) 205.
15. S. J. WITZEMAN, D. W. NOTTINGHAM and F. D. RECTOR, *J. Coat. Technol.* **62** (1990) 101.
16. R. J. CLEMENS and F. D. RECTOR, *ibid.* **61** (1989) 83.
17. F. D. RECTOR, W. W. BLOUNT and D. R. LEONARD, *ibid.* **61** (1989) 31.
18. A. I. YEZRIELEV, K. R. RIGOPOULOS, R. W. RYAN, K. K. KUO and G. A. KNUDSEN, US Patent 5976706, 1999.
19. W. J. BLANK, *Polym. Mater. Sci. and Eng.* (PMSE) **77** (1997) 391.
20. R. BUTER, *Farbe & Lack* **86**(4) (1980) 307.
21. R. NARAYAN and K. V. S. N. RAJU, *Paintindia* **51**(7) (2001) 35.
22. *Idem.*, *Prog. Org. Coat.* POC **30** (2002) 1–9 (in press).
23. K. V. S. N. RAJU and M. YASSEN, *Prog. Org. Coat.* **10** (1982) 532.
24. ISO, "Paint & Varnish General Test Methods" ISO 1514:1993, 26 p.
25. J. D. SKROVANEK, *Prog. Org. Coat.* **18** (1990) 89.
26. F. N. JONES, *J. Coat. Technol.* **68**(846) (1996) 28.
27. D. J. GOLOB, T. A. ADOM JR. and R. W. WHITSON, *Polym. Mater. Sci. Eng.* **63** (1990) 826.
28. P. M. DUNCAN and M. R. VAN DE MARK, *Mod. Paint Coat.* **80**(6) (1990) 51.
29. S. SHOEMAKER, *J. Coat. Tech.* **62**(787) (1990) 49.
30. J. D. HOOD, W. W. BLOUNT and W. T. SADE, *ibid.* **58**(739) (1986) 49.
31. W. J. BLANK, *ibid.* **60**(764) (1988) 43.
32. R. NARAYAN, Ph.D. Dissertation, ISM Dhanbad, India, 2002.
33. R. B. PRIME, J. M. BURNS, M. L. KARMIN, C. H. MOY and H. B. TU, *J. Coat. Technol.* **60**(761) (1988) 55.
34. D. W. CRAWFORD, *Thermochemica Acta* **357/358** (2000) 162.
35. M. B. ROLLER, *J. Coat. Technol.* **54**(691) (1982) 33.
36. ZENO W. WICKS JR., *ibid.* **58**(743) (1986) 23.
37. L. W. HILL, *Polym. Mater. Sci. Eng.* **77** (1997) 387.
38. J. K. GILHAM, *Polym. Eng. Sci.* **26** (1986) 1429.
39. S. DESAI, I. M. THAKORE, B. D. SARAWADE and S. DEVI, *Eur. Polym. J.* **36** (2000) 711.

*Received 9 April*
*and accepted 10 May 2002*