Upgrading the Adhesion Properties of a Fast-Curing Epoxy Using Hydrophilic/Hydrophobic Hyperbranched Poly(amidoamine)s

Hisham A. Essawy, Heba A. Mohamed, Nadia H. Elsayed

Department of Polymers and Pigments, National Research Center, Dokki 12311, Cairo, Egypt
Correspondence to: H. A. Essawy (E-mail: hishamessawy@yahoo.com)

ABSTRACT: A homologous series of hyperbranched polymers (HBPs) was prepared following a well-defined method and their formation in a polymeric form bearing different extents of branching with amine functional groups at the terminals was verified using different techniques such as Fourier Transform Infrared, [1]H Nuclear Magnetic Resonance, Differential Scanning Calorimetry, and Gel Permeation Chromatography. Toughening of a commercially available fast cure epoxy was aimed through reactive blending with the formed HBPs that exhibit variation in polarity and branching according to the relevant synthesis strategy employed for each polymer. The mechanical properties (impact resistance, pull-off adhesion, and bending) of the resulting coating films pertaining to each epoxy formulation after adhering to metal substrates revealed obvious progress in their performance with respect to a control sample that was hardened exclusively in absence of any HBP. The results were explained on the light of the ability of this class of materials to impose flexibility and dilute the intensive crosslink density associated frequently with the rapid curing of epoxy systems. The extent of gained enhancement for each formulation was accounted for by the molecular architecture of the HBPs, their degrees of branching, polarity, and relative reactive contents of primary amino groups in each case. In addition, the influence of these parameters on a proper wetting over the substrate and morphology of the films in each case was also studied using scanning electron microscopy. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Epoxy resins are extensively used in various fields such as adhesives, coatings, and other high performance materials. They exhibit generally superior characteristics such as high chemical and corrosion resistance, good mechanical properties, and excellent thermal resistance.[1] Due to the high crosslink density and low toughness of epoxy resins after curing, they suffer from several drawbacks. For example, brittleness, poor resistance to crack propagation, and low impact strength. These drawbacks are also common for other thermosetting resins.[2] It is desirable to enhance toughness of thermosetting resins without influencing other useful properties.[3,4] Conventional modifiers usually employed for epoxy resins such as rubbers, thermoplastics or glass particles are known for their ability to affect the resin glass transition temperatures (T_g) by different levels.[5] However, this was always accompanied by processing limitation of the resin. No efficient toughening agent thus seemed to be applicable to epoxy resins without affecting the general performance of the resins.

Mezzenga et al.[6] reported in an intensive study that property improvements in epoxy composites can be achieved using some commercially available dendritic hyperbranched polymers (HBPs) as additives (can be fully soluble or phase-separating). Surprisingly, the additives showed more efficient toughening and internal stress reduction properties in case of the phase-separating additives, which could be ascribed to the modified branched network morphology. Full solubility or phase-separation is a function of solubility and polarity of these materials. Further, the authors expected that the unique structure of these polymers might solve problems related to processing limitations.

PAMAM[7,8] received great attention in the last few years because it can be prepared in a simple way with a diversity of chemical forms. A variety of structures can be tailored during synthesis by reaction of a monomer like methylacrylate (MA) with a wide range of amines, such as diethylenetriamine (DETA) or ethylenediamine (EDA), via alternative Michael addition and amidation steps thus the resulting structure grows in a divergent manner. This leads to a variable number of amido and tertiary amino units in their backbone and either many primary amino groups in their terminal HB chains if the charged MA : amine

ratio is around 1 (hydrophilic) or many methoxy groups if the charged MA : amine ratio is around 2 (hydrophobic). Thus, the most important variable parameter is the feed ratio of the reaction components, which results in either hydrophilic or hydrophobic HBPs. Therefore, it is actually a prominent parameter in determining the compatibility with the epoxy system of interest. In addition, the produced HBPs can additionally show different properties according to the type of amine employed. The amine type is thus a key factor in determining the extent of branching and types of repeating units. This causes in turn a dramatic difference in their solubility, polarity, and glass transition temperatures.[8]

HB PAMAM commercialization, in different chemical forms, is fast mounting nowadays. This advantage along with the ease of preparation in one-step reaction translates into cheaper price with respect to other commercially available HBPs. Thus, our attention was drawn in this study for the use of different chemical forms of PAMAMs in adhesive formulations of a fast curing epoxy as toughening additives and investigating the effect of this inclusion on the properties of the resulting coating films and adhesion strength on metallic substrates.

Therefore, four different types of HBPs were prepared in one-step reactions according to previous reports.[8,9] The types of HBPs are HP(MA-EDA) 1; HP(MA-EDA) 2; HP(MA-DETA) 1.2; HP(MA-DETA) 2. The number after each structure refers to the feed ratio of MA to EDA/DETA, so the samples denoted with 2 are considered hydrophobic because higher conversion of the amino groups into methoxy groups took place during the Michael addition. This increases accordingly the tendency of these hydrophobic samples towards apolar media. On the contrary, the samples denoted with 1 or 1.2 are considered hydrophilic because only a minor portion of the total primary amino groups was converted to methoxy groups. In this way, the compatibility of the prepared HBPs with a diversity of epoxy systems can be broadly tailored.

To make the difference between these structures more explicit, they can be approximately arranged in the following order on the basis of polarity: HP(MA-EDA) 1> HP(MA-DETA) 1.2 > HP(MA-EDA) 2 > HP(MA-DETA) 2. However, they can be arranged in the following order according to primary amino group contents: HP(MA-EDA) 1> HP(MA-DETA) 1.2 > HP(MA-DETA) 2 = HP(MA-EDA) 2 while according to degree of branching the following order is suggested: HP(MA-DETA) 2 > HP(MA-EDA) 2 > HP(MA-DETA) 1.2 > HP(MA-EDA) 1. Trials to measure exactly the degree of branching of these polymers failed because of the rather complicated structure and existence of different types of repeating units.[8]

MATERIALS

The MA, DETA, and EDA were purchased from Aldrich. Fast curing epoxy resin, under trade name EPOX-635412, was delivered with its own hardener from US Composites Company. All other chemicals were of laboratory grade and used without further purification.

TECHNIQUES

Synthesis of HBPs

EDA and DETA were reacted, each individually, with MA in different ratios of MA/amine (1 and 2 for EDA and 1.2 and 2 for DETA).[8] The reaction goes simply in each case by dropwise addition of MA into a flask containing the required molar ratio of amine dissolved in an appropriate amount of methanol under continuous stirring at room temperature for about 2 days then the solvent was removed under vacuum. The reaction was then kept to progress for 1 h at 60°C, 2 h at 100°C, 2 h at 120°C, and 2 h at 140°C while applying vacuum beyond each step to remove excess reagents.

Preparation of Epoxy Formulations with HBPs

Several epoxy formulations were designed into four main groups. Group 1 [based on HP(MA-EDA) 1] was divided into eight samples, A1–A8, that differ in their HBP concentration as toughening additive and adhesion promoter as well. The HBP was incremented by 0.5% in the range 0.5–4% based on the total epoxy weight. Group 2, denoted as B1–B8, was based similarly on HP(MA-EDA) 2 while C1–C8 stands for samples based on HP(MA-DETA) 1.2 (group 3). As HP(MA-DETA) 2 was not so compatible with the solvents mixture employed during blending with the appropriate HBP so its formulations were designed into four samples only in the range of 0.5–2% (D1–D4) to avoid intensive phase separation during processing (group 4). In all cases, epoxy (80%) and the basic hardener (20%) contents were always kept constant. A blank sample (Z) was also included where no HBP was used at all but the sample was cured lonely with the provided commercial hardener supplied with the epoxy. Briefly, HBP is dissolved in a least amount of butanol : ethanol (1 : 1) then the mixture was added to the basic hardener (provided by the supplier) before finally mixed with the epoxy. For all formulations, the basic hardener was added to the epoxy by volume ratio of 1 : 4. In case of group 4 formulations, the butanol : ethanol mixture was replaced by chloroform : ethanol mixture (1 : 1) due to solubility limitations in the former solvents mixture. The prepared formulations were applied to substrates of either mild steel or tin panels using a brush within 15 min after mixing the hardener with the epoxy at room temperature. The mechanical properties evaluations were conducted after 7 days to ensure complete drying of the films.

Characterizations

Fourier transform infrared (FTIR) spectra of the HBPs were collected on a JASCO FTIR-6100E spectrometer, Japan, in normal transmittance mode for HP(MA-EDA) 1 and HP(MA-DETA) 1.2 (hydrophilic samples) whereas in attenuated reflectance mode for HP(MA-EDA) 2 and HP(MA-DETA) 2 (hydrophobic samples) because of samples rigidity. Baseline correction was applied to all spectra. JEOL ECA-500 MHz ^{1}H Nuclear Magnetic Resonance (NMR) spectrometer was used for recording the NMR measurements of the polymers using CDCl$_3$ as a solvent. The T_g of the polymers were determined under nitrogen atmosphere using differential scanning calorimeter (DSC), type NETZSCH STA 409 C/CD, operated at a heating rate of 10°C/min. Molecular weights determination of the polymers was
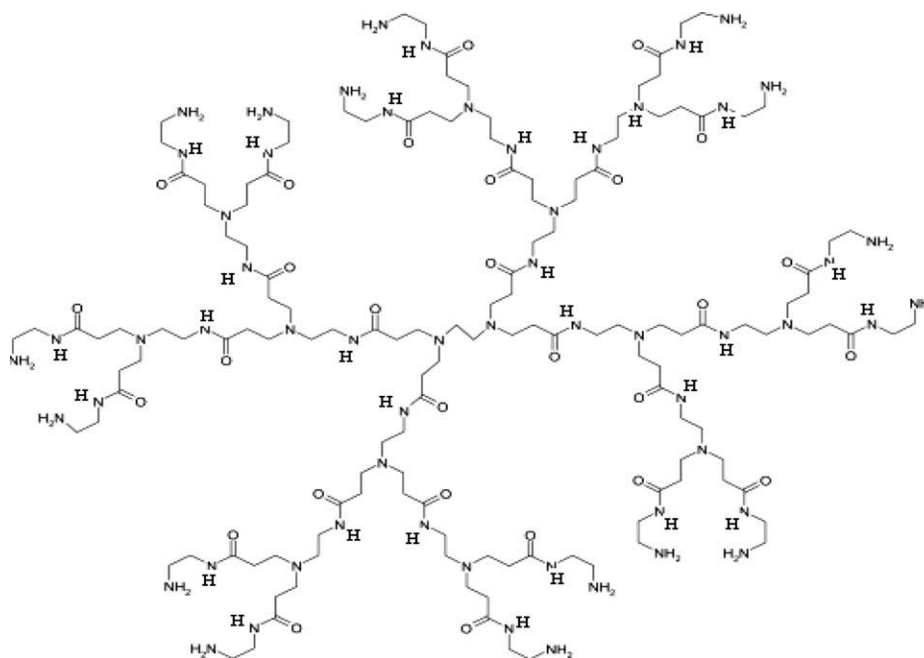
Scheme 1. General chemical structure of HB(PAMAM) with EDA as a core.

performed on a Gel Permeation Chromatograph (GPC), Germany, equipped with a refractive index detector, by injecting about 100 μL of polymer solution in DMF at room temperature, through a teflon filter with a mesh size of 450 nm, into Agilent 1100 columns connected in series. The measurements were carried out against a polystyrene standard after prior precipitation in THF in case of the hydrophilic samples to get rid of any trapped unreacted EDA or DETA. A scanning electron microscope (SEM), model JEOL-JXA-840A, with 30 kV operating voltage, was used to examine the morphology of primed steel panel substrates with the epoxy adhesive formulations.

Mechanical Properties

Impact resistance evaluation was performed according to ASTM D2794–93(2010). The inch-pounds (kg/m) at the impact failure end points were recorded as an average of several readings. A standard test method for pull-off adhesion strength of the coating films, using a portable adhesion tester (Posi Test Pull-off adhesion digital tester), was used according to ASTM D4541-09e1. Bending evaluation of films adhered to tin panels was performed on Sheen instruments LTD, England, according to ASTM D1737-85 to determine the cracking propagation resistance of the films. In all cases, measurements were taken in triplicates at least for each reading.

RESULTS AND DISCUSSION

Generally, the terminal groups of HBPs can strongly affect their reactivity[10] and other properties such as glass transition temperatures,[11] viscosity,[12] and solubility.[13] This can present enormous potential for applications in industry, for example, toughening additives,[14] rheology modifiers,[15] and low shrinkage restorative and reactive formulations.[16] HBPs applications in different coating technologies had been thus presented in the literature.[17,18]

Scheme 1 shows an example representing amino-terminated HBP with EDA as a core. In general, the amino-terminated PAMAMs are possessing high number of reactive sites in the form of primary amino groups and amide groups as well (Scheme 1) on the contrary to the methoxy-terminated PAMAMs where in a typical case some of the primary amino groups are converted into $-N(CH_2CH_2(C=O)OCH_3)_2$ groups in the presence of excess of MA (not shown in Scheme 1). The primary amino groups are expectedly capable of reaction with oxirane groups in an epoxy system through ring opening polymerization to cause hardening from one side and improve the adhesion characteristics to metallic substrates from another side. The high degree of branching and absence of chain entanglements with respect to linear counterparts is regarded as the source of the desired flexibility after incorporation into the epoxy network. This approach can be extended to any highly crosslinked resin, which may improve at least some properties without affecting others.
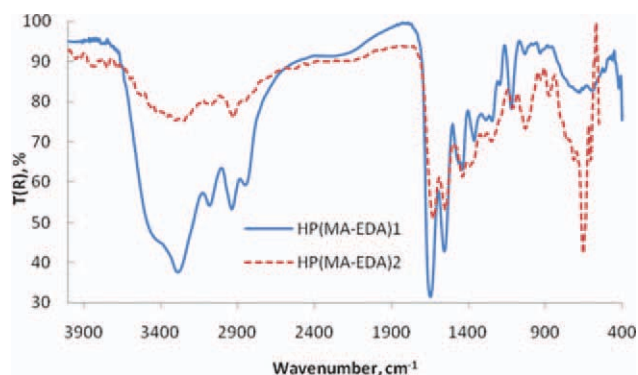
Figure 1. FTIR spectra of HP(MA-EDA)1 and HP(MA-EDA)2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
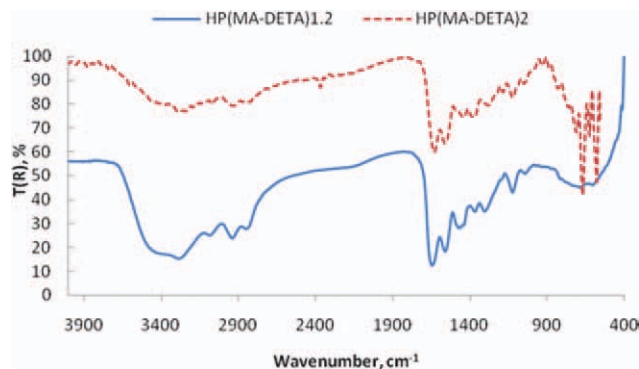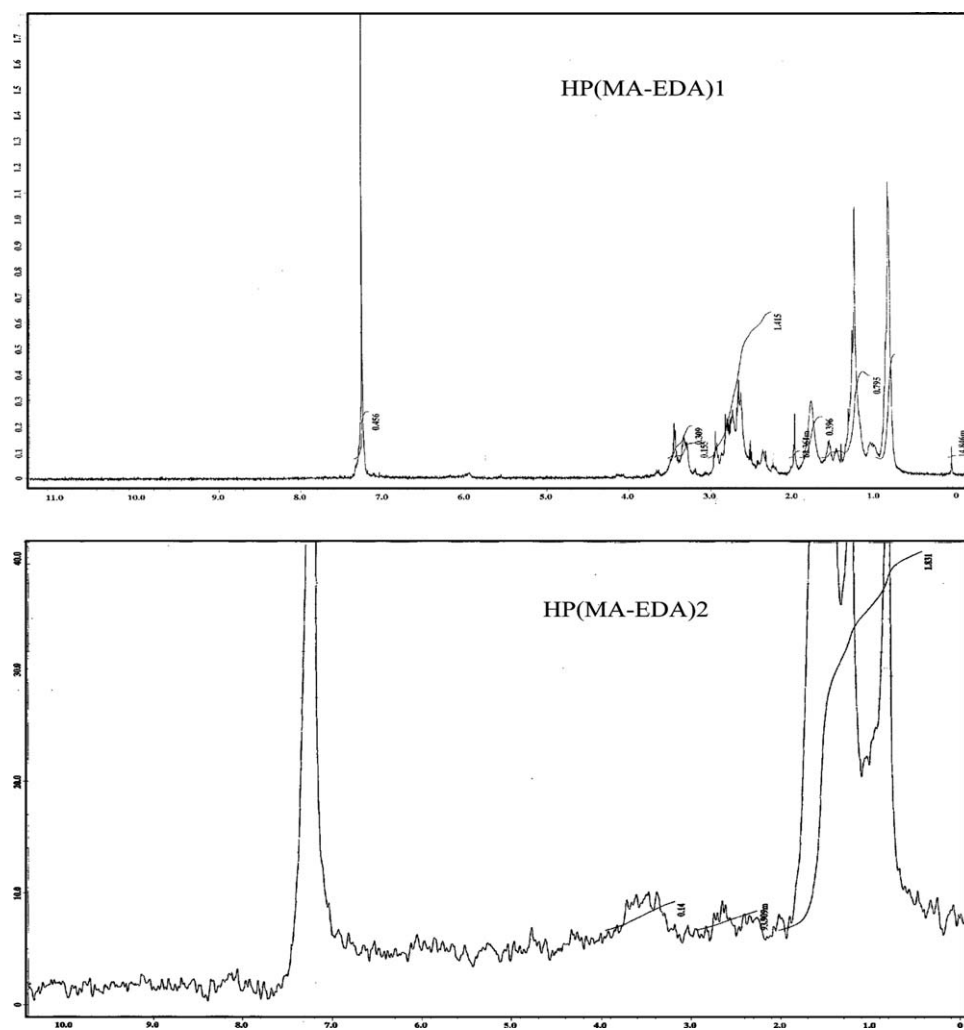
Figure 2. FTIR spectra of HP(MA-DETA)1.2 and HP(MA-DETA)2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The formation of HB PAMAMs in different forms with a reasonable divergent growth was confirmed by different techniques. Figures 1 and 2 exhibit the FTIR spectra of the prepared polymers. The spectra of HP(MA-EDA)1 and HP(MA-DETA)1.2 are very similar. In both cases, characteristic peaks of PAMAM amino groups in its structure, irrespective of the employed units for providing branching (EDA or DETA), are obvious. For HP(MA-EDA)1, a peak at 3286 cm^{-1} belongs to NH_2 groups in addition to another one at 2937 cm^{-1} ascribed to CH_2 groups. The carbonyl peak of acylamino groups is also apparent at 1644 cm^{-1} along with a peak at 1555 cm^{-1} that represents the NH and CN in the acylamino groups. In case of HP(MA-DETA)1.2, a slight perturbation can be recognized for the corresponding peaks; namely 3285 cm^{-1} for NH_2 groups and 2938 and 2846 cm^{-1} for the CH_2 groups. Further, the carbonyl peak appears at 1644 cm^{-1} while the 1559 cm^{-1} peak refers to the NH and CN in the acylamino groups. The obtained spectra in both cases are very close to the collected IR data by Liu et al.[8] for the same polymers, which may support the formation of the PAMAM in its amino-ended form.

However, carefully examining the attenuated reflectance infrared spectra for the hydrophobic samples: [HP(MA-EDA)2 and HP(MA-DETA)2], we found almost the same characteristic peaks assigned for the different groups present in the hydrophilic samples with the difference that the intensity of the NH_2 peaks largely diminished as a result of their consumption in the

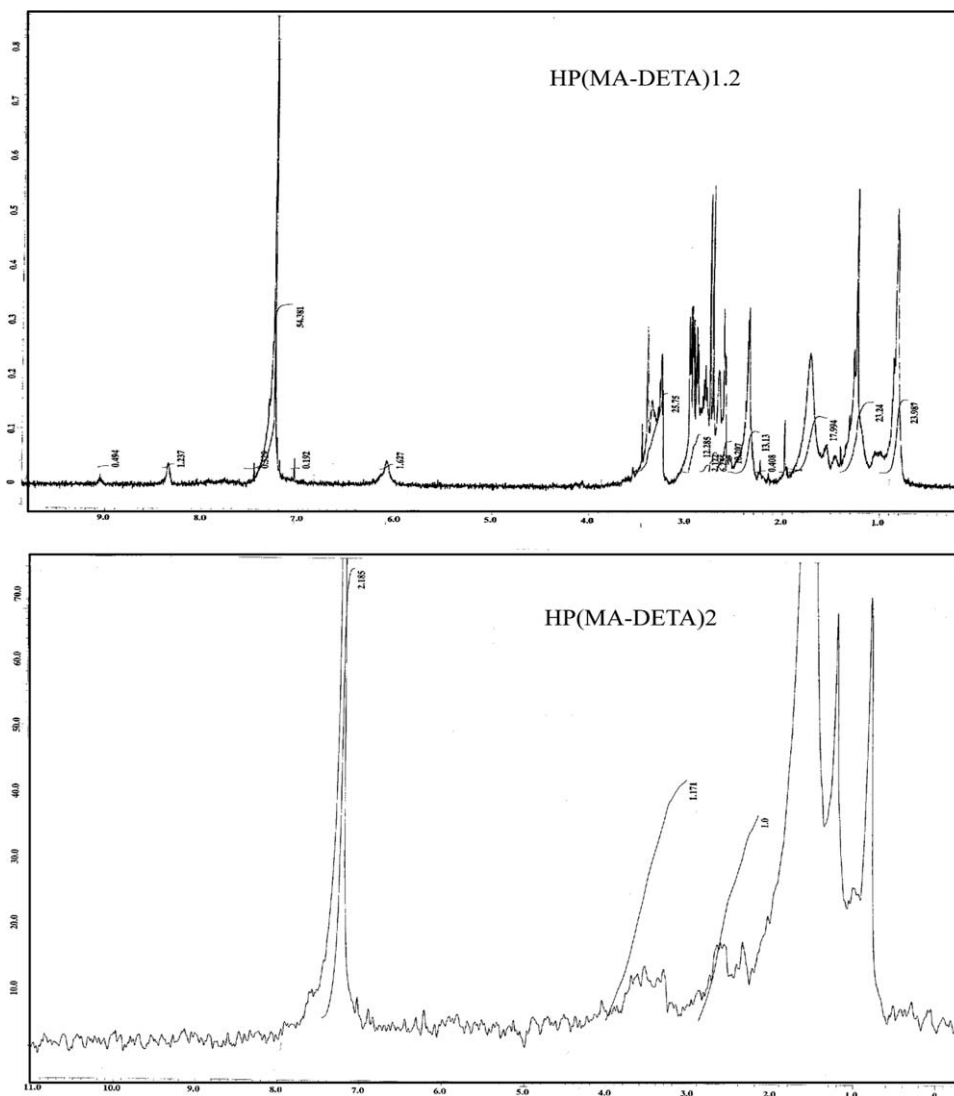**Figure 3.** ^{1}H NMR spectra of HP(MA-EDA)1 and HP(MA-EDA)2.

Figure 4. ^{1}H NMR spectra of HP(MA-DETA)1.2 and HP(MA-DETA)2.

conversion to methoxy groups. This may support the formation of PAMAM in its methoxy-ended form. It could not be relied on the peak intensity of the methyl groups at 1400 cm^{-1} for quantitative comparison between the hydrophilic and hydrophobic samples due to the different modes of collecting the spectra.

To further prove the polymers formation with the anticipated structures especially the availability of reactive amino groups even in case of hydrophobic samples, where the feed ratio of MA per one amine was equal to 2, ^{1}H NMR data measurements were recorded for the samples.

The corresponding ^{1}H NMR (CDCl$_3$) spectra of the polymers are displayed in Figures 3 and 4. In case of HP(MA-EDA)1 [Figure 3(a)] the signals referring to NH$_2$, NH (centered at 1.73 and 2.4 ppm, respectively), a group of signals assignable to CH$_2$ groups of different chemical environments (2.7–3.1 ppm) and some signals (3.25–3.5 ppm) that belong to CH$_3$ neighboring oxygen, are obvious. Collecting the spectra of HP(MA-EDA)2 [Figure 3(b)] was rather complicated due to the weak solubility

in CDCl$_3$, a peak characterizing the primary amine and acylamino groups (2.2–2.4 ppm), different signals of CH$_2$ groups with varying chemical environments (covering the range 2.5–3.6
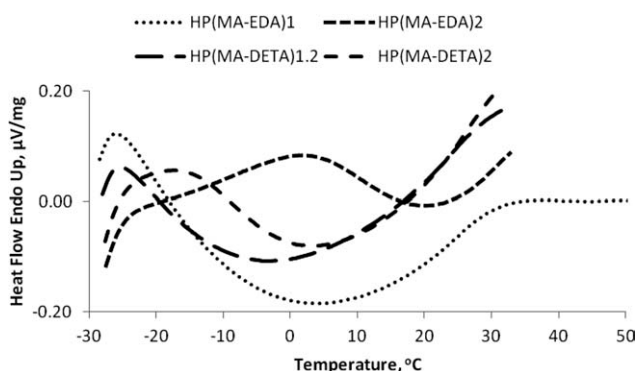

Figure 5. DSC curves of HP(MA-EDA)1, HP(MA-EDA)2, HP(MA-DETA)1.2 and HP(MA-DETA)2.
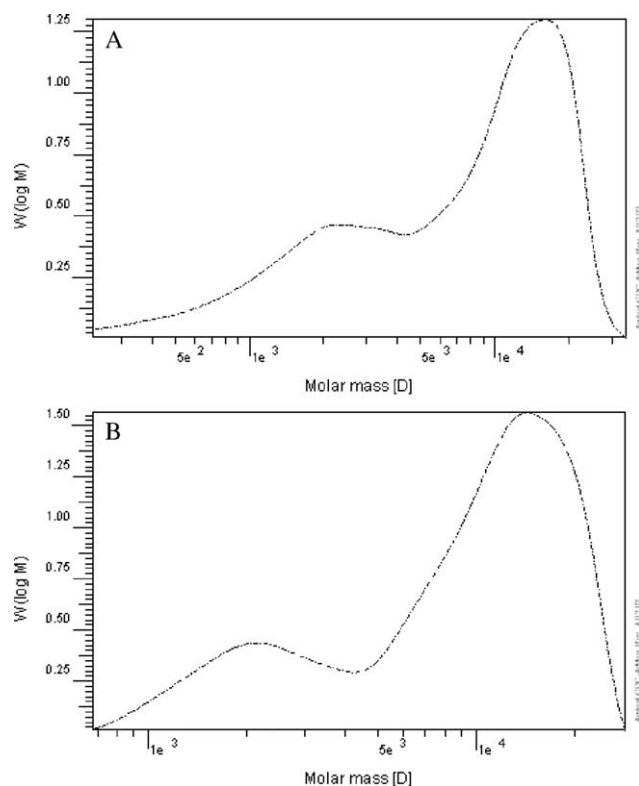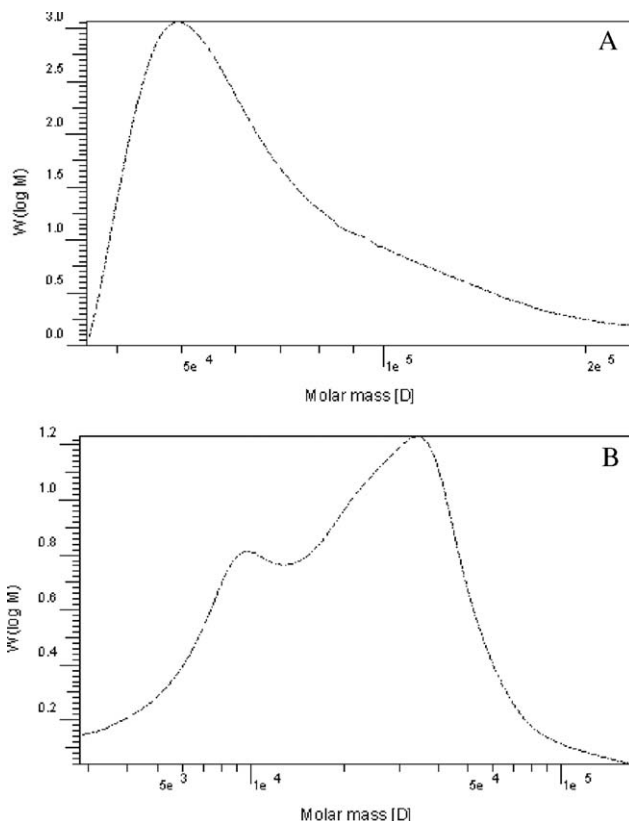
Table I. Molecular Weights Data Determined for the HBPs Using GPC

	$M_w \times 10^3$ (g/mol)	$M_n \times 10^3$ (g/mol)	PD
HP(MA-EDA) 1	9.67	3.14	3.1
HP(MA-EDA) 2	74.2	62.6	1.18
HP(MA-DETA) 1.2	10.78	5.2	2
HP(MA-DETA) 2	26.88	14.45	1.86

Figure 7. GPC profiles of a) HP(MA-EDA)2, b) HP(MA-DETA)2.

ppm) and a little CH$_3$—O signal (4.1 ppm) are easily detectable. In all collected spectra, the peak at 7.27 ppm refers to CHCl$_3$ as impurity in CDCl$_3$. The collected spectra for the PAMAMs based on DETA [HP(MA-DETA)1.2 and HP(MA-DETA)2, Figure 4(a, b)] appeared very similar to their analogous structures formulated with EDA but with tiny shifts that are mainly related to the difference in chemical structure between DETA and EDA.

Therefore, based on the recorded NMR data, we got strong evidence that the hydrophobic samples were still showing reactivity toward epoxy with their residual amino groups and that not all the amino groups were consumed during the conversion steps to methoxy groups.

Thermal analysis of the polymers was conducted using DSC for determination of the T_g. The runs for all polymers are collected together as can be shown in Figure 5. T_g values were nearly recorded at the meeting points of straight lines extended from around the onset and completion edges of the heat capacity steps in each case due to the broadness of the steps

thus found 5°C for HP(MA-EDA) 1; 20°C for HP(MA-EDA) 2; −3°C for HP(MA-DETA) 1.2; and 3°C for HP(MA-DETA) 2, respectively. These values are a little bit different from those obtained in the guiding study[8] under similar synthesis conditions. Such T_gs suggest obtaining PAMAM structures with a high degree of branching. Thus these structures are liable for use as toughening agents for thermosetting systems exhibiting high crosslink density upon curing. This can help to improve the epoxy properties, for example, less brittleness, more resistance to crack propagation and enhancing ability of withstanding stress.

Characterization with GPC for determination of molecular weights of the polymers is revealed in Table I and Figures 6 and 7. With respect to HP(MA-EDA) 1 and HP(MA-DETA) 1.2 [Figure 6(a, b)], it can be observed that the corresponding profiles of these polymers are bimodal, which means that the polymers are comprising 2 main fractions of polymeric species. However, a major part of these fractions is exhibiting a relatively high molecular weight in the range 5000–16,000 g/mol in both cases. In addition, the weight average molecular weights are very close for these polymers (10,000 g/mol) while HP(MA-EDA) 1 is exhibiting a higher PD (3.1) as compared to 2 for HP(MA-DETA) 1.2. Generally, the high PD may contribute to the broadening of the T_g steps observed in Figure 5 indicating the formation of different polymeric species having a big difference in molecular weight or branching.

However, Table I shows that the hydrophobic samples, where higher proportions of MA were applied with respect to the

Figure 6. GPC profiles of a) HP(MA-EDA)1, b) HP(MA-DETA)1.2.

Table II. Epoxy Adhesive Formulations Based on HBPs

Epoxy formula composition (g)	Blank (Z)	Group 1 A1–A8	Group 2 B1–B8	Group 3 C1–C8	Group 4 D1–D4
Epoxy	80	80	80	80	80
Hardener	20	20	20	20	20
HBP	–	0.5–4.0	0.5–4.0	0.5–4.0	0.5–2.0

amine [HP(MA-EDA) 2 and HP(MA-DETA) 2], acquired much higher molecular weights (compare Figure 7 with Figure 6). This may support an assumption that the hydrophilic samples were discriminated by their known strong interaction with the GPC columns via the high content of amino groups. As well, the measured molecular weights data for star and branched polymers using GPC technique should be carefully considered if their measurements are carried out against a linear standard or using a refractive index detector. Under such cases, lower values than the actual ones are supposed to be obtained due to their smaller hydrodynamic radii with respect to linear polymers.[19] Further, the difference in power of solvency of DMF for HP(MA-EDA) 2 and HP(MA-DETA) 2 with respect to the hydrophilic counterparts is also playing a role in this context due to also the influence of this on the hydrodynamic radii.

Recently, our group prepared various dendritic PAMAMs via a multistep sequential addition route and attempted successfully to use them as multifunction additives to a type of thermosetting resins (urea-formaldehyde), which are widely applicable in industry as a wood adhesive system.[20–23] It was found that most of the resin properties were significantly improved. Despite the fact that the sequential addition route is laborious and tedious, it provides more appropriate growth giving rise to well-defined generations. However, it was found that the overall behavior after modification became too complicated as a function of their generation and terminal functional groups as well. Accordingly, the one-pot route was tracked in this work for simplicity and to infer a more practical way to the proposed approach.

The fast curing of the epoxy used in this work results usually a rigid laminate. Hence, it is foreseen that the intervention with HBPs may enhance some properties of its coating or adhesive films from one side and facilitate the processing from another side. To check the wide-ranging viability of this approach we selected purposely a commercial type of fast curing epoxy.

Table II lists the recipes of all epoxy formulations designed with the HBPs as toughening additives. Measurements of mechanical properties were carried out on coating films of the epoxy formulations after curing to demonstrate the action of the additives.

Impact resistance was the property that improved outstandingly in the presence of the HBPs as reactive toughening agents (Figure 8). The blank exhibited impact resistance of 0.635 Kg/m, increased significantly for all formulations with HBPs concentrations above 1%. However, this occurred for all formulations by

different extents except for A1 and D2–D4. The maximum impact resistance was obtained distinctively for A8, B7, B8, and C4–C8 (1.84 Kg/m), which corresponds to a 3-fold increase with respect to the blank.

This can be explained by the fact that after these additives became parts of the epoxy network structure, their inclusion expands the distance between crosslink points throughout the network structure. In this way, as soft segments positioned between highly rigid segments, they play the role of shock absorbing domains. These domains can reduce the crosslink density and provide sufficient flexibility to the rigidified epoxy film after curing. Hence, the impact resistance was markedly improved. This finding is in accordance with results obtained by other researchers who used other HBPs or low generation PAMAM and found them as effective toughening agents for thermosetting materials such as bismaleimide,[24] urea-formaldehyde resins,[25] and DGEBA epoxy.[26] However, they did not extend their use for adhesion or coating purposes.

Unfortunately, this improvement did not extend to formulations of D2–D4 that are based on HP(MA-DETA) 2. This is assumed to originate from the poor compatibility between the epoxy from one side and HP(MA-DETA) 2 from another side leading to some extent of phase separation and improper curing.

The influence of the amino groups of the additives on promoting the coating adhesion to metal substrates was estimated by Pull-off adhesion test of epoxy films after adhesion on the substrates. The adhesion strength values of films representing the different coating formulations on metal substrates as a function of HBP type for each concentration are shown in Table III.

The pristine sample without any addition of HBP gave rise to 3.36 MPa. The formulations of groups 1–3 behaved almost the same with respect to their adhesion potential after the addition
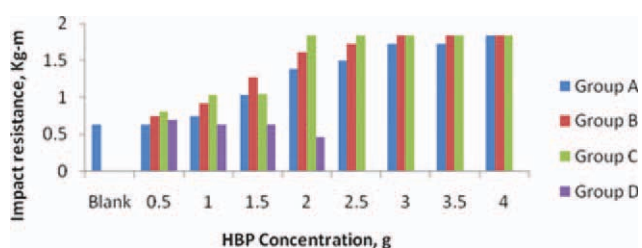

Figure 8. Impact resistance values corresponding to the epoxy formulations co-hardened by HBPs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Pull-Off Adhesion of Epoxy Formulations

HBP (g)	Formula symbol	Pull-off adhesion (MPa)	Group 1	Group 2	Group 3	Group 4
0	Z	3.36	–	–	–	–
0.5	X1	–	3.36	3.36	3.49	3.36
1.0	X2	–	3.61	3.62	3.73	3.34
1.5	X3	–	3.87	3.96	4.11	3.29
2.0	X4	–	4.12	4.13	4.16	3.25
2.5	X5	–	4.12	4.13	4.08	–
3.0	X6	–	3.95	3.95	3.91	–
3.5	X7	–	3.91	3.87	3.84	–
4.0	X8	–	3.87	3.66	3.61	–

of each corresponding HBP (Table III), which may reflect that even for the hydrophobic HBPs, a significant amount reactive amino groups were available to participate in the curing and adhesion processes which may have proceeded competitively. The pull-off adhesion starts to increase reaching maximum at concentrations of HBPs around 2–2.5% then started to go
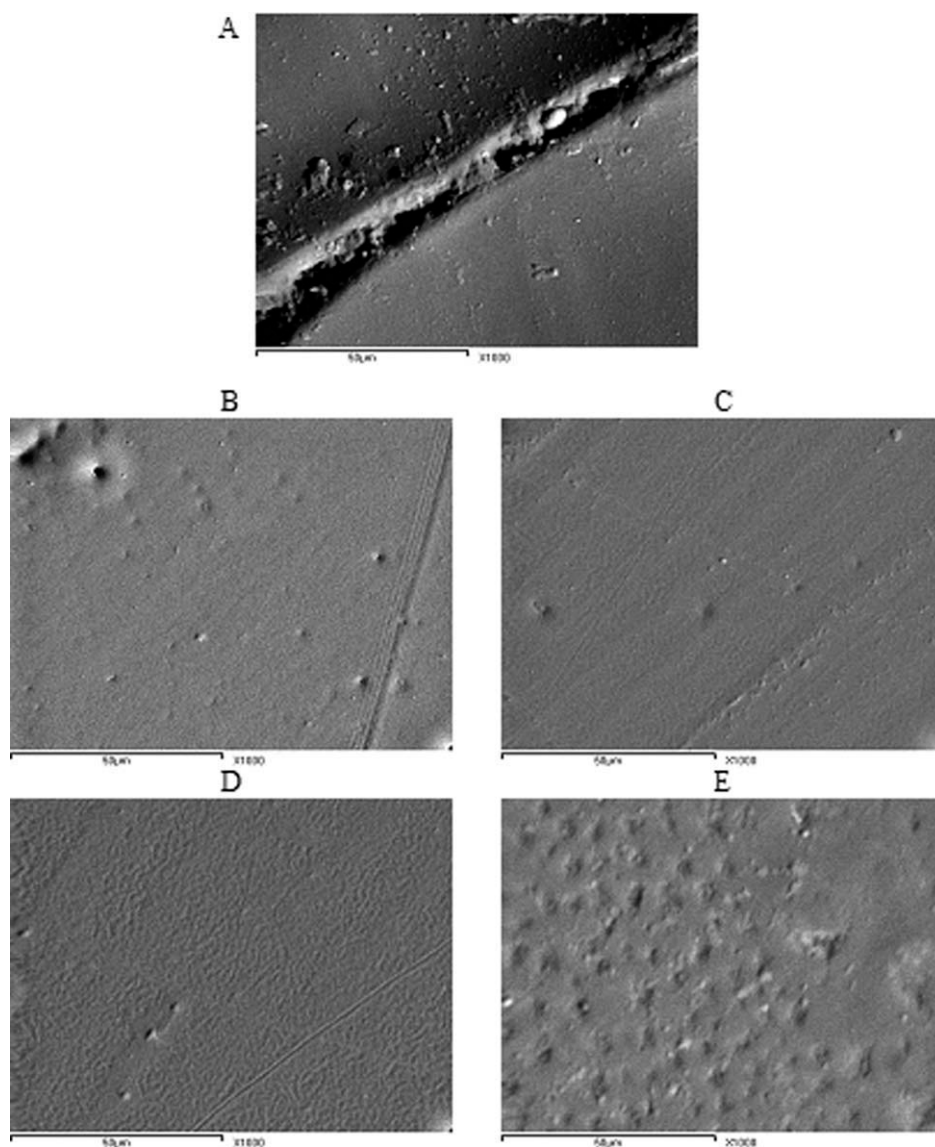
Figure 9. SEM photographs of coating films of a) neat epoxy and b) A4, c) B4, d) C4, e) D3, formulations on steel adherends.

down with more addition but remained even better than the control. Again, group 4 did not respond positively to the addition of HBP, which may be attributed so simply to phase separation encountered during curing thus could not permit the chains to expand at ease in the medium to expose their available amino groups to be involved in the curing process and network formation. Eventually, we can therefore suppose that these additives can also interact with the metal surface and cause maximum enhancement up to a certain concentration (2–2.5%). Above this limit, the adhesion was overwhelmed most likely by the over-plasticizing effect of the additives or due to preference of the epoxy to self-cure cohesively in the presence of increasing amounts of HBPs rather than to adhere robustly to the substrate. This suggestion could be supported visually by occurrence of interfacial failure in the majority of samples. It is worthy to note that the thickness of the coating films was not exceeding 100 μm, which is the main reason why the pull-off adhesion results of these samples seem of poorer quality as compared with commercial epoxy hardened by conventional polyamines.

Bending is another property that is very much related to the acquired elasticity or ductility in material. The general mode of fracture after interference with HBPs during curing should influence this property. Bending tests revealed that most of the adhered films on tin substrates survived and passed the test successfully except the blank and in very few cases (A1, B1, and D1–D4) where the failure was obtained in the form of intensive cracking within the coating films. With respect to A1 and B1, it seems that concentration factor virtually plays a role in this case so the HBP was not sufficient to take part in the curing reaction and modification of the network structure while for formulations of group 4 the phase separation prevails so the HP(MA-DETA) 2 existed as a nonreactive additive in this case and did not contribute effectively into the formed network. As a result, poor resistance of the coating film to cracking is attained leading eventually to a failure.

The morphology and homogeneity of the epoxy coating layers [neat epoxy (blank) in addition to A4, B4, C4, and D3 formulations] on steel substrates were examined using SEM as illustrated in Figure 9.

The SEM images reveal uniform coating and good interfacial interactions on steel adherents for the formulations based on the HBPs. The films looked even better than the blank that exhibited wetting difficulty and weak interfacial adhesion represented by appearance of surface defects within the coating layer. D3 was an exception and actually associated with poor spreading and emergence of some agglomerations. This may have been induced by the rapid curing and initiation of phase separation at an early stage of the reaction in this case. This ensures that the proper wetting and nonhindered spreading was aided by the HBPs insertion in the other cases through reactive blending with the epoxy itself in addition to their involvement in interfacial adhesion on the metallic substrates.

The above results altogether confirm that different forms of PAMAMs can be used to provide a sustainable toughening and enhancing adhesion effects for thermosetting adhesive systems under optimized conditions without affecting other properties. These advantages could be applied for a fast-curing type of epoxies, which are known to cure in a short time on the expense of some properties. Additionally, PAMAMs are advantageous with respect to other comparable additives because they are less volatile, less poisonous, and can be well tailored in many chemical forms to meet compatibility requirements with a wide range of epoxy systems.

CONCLUSIONS

Adjusting MA/amine feed ratio along with extent of branching according to the amine type, during simultaneous Michael addition and amidation reactions, can be a versatile tool to obtain a series of reactive HB poly(amidoamine)s showing remarkable different chemical characteristics. The relevant contents of their primary amino groups and hydrophilicity (hydrophobicity) are the main reasons beyond exhibiting broad reactivity. Thus, their compatibility can be well tailored to fit the use as multifunction additives to modify properties of many epoxy systems with wide varieties of chemical structures.

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