

## Thermomechanical and Chemorheology Properties of a Thermosetting Acrylic/Melamine Clearcoat Modified with a Hyperbranched Polymer

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**ABSTRACT:** The work presented here aims at studying the thermomechanical and chemorheological properties of an automotive clearcoat containing an acrylic/melamine resin modified with a hyperbranched poly ester-amide (HBP) additive. Rheological experiments were conducted at ambient (25°C) and curing temperature (140°C). Dynamic mechanical thermal analysis and hardness measurements were performed to reveal the influence of HBP content on the behavior of the cured samples. It was found that the viscosity of the resin containing HBP samples considerably decreased. Although curing degree and mechanical properties were improved at low HBP loadings, a reverse effect was seen at higher contents. Dynamic rheological results during curing showed that although low amount of HBP resulted in an early gel point (GP), higher HBP loading postponed the GP. This loading-dependent behavior was explained by the influence of HBP on viscosity and reactivity of the system on which the curing performance was influenced oppositely. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1929–1938, 2013

**KEYWORDS:** coatings; viscosity and viscoelasticity; dendrimers; hyperbranched polymers and macrocycles; thermosets; blends

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### INTRODUCTION

Dendritic polymers are macromolecules produced from polymerization reaction of multifunctional monomers. A poly-functional monomer acting as a core provides sites for interacting with other multifunctional monomers. “Dendritic” is originated from a Greek word “Dendron” which means “tree.” Today, synthesis, properties, and applications of dendritic polymers have been well documented.<sup>1,2</sup> Dendritic polymers are classified into dendrimers and hyperbranched polymers depending on their branching architecture. Although dendrimers have a perfect structure due to a precise control in their synthesis process, hyperbranched polymers have an imperfect branching structure. This makes hyperbranched polymers to be much cheaper compared with dendrimers. Accordingly, this eases the mass production of hyperbranched polymers and develops their applications in different industrial products. Hyperbranched polymers can be utilized in a diverse range of applications such as catalysis, sensors, delivery systems, polymeric blends, and especially coatings.<sup>2</sup> Low melt viscosity, high solubility in organic solvents, well-defined structure, large degree of functionality, and the possibility for modification of functional groups make hyperbranched polymers highly versatile materials for coating applications.<sup>3,4</sup> Hyperbranched polymers have been used as main resin

in production of powder coatings,<sup>5–8</sup> UV-curing resins,<sup>9–12</sup> high solid coatings,<sup>4</sup> water-borne coatings,<sup>13</sup> and also as multifunctional crosslinkers in some thermosetting systems.<sup>14–16</sup> Hyperbranched polymers have also been proposed as toughening agents for thermosetting systems, especially for epoxy-based polymers.<sup>17–23</sup> Hyperbranched polymers in comparison to conventional toughening agents such as rubber and thermoplastic particles, have shown to toughen the epoxy resins more effectively without any significant decrease in modulus. Despite extensive use of hyperbranched polymers as toughening agent for epoxy resins, their effects in other thermosetting systems have rarely been reported. In few attempts, vinyl-urethane hybrid resins and bis-maleimide containing thermosetting systems were toughened by various polyether and/or polyester-based hyperbranched polymers.<sup>24–26</sup>

Acrylic resins cured with melamine crosslinkers are the most common types of thermosetting polymers being used as automotive clearcoats.<sup>27–29</sup> In this system, the intended reaction occurs between hydroxyl groups of acrylic resin and methoxy groups of the methoxylated melamine resin.<sup>30</sup> While they meet the need for having a high modulus, their high glass transition temperature and relatively low elongation at break make them a brittle network. This can affect the mechanical properties such as chip and scratch resistance needed for such applications.<sup>31–34</sup>



**Table I.** Formulation of Various Modified Clear Coats

Sample No.	HBP (g)	Acrylic (g)	Melamine (g)
HBPO	0.00	70.00	30.00
HBP5	1.29	66.39	30.00
HBP10	2.59	62.90	30.00
HBP25	6.48	52.41	30.00
HBP50	12.96	34.94	30.00

(Shimifann, model MX0102) at ambient temperature with the speed of 1500 rpm for 60 min.

The modified clearcoats were applied on precleaned glass substrates. Samples were then cured at 140°C for 20 min. The thickness of cured films was  $65 \pm 5 \mu\text{m}$  (according to ASTM D7091). Free films were also prepared by immersing the glass coated substrates in water, followed by removing after 10 min.

To study the rheological properties of the clearcoat solutions, all formulations were prepared by dissolving in butyl acetate to reach a total solid content of 60%. The rheological properties of the pure and modified clearcoat solutions were analyzed by a cylindrical rheometer (Anton Paar Model: MCR300) in a rotational mode at ambient temperature.

Isothermal rheological experiments were utilized to study the viscoelastic parameters of various clearcoat formulations. To this end, a rheometric mechanical spectrometer (Paar Physica USD200), with a parallel plate geometry (diameter = 25 mm; gap = 1 mm) at 140°C at 1% strain and angular frequency  $\omega$  of  $10 \text{ s}^{-1}$  was used. Attempts were made to adjust the total solid contents of all samples at 60% using butyl acetate.

The effects of HBP addition on the crosslinking density and glass transition temperature ( $T_g$ ) were studied by means of a Tritec 2000 dynamic mechanical thermal analysis (DMTA). Experiments were carried out on free films at 1 Hz. DMTA was done in a tension mode. Length, width, and thickness of the samples were 20, 5, and 0.07 mm, respectively. The heating range was between 25 and 200°C, and the heating rate was 5°C/min (according to ASTM E1640-04).

Microhardness of the clear coats containing various loads of HBP was determined using a microindenter of a Leica VMHTMOT equipped with a berkovich diamond tip (three-faced pyramid) according to the following equation:

$$H = 1854.4 \times P/d^2 \quad (1)$$

where  $H$  is the hardness,  $P$  is the applied load, and  $d$  is the diagonal length of the indented area. A normal force of 19.6 N was applied for 15 s.

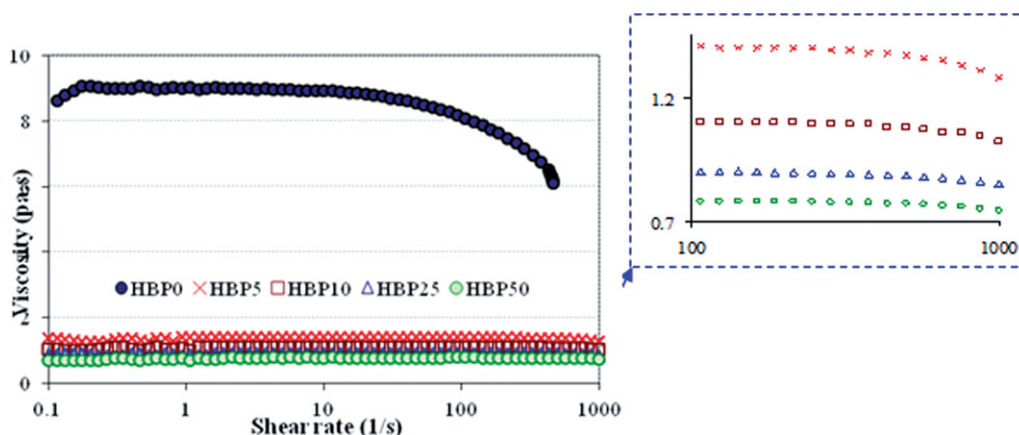
## RESULTS AND DISCUSSION

To discuss the effect of clearcoat modification using HBP, viscosity measurements were first conducted. Figure 2 exhibits viscosity versus shear rate for various loadings of HBP.

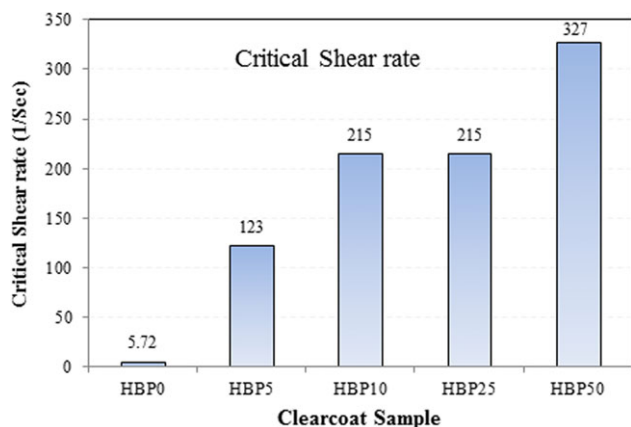
It can be seen that adding HBP to the formulations is highly effective to reduce the viscosity. This may be attributed to the difference between the intrinsic viscosity and chain structure of acrylic resin and HBP macromolecules.<sup>36</sup> The intrinsic viscosity of HBP (0.16 dL/g) was much lower than that of the thermosetting acrylic resins (around 1 dL/g). This is due to much lower molecular weight of HBP compared to that of acrylic resin. This difference in molecular weight results in a drop in intrinsic and also apparent viscosity of the blended solutions.

On the other hand, the more compact structure of HBP in comparison to the long linear chains of acrylic resin may result in a less chain entanglement in formulation, leading to a significant decrease in viscosity.<sup>37–40</sup> In addition, it is probable that the globular location of HBP molecules is between linear chains of acrylic resin. This disrupts the entanglement of linear chains and makes it act as a spacer.<sup>38</sup> It is also seen that as the HBP content increases from 0 to 5%, the viscosity of the clearcoats considerably drops, after which (from 5 to 50%), the HBP is less effective to depreciate the viscosity.

A considerable reduction in viscosity as a result of a low level of modifier (only 1.3 wt % for HBP5 sample) can reduce the amount of solvents used for adjusting the clearcoat viscosity. This is beneficial from the economical and environmental viewpoint. This reduces the cost of the clearcoat and also provides a



**Figure 2.** Viscosity versus shear rate for various clearcoats modified with HBP. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3.** Variations of critical shear rate versus HBP content. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

basis for preparation of clearcoat formulations with higher solid contents, which emits less volatile organic matters to the atmosphere.

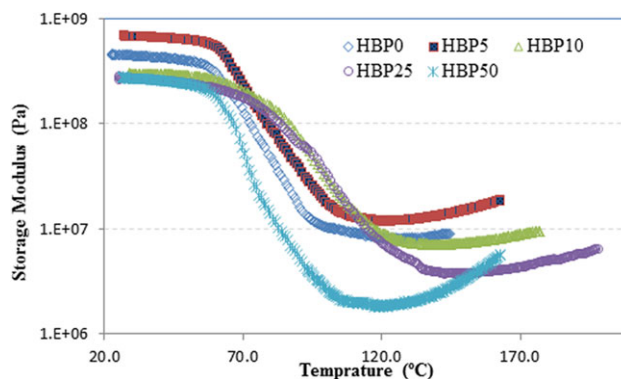
As Figure 2 clearly depicts, all formulations display a Newtonian behavior at low shear rates but a shear-thinning characteristic at higher shear rates. A closer look into the high shear rate region can show this behavior more obviously. This observation is similar to the results obtained by Hsieh and coworkers,<sup>41</sup> in which they found that the blends containing HBPs behaved Newtonian if one of the components was acting like Newtonian fluids. In this case, it is also seen that HBP shifts the behavior of the blend solution from a shear-thinning solution to a Newtonian one.

Further evaluations on the flow curves in Figure 2 illustrate that as the HBP content increases, critical shear rate, at which the behavior changes from Newtonian to shear thinning, shifts to higher shear rates. To further clarify the critical shear rate point for HBP-modified clearcoats, the higher shear rate region (100–1000 s<sup>-1</sup>) has been enlarged in Figure 2. The critical shear rate values of all clearcoats are presented in Figure 3.

As can be seen in Figure 3, the higher the HBP content, the greater is the critical shear rate. This again may imply fewer entanglements in the solution containing HBP. This suggests the change in behavior of the blends from a pseudoplastic solution to a Newtonian type. These results are in agreement with the findings of Nunez and coworkers who blended hyperbranched polyesters with a linear poly(2-hydroxyethyl methacrylate) system.<sup>38</sup>

#### DMTA Analysis of HBP Containing Films

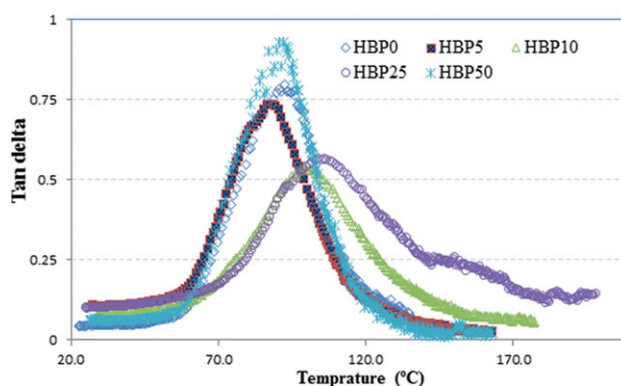
DMTA experiments were carried out to reveal the influence of HBP loading on the main characteristics of films including  $T_g$ , crosslinking density and homogeneity.<sup>42–44</sup> Variations of storage modulus and  $\tan \delta$  versus temperature are shown in Figures 4 and 5 respectively. The values of different data deduced from DMTA graphs such as storage modulus at 25°C and that of the rubbery plateau zone ( $E'_{min}$ ), crosslinking density,  $T_g$ , and the height and width of loss peak are given in Table II. Crosslinking density was calculated from rubbery plateau zone of storage



**Figure 4.** Storage modulus vs. temperature for all clearcoats. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

modulus ( $v_c = E/3RT$ ), where  $v_c$  is crosslinking density and  $R$  is gas constant.  $E$  and  $T$  are storage modulus and temperature at the initial point of rubbery zone, respectively.

As can be seen in Figures 4 and 5 and Table II, HBP can act in different ways depending on its loading in the film. In the case of crosslinking density, HBP increases the total crosslinking of the clearcoat when it is introduced to formulations up to 5%. After this content, it significantly decreases the crosslinking density of the system. For example, in HBP50 sample it has a poor (low) crosslinking density.  $T_g$  variations of the samples reveal that the impact of HBP on  $T_g$  does not follow a systematic trend and is dependent on the loading percent of HBP. While  $T_g$  decreases for HBP5, it increases for samples modified with higher loadings of HBP (HBP10 and HBP25). For HBP50, it is seen that  $T_g$  abruptly decreases. Lower  $T_g$  of HBP5 compared with that of the pristine clearcoat reveals that HBP molecules, due to presence of fewer and less extensive entanglements in the blend, produce a more flexible structure. It has been demonstrated that globular hyperbranched polymers can increase the free volume of the mixture, when they are blended with a compatible linear polymer.<sup>45</sup> The greater free volume results in lower  $T_g$ . But it seems that this behavior is not further seen at higher loadings of HBP. Increased  $T_g$  of the HBP10 and HBP25 clearcoats, despite decreased values of their crosslinking density,



**Figure 5.** Loss peak versus temperature diagrams for all clearcoats. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.** Some Basic Characteristics of Clearcoats Obtained from DMTA Diagrams

Sample No.	$E'$ at 27°C (Pa)	$E'_{\min}$ (Pa)	Crosslinking density (mmol/cm <sup>3</sup> )	$T_g$ (°C)	Peak width (°C)	Peak height
HBP0	$4.51 \times 10^8$	$8.05 \times 10^6$	0.865	91.8	0.78	29
HBP5	$7.03 \times 10^8$	$12.05 \times 10^6$	1.036	88.0	0.76	31.5
HBP10	$3.03 \times 10^8$	$7.15 \times 10^6$	0.677	99.2	0.55	42.45
HBP25	$2.76 \times 10^8$	$3.79 \times 10^6$	0.654	106.5	0.52	50.45
HBP50	$2.75 \times 10^8$	$1.82 \times 10^6$	0.163	92.5	0.92	31.5

may imply that other forms of interactions such as physical and hydrogen bonding (instead of covalent bonding or chain entanglements) have to be taken into consideration. Hybrane 1500 has a polyester-amide backbone in the interior part (numerous ester and amide linkages) and has 10 hydroxyl groups on its peripheral part.<sup>39,46</sup> The monomers used in preparation of acrylic resin were styrene/methyl methacrylate/ butyl methacrylate and 2-hydroxy ethyl methacrylate (HEMA). Despite the fact that these monomers have weak or medium strength in hydrogen bonding formation (except for HEMA), both ester-amide linkages and hydroxyl groups of HBP are potentially stronger groups to interact via hydrogen bonding with each other or other components in the clearcoat formulation such as melamine. Therefore, replacing an acrylic resin composed of less polar acrylate monomers with a more polar polymer (HBP) would significantly increase the intramolecular and intermolecular forces, leading to a decrease in free volume and a less flexible structure that has a higher  $T_g$ .<sup>47-49</sup> For HBP50, it seems that the effect of hydrogen bonding is compensated for much lower crosslinking density in HBP50, leading to a comparable  $T_g$  value relative to that of the blank clearcoat. Another reason for higher  $T_g$  of samples containing high loadings of HBP could be the higher probability of methylene bridges ( $-N-CH_2-N-$ ) formation in the coating structure as a result of melamine self-condensation (see FTIR results). The formation of these linkages that are less flexible compared with ether linkages is more probable, when there is not enough or less reactive hydroxyl groups in the system.<sup>50</sup>

It is seen from DMTA results that as the HBP is increased, the height of loss peak decreases whereas the width increases (except for HBP50). It means that the homogeneity of the system decreases, as a result of this modification. For HBP50, due to low crosslinking density, the homogeneity increases again.

The viscoelastic properties during curing can provide a good insight into the curing degree of the thermosetting polymers.<sup>51</sup> Rheological experiments were done to study how HBP macromolecule can influence the curing performance of its blend with acrylic/melamine system. The storage modulus, loss modulus, damping factor, and complex viscosity versus curing time diagrams in an isothermal experiment (140°C) are depicted in Figure 6.

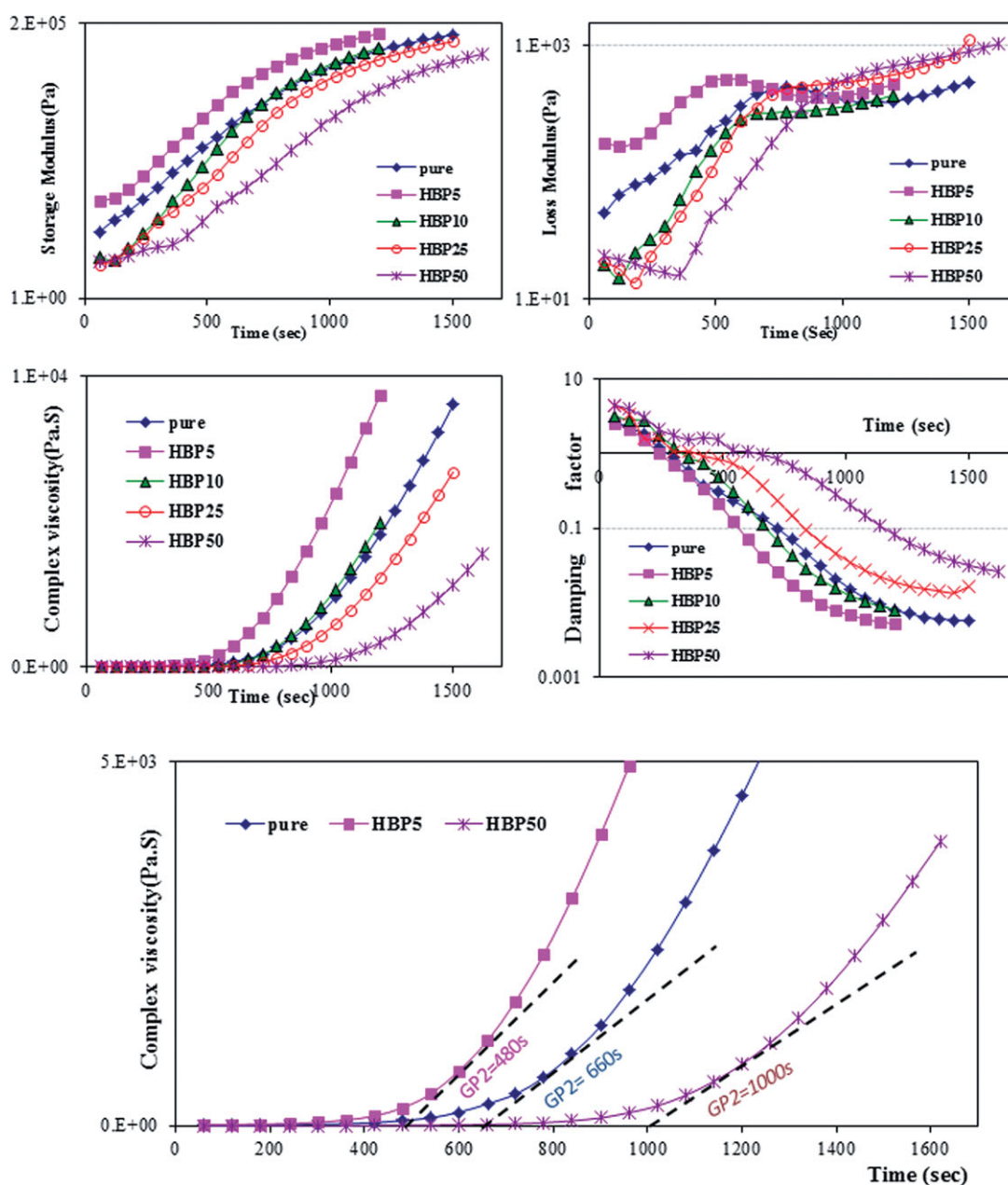
As expected, when the curing process starts, storage modulus of all clearcoats sharply increases at the very beginning of the curing stage. As the time elapses, storage modulus tends to decrease, reaching a constant value at the end of the curing

time. It can also be observed that as the HBP content increases in clearcoat formulations, the slope of storage modulus decreases except for HBP5 that has a similar or even sharper trend.

In case of loss modulus, it is seen that although the loss modulus of HBP0 increases immediately after the curing commences, loss moduli of HBP-containing samples tolerate a slight decrease at the beginning of the curing, after which they start to increase. Further evaluations depict that as the HBP content is increased, the duration, which is the time during which the loss modulus decreases, is extended to longer times. This may be explained by hydrogen bonding formation in the blend. When the sample is exposed to isothermal curing condition at 140°C, the solvent molecules start leaving the sample and the polymeric chains come closer to each other. When the polymeric chains are close enough, they interact via intermolecular forces like hydrogen bonding and then start chemical bonding, provided that the functional groups come close to each other. In the blends containing HBP, after solvent evaporation, HBP can form a relatively strong hydrogen bonding, making the polymeric chains less flexible, therefore leading to an initial drop in loss modulus. As the HBP increases, the hydrogen bonding become stronger and therefore the chains become more involved in physical interaction.<sup>47</sup> Therefore, greater energy is needed to overcome physical bonding. So, the start of their crosslinking reactions is delayed to longer times.

The gel point (GP) and variation in viscosity of samples offer valuable information about curing degree. GP is defined as the time frame at which the weight-average molecular weight reaches infinity. Different criteria have been used for determination of GP. The point that  $G'$  and  $G''$  crosses or damping factor ( $G''/G'$ ) becomes equal to unity or the point at which viscosity abruptly increases and goes to infinity can be considered as the GP,<sup>52</sup> the values of which are given in Table III. GP2 values have been extracted from Figure 6 (complex viscosity vs. time diagrams). It was calculated by extrapolating the tangential line over the curvature of complex viscosity where it abruptly rises. This method has been clarified in the last diagram of Figure 6.

The increase in storage modulus of each sample during its curing is defined as  $\Delta G'$ . This factor is calculated by difference in storage modulus values at the end of curing ( $t = 20$  min) and the beginning ( $t = 0$ ) of the curing process. This value ( $G'_{20} - G'_0$ ) for all samples is given in Table III. Due to the insignificant value of  $G'_0$  compared to  $G'_{20}$ ,  $\Delta G'$  is so close to  $G'_{20}$ . As the HBP content increases,  $\Delta G'$  increases for the HBP5 and



**Figure 6.** Different rheometrical parameters during curing of clearcoats. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

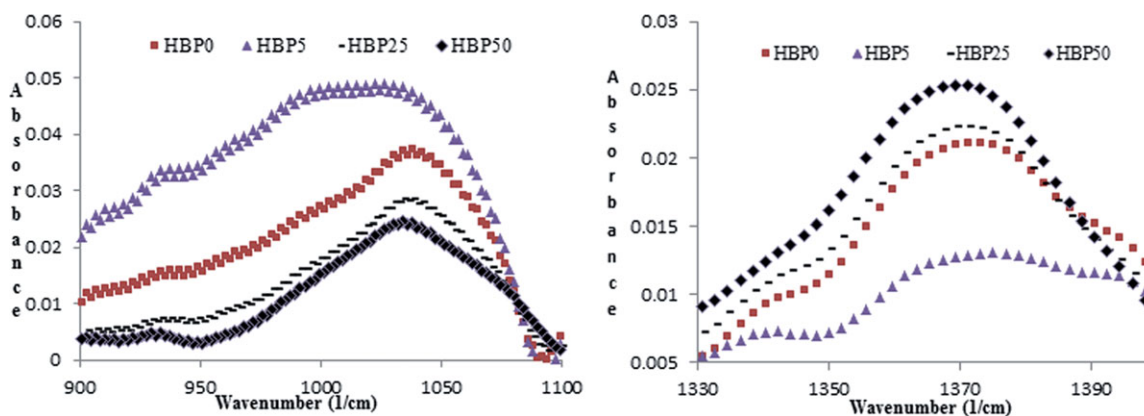
then decreases for samples containing higher HBP contents.  $\Delta G'$  is a result of solvent evaporation and formation of three-dimensional network in the matrix. As the total solid content for all samples was identical, this might only be a reflection of chemical network formation. The same trend for  $\Delta G'$  and cross-linking density (in Figure 4 or Table II) confirms such observations.

According to GP values, although gel time shifts to shorter times for HBP5, those of samples containing greater loadings of HBP shift to longer times. For HBP50, gel time reaches a value much higher than that of the blank sample, that is, HBP0. Functionality, viscosity, reactivity, and temperature are the most influential factors that affect the GP. As in all

samples, temperature and functionality were kept identical during curing, two other factors, that is viscosity and reactivity, seem to control the GP.

**Table III.** GP and  $\Delta G'$  Values for Various Clearcoats During Curing

Sample No.	GP1 (s)	GP2 (s)	$\Delta G'$ (Pa) ( $G'_{20} - G'_0$ )
HBP0	275	660	$4.55 \times 10^4$
HBP5	250	480	$9.36 \times 10^4$
HBP10	330	660	$4.99 \times 10^4$
HBP25	400	780	$3.09 \times 10^4$
HBP50	640	1000	$8.45 \times 10^3$



**Figure 7.** Two narrow cuts (900–1100  $\text{cm}^{-1}$  and 1330–1400  $\text{cm}^{-1}$ , respectively, being assigned to ether linkages and methylene bridge) of FTIR spectra of different clearcoats containing various loads of HBP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Viscosity results in Figure 2 revealed that all HBP containing clearcoats had a much lower viscosity values compared with blank sample. The lower viscosity of formulation results in greater mobility of the polymeric chains and thus higher chance of molecular reaction between functional groups. In case of reactivity, incorporation of HBP in the formulations seems to decrease the reactivity. Comparison of the hydroxyl groups of acrylic resin with those of HBP molecule illustrates that the former is a primary alcohol and the latter is a secondary one. It is well known that due to spatial hindrance; the secondary alcohols are less reactive compared to primary alcohols. Therefore, incorporation of HBP into clearcoat has two opposite effects on the curing degree. Its viscosity effect is in favor of curing, whereas its reactivity is against it.

According to the results observed, it seems that competition between viscosity and reactivity is the detrimental factor in controlling the curing and thus the resulting characteristics of the modified clearcoats. In comparison to blank clearcoat, viscosity has significantly been reduced with only 5% of functional groups replaced. Therefore, the impact of viscosity effect is more influential than the reactivity. This results in curing performance enhancement, leading to earlier GP and network build-up and higher crosslinking density. For samples having higher HBP contents (HBP10, HBP25, and HBP50), viscosity does not significantly decrease compared with HBP5. It seems that for HBP10, the effect of viscosity has been completely compensated for by the effect of reactivity (even the reactivity effect slightly dominates). The similar trend between gel times and crosslinking values for HBP0 and HBP10 is in favor of this supposition. For HBP25 and HBP50 clearcoats, the reactivity of the system has significantly decreased (especially in case of HBP50), whereas the viscosity effect has slightly reduced. For these samples, the lower reactivity effect dominates the role of viscosity effect, leading to longer gel times. Shift of GP to longer times postpones the network formation. Therefore, delayed curing process after 20 min leaves the samples immature, showing a low level of crosslinking. This can also be discussed by the storage modulus diagrams of these samples in both rheology measurements and DMTA experiments. Monotonic increase in storage modulus (Figure 6) without showing a stable state at

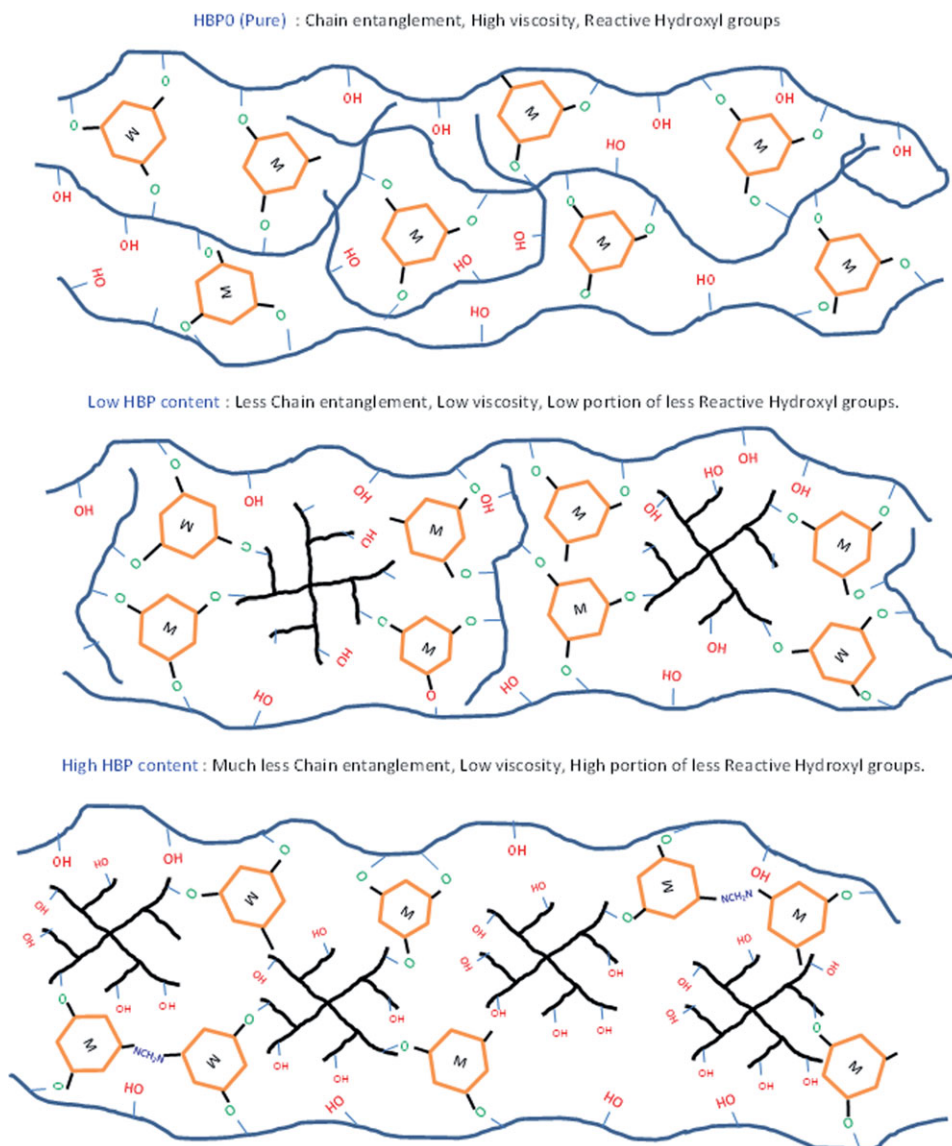
the end of curing process ( $t = 20$  min) for samples HBP25 and HBP50 together with a sharp increase in storage modulus of the cured state of these two samples after the rubbery zone (postcuring) might reflect this immaturity.<sup>53</sup>

To investigate the effect of HBP loading on the curing of clearcoats, the chemical structure of modified clearcoats should be characterized. As a result of curing reactions in acrylic/melamine systems, two main linkages are formed, that is, ether linkages and methylene bridges.<sup>54</sup> Although ether linkages are resulted from reaction between acrylic and melamine macromolecules, methylene bridges are formed as a result of self-condensation of melamine. To follow the presence and formation of these bonds, FTIR can be utilized. The presence of the former and the latter linkages can be evidenced by variations in 1000–1100  $\text{cm}^{-1}$  and 1300–1400  $\text{cm}^{-1}$  parts of FTIR spectra, respectively.<sup>55</sup> These two parts of FTIR spectra of different clearcoats have been highlighted in Figure 7. The spectra have been normalized with respect to the C–N (attached to triazine heterocycle peak around 1560  $\text{cm}^{-1}$ ), which remains unchanged for all clearcoats. To quantify these comparisons, the normalized absorbance values of –N–CH<sub>2</sub>–N– and ether ([the area under –N–CH<sub>2</sub>–N– peak and ether frequency bands]/[the area under C–N peak]) were calculated and presented in Table IV.

According to Figure 7 and values presented in Table IV, the ether linkage increases from HBP0 to HBP5 and then decreases in samples containing higher loadings of HBP. In case of methylene bridge, although its value decreases in HBP5 compared with HBP0, it increases for clearcoats containing higher HBP loadings. These findings accompanied with DMTA results can

**Table IV.** Relative Normalized Intensities of Ether Linkages and Methylene Bridge of Different Clearcoats Containing Various Loads of HBP

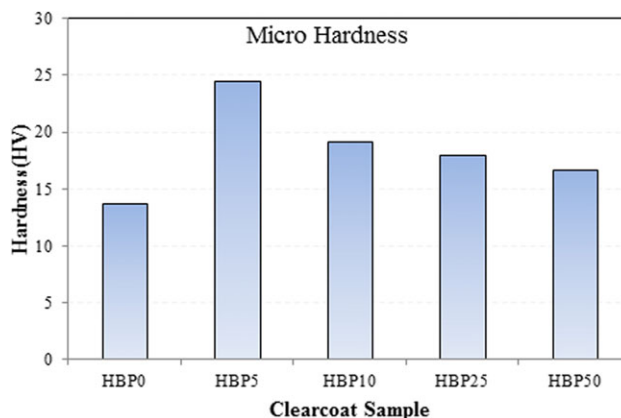
Sample No.	HBP0	HBP5	HBP25	HBP50
Ether linkage	0.70	0.83	0.52	0.42
Methylene linkages	0.31	0.24	0.32	0.36
Total (ether + methylene linkages)	1.01	1.07	0.84	0.78



**Figure 8.** The schematic orientation of coating components in different clearcoats (Hexagonal is melamine). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

provide a general insight on the type of crosslinking in the modified clearcoats. In low loading of HBP, the lower viscosity of the system facilitates the reaction between acrylic and melamine resin that leads to an increase in crosslinking density. At higher loadings of HBP, due to the decrease in the reactivity of hydroxyl groups, the chance of reaction between the acrylic and melamine decreases. This provides an environment for unreacted functional groups of melamine resin to self-condense with each other.<sup>50</sup> The greater amount of methylene bridges that are less flexible than ether linkages can account for the higher  $T_g$  in clearcoats containing higher loadings of HBP (HBP10 and HBP25), as claimed before in DMTA results.

In Table IV, the summation of intensities of ether and methylene bridges is also reported. As seen, the total value increases from HBPO to HBP5 and then decreases. This trend is similar to that of crosslinking density. As most of crosslinkings in the



**Figure 9.** Microhardness results of different clearcoats. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



clearcoat are either ether or methylene bridge type, this similar trend is reasonable.

According to results obtained so far, especially thermomechanical as well as FTIR results, a general overview for the chemical structures of different clearcoats modified with various loadings of HBP can be understood. A schematic representation of molecular structure is proposed in Figure 8. It has to be considered that due to complex mixtures of acrylic and melamine resins, variety of reactions for melamine resin, and also to the reversibility of most of curing reactions, it is not easy to elucidate the exact structure of the final network.

### Hardness

To find out the effect of HBP on mechanical properties of clearcoats, hardness of samples were measured. Mechanical properties such as hardness can be indicative of curing performance of the clearcoat.<sup>32</sup> Microhardness results of different clearcoats are depicted in Figure 9.

As clearly seen in Figure 9, the hardness sharply increases when only 5% of hydroxyl groups are replaced by HBP-type hydroxyls. For higher loadings of HBP, hardnesses decrease but still are higher compared with HBP0. The higher hardness values of HBP10, HBP25, and HBP50, despite their lower crosslinking density compared with neat clearcoat, show that other forms of intermolecular interactions rather than chemical crosslinking have to be responsible for resisting against the indenter tip. As previously stated, incorporating HBP in formulations induces greater sites for hydrogen bonding formation. Low molecular weight of HBP enables them to enter in the space between polymeric chains and form hydrogen bonding with other components via numerous hydroxyl groups available on their peripheral. As the content of HBP increases, physical intermolecular/intramolecular forces increase, leading to higher resistance against indenter tip penetration. In case of HBP5, both hydrogen bonding formation and higher crosslinking density reinforce the network causing an abrupt increase in hardness. But higher loadings of HBP seem to give rise to an extensive physical interaction compared with blank sample.

### CONCLUSION

A typical automotive clearcoat modified with a hyperbranched poly ester-amide (HBP) was studied to investigate the influence of HBP loading on the main rheological, thermomechanical, and mechanical characteristics of the coating. The results revealed that there is an optimum content for HBP. It was found that beside a significant reduction in viscosity of the system, HBP can improve the curing degree and cause an earlier gel time, leading to higher crosslinking density and hardness when it is added at low contents. It was attributed to the viscosity effect. In higher loadings of HBP, it was revealed that the viscosity effect was compensated for with the reactivity effect that caused a less efficient curing degree. This resulted in less crosslinking density and inferior mechanical properties compared with the samples containing optimum HBP content.

### REFERENCES

1. Yates, C. R.; Hayes, W. *Eur. Polym. J.* **2004**, *40*, 1257.
2. Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183.
3. Johansson, M.; Glauser, T.; Jansson, A.; Hult, A.; Malmström, E.; Claesson, H. *Prog. Org. Coat.* **2003**, *48*, 194.
4. Benthem, R. A. T. M. *Prog. Org. Coat.* **2000**, *40*, 203.
5. Johansson, M.; Malmstrom, E.; Jansson, A.; Hult, A. *J. Coat. Technol.* **2000**, *72*, 49.
6. Wei, H.; Liang, H.; Zou, J.; Shi, W. *J. Appl. Polym. Sci.* **2003**, *90*, 287.
7. Cheng, X.; Huang, Z.; Liu, J.; Shi, W. *Prog. Org. Coat.* **2007**, *59*, 284.
8. Zhu, S. W.; Kou, H. G.; Wei, H. Y.; Lin, D.; Shi, W. *Chin. J. Polym. Sci.* **2001**, *19*, 155.
9. Xu, G.; Shi, W. *Prog. Org. Coat.* **2005**, *52*, 110.
10. Gao, Q.; Li, H.; Zeng, X. *J. Coat. Technol. Res.* **2011**, *8*, 61.
11. Simic, S.; Dunjic, B.; Tasic, S.; Bozic, B.; Jovanovic, D.; Popovic, I. *Prog. Org. Coat.* **2008**, *63*, 43.
12. Schmidt, L. E.; Schmäh, D.; Leterrier, Y.; Månson, J. A. E. *Rheol. Acta* **2007**, *46*, 693.
13. Bao, C. L.; Wang, L. S.; Zhang, A. Q. *J. Taiwan Inst. Chem. Eng.* **2009**, *40*, 174.
14. Karakaya, C.; Gunduz, G.; Aras, L.; Mecidoglu, I. A. *Prog. Org. Coat.* **2007**, *59*, 265.
15. Johansson, K.; Bergman, T.; Johansson, M. *Appl. Mater. Int.* **2009**, *1*, 211.
16. Maslanka, S.; Sułkowski, W. W.; Sułkowska, A. *J. Therm. Anal. Calorim.* **2010**, *102*, 1051.
17. Boogh, L.; Pettersson, B.; Manson, J. A. E. *Polymer* **1999**, *40*, 2249.
18. Fu, J. F.; Shi, L. Y.; Yuan, S.; Zhong, Q. D.; Zhang, D. S.; Chen, Y.; Wu, J. *Polym. Adv. Technol.* **2008**, *19*, 1597.
19. Sangermano, M.; Messori, M.; Galleco, M.M.; Rizza, G.; Voit, B. *Polymer* **2009**, *50*, 5647.
20. Lv, S.; Yuan, Y.; Shi, W. *Prog. Org. Coat.* **2009**, *65*, 425.
21. Morell, M.; Erber, M.; Ramis, X.; Ferrando, F.; Voit, B.; Serra, A. *Eur. Polym. J.* **2010**, *46*, 1498.
22. Mezzenga, R.; Manson, J. A. E. *J. Mater. Sci.* **2001**, *36*, 4883.
23. Cicala, G.; Recca, G. *Polym. Eng. Sci.* **2008**, *48*, 2382.
24. Xu, J.; Wu, H.; Mills, O. P.; Heiden, P. A. *J. Appl. Polym. Sci.* **1999**, *72*, 1065.
25. Karger-Kocsis, J.; Frohlich, J.; Gryshchuk, O.; Kautz, H.; Frey, H.; Mülhaupt, R. *Polymer* **2004**, *45*, 1185.
26. Gryshchuk, O.; Jost, N.; Karger-Kocsis, J. *Polymer* **2002**, *43*, 4763.
27. Yari, H.; Moradian, S.; Ramezanzadeh, B.; Kashani, A.; Tahmasebi, N. *Polym. Degrad. Stab.* **2009**, *94*, 1281.
28. Ramezanzadeh, B.; Mohseni, M.; Yari, H.; Sabbaghian, S. *J. Therm. Anal. Calorim.* **2010**, *102*, 13.
29. Mohammad Rabea, A.; Mohseni, M.; Yari, H.; Ramezanzadeh, B. *J. Appl. Polym. Sci.*, DOI: 10.1002/app.38627.

30. Vargha, V.; Körmendy, Z. J. *Therm. Anal. Calorim.* **2005**, *79*, 195.
31. Ramezanzadeh, B.; Moradian, S.; Tahmassebi, N.; Khosravi, A. *Prog. Org. Coat.* **2011**, *72*, 621.
32. Yari, H.; Moradian, S.; Tahmasebi, N.; Arefmanesh, M. *Tribol. Lett.* **2012**, *46*, 123.
33. Hara, Y.; Mori, T.; Fujitani, T. *Prog. Org. Coat.* **2000**, *40*, 39.
34. Gregorovich, B. V.; Adamsons, K.; Lin, L. *Prog. Org. Coat.* **2001**, *43*, 175.
35. Yari, H.; Mohseni, M.; Ranjbar, Z. In 8th Coatings Science International 2012 (COSI2012), Noordwijk, The Netherlands, June **2012**.
36. Han, K.; Li, W.; Wu, C.; Yu, M. *Polym. Int.* **2006**, *55*, 898.
37. Sendjarevic, I.; McHugh, A. J. *Macromolecules* **2000**, *33*, 590.
38. Nunez, C. M.; Chiou, B. S.; Andrady, A. L.; Khan, S. A. *Macromolecules* **2000**, *33*, 1720.
39. Lin, Y.; Zhang, K. Y.; Dong, Z. M.; Dong, L. S.; Li, Y. S.; *Macromolecules* **2007**, *40*, 6257.
40. Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
41. Hsieh, T.-T.; Tiu, C.; Simon, G. P. *Polymer* **2001**, *42*, 7635.
42. Ramezanzadeh, B.; Attar, M. M.; Farzam, M. *J. Appl. Polym. Sci.* **2011**, *103*, 731.
43. Zhang, D.; Jia, D.; Chen, S. *J. Appl. Polym. Sci.* **2009**, *98*, 819.
44. Morancho, J. M.; Cadenato, A.; Ramis, X.; Fernández-Francos, X.; Flores, M.; Salla, J. M. *J. Appl. Polym. Sci.* **2011**, *105*, 479.
45. Ratna, D.; Simon, G. P. *J. Appl. Polym. Sci.* **2010**, *117*, 557.
46. Zhang, W.; Zhang, Y.; Chen, Y. *Iran. Polym. J.* **2008**, *17*, 891.
47. Davy, K. W. M.; Kalachandra, S.; Pandain, M. S.; Braden, M. *Biomaterials* **1998**, *19*, 2007.
48. Cowie, J. M. G.; McEwan, I.; McEwen, I. J.; Pethrick, R. A. *Macromolecules* **2001**, *34*, 7071.
49. Arrighi, V.; Cowie, J. M. G.; Ferguson, R.; McEwen, I. J.; McGonigle, E. A.; Pethrick, R. A.; Princi, E. *Polym. Int.* **2005**, *55*, 749.
50. Hirayama, T.; Urban, M. W. *Prog. Org. Coat.* **1992**, *20*, 81.
51. Dusek, K.; Duskova-Smrckova, M. *Prog. Polym. Sci.* **2000**, *25*, 1215.
52. Ratna, D.; Varley, R.; Simon, G. P. *J. Appl. Polym. Sci.* **2004**, *92*, 1604.
53. Yari, H.; Mohseni, M.; Ramezanzadeh, B. *J. Appl. Polym. Sci.* **2009**, *111*, 2946.
54. Jones, F. N.; Chu, G.; Samaraweera, U. *Prog. Org. Coat.* **1994**, *24*, 189.
55. Nguyen, T.; Martin, J.; Byrd, E.; Embree, N. J. *Coat. Technol.* **2002**, *74*, 65.