

Poly(ester-amine) Hyperbranched Polymer as Toughening and Co-curing Agent for Epoxy/Clay Nanocomposites

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The marriage between hardness and flexibility of epoxy resins (improved toughness) is a desired feature, which broads their application in various industrial fields, especially for high impact resistance purposes. Accordingly, this work aims to improve toughness properties of epoxy resin (Epon-828)/Ancamine (curing agent) system using amino-terminated hyperbranched poly(ester-amine) [Poly(PEODA-NPA)] (HP) as toughening and/or co-curing agent, in presence of organo-modified Montmorillonite clay (OMMT) as a reinforcing filler. HP was synthesized via Michael addition reaction of poly(ethylene glycol) diacrylate (PEODA) to *N*-methyl-1,3-propanediamine (NPA). Chemical structure and molecular weight of HP were elucidated using infrared (FTIR) spectroscopy and gel permeation chromatography (GPC) techniques, respectively. Epoxy/OMMT nanocomposites toughened with HP (at different concentrations) showed remarkable improvement in their toughness without any adverse effect on the other physico-mechanical properties. The optimum concentration of HP and OMMT was found to be 20 wt % and 1–3 wt% of the epoxy resin, respectively. The extent of exfoliation and dispersion of OMMT platelets within the epoxy cured films was assessed by X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements. In addition, thermal gravimetric analyses (TGA-DTA) of epoxy/OMMT nanocomposites toughened with HP showed a slight increase in their decomposition temperature, particularly at low OMMT loading. POLYM. ENG. SCI., 53:1011–1020, 2013. © 2012 Society of Plastics Engineers

INTRODUCTION

In the past decades, thermosetting polymers and particularly epoxy resins have extensive applications in various industrial fields such as coatings, adhesives, laminated boards, molding resins, electro-insulating varnishes, high performance composite materials, and aerospace industries

[1, 2]. This can be attributed to their terrific features like excellent mechanical and chemical properties, including high tensile strength and modulus, super adhesion to various substrates, excellent moisture and chemicals resistance, low shrinkage in cure, and excellent dimensional stability. However, some properties need further improvement to fulfill more demanding applications, especially for high impact resistance purposes [3–6]. Thus, the marriage between hardness and flexibility (improved toughness) is a highly desired feature, which opens the way for more industrial applications for epoxy resins. To achieve this target, many researchers have incorporated a second component to improve toughness properties of epoxy resins, including rubber, amino-terminated butadiene nitrile rubber, polyurethane, silicone and some other thermoplastics as modifiers for the epoxy resins [7–12]. On the other hand, the incorporation of a nanoscopic reinforcing phase such as SiO₂ particles, TiO₂, ZnO and particularly expandable layered silicates, like Montmorillonite (Na⁺MMT) clay, to a polymer matrix imparts extraordinary properties, which enable more applications outside the boundaries of traditional composites, even at low filler loadings [13–15]. Beside its low price, the extensive use of the naturally abundant Montmorillonite (Na⁺MMT) clay as a reinforcing filler for epoxy resins is attributed to the intercalation and/or exfoliation of its layers during mixing with epoxy matrix, which enhance the interfacial interaction between the two phases. The improvement in mechanical, barrier, thermal, and optical properties has been reported for various epoxy/clay composites at low filler loading [16–25]. In addition, it is worth to mention that the crosslinking or curing agent has crucial influence on the final properties and applicability of epoxy resins. Commercial amines, particularly low molecular weight cycloaliphatic amines are widely used for curing of epoxy resins at room temperature due to their high reactivity, and consequently lead to highly cured epoxy resin with high hardness and low toughness. However, most of commercial amine hardeners are highly volatile, toxic, usually

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dissolve in organic solvents, cause skin irritation and sensation, and very sensitive to CO₂ in air which consequently strict stoichiometry with respect to epoxy resin [26]. To prevent or restrict the use of these types of curing agents, it was important to tailor a high molecular weight amine (low volatility) to be used as an alternative for commercial amines or used as co-curing agent, and also to improve the toughness of the epoxy resin, simultaneously. We suggest that the most important materials that can achieve this purpose are hyperbranched polymers. Recently, hyperbranched polymers and dendrimers have attracted much attention because of their brilliant architectures as highly branched polymers, and their unique properties including lower viscosity, higher solubility, in addition to the large number of their terminal groups which offer versatile crosslinking possibilities, as compared with their equivalent linear analogues. In addition, hyperbranched polymers are synthesized via one pot reaction and do not require successive purification stages like dendrimers [27–31]. Several types of hyperbranched polymers have been prepared such as polyphenylenes, polyethers, polyesters, polyamides, polycarbonates, poly(etherketones), and polyurethanes [32–38]. Indeed, hyperbranched polymers are readily feasible for various potential applications such as multifunctional initiators, rheology control compounds for surface modification, nanofillers for polymer nanocomposites, nanoporous generators for low dielectric constant insulators, coatings and even in biomedical applications as drug delivery systems [39–49]. Practically, Simon et al. have noticed an improvement in the impact properties upon using a ternary blend nanocomposites based on a combination of epoxy resin, hyperbranched epoxy and a layered silicate [50]. Recently, an improvement in the surface hardness, scratch resistance, and flexibility of hyperbranched polyester resin (Boltorn H30)/clay nanocomposite was noticed in presence of hexakis (methoxymethyl) melamine (HMMM) as crosslinker [51]. It was found that the hyperbranched polyesters promoted the exfoliation, and stabilized the exfoliated structure of the clay platelets after drying, which was mostly caused by the compact globular structure of the hyperbranched polymer, with a large number of polar end-groups and a relatively hydrophobic core, preventing the molecules from collapsing onto the clay layers [52–55]. Furthermore, a high-water-content, moldable, and self healing hydrogel with excellent mechanical strength was obtained by using native MMT in combination with a dendritic polyester based on 2,2-bis(methylol) propionic acid (Bis-MPA) [56].

Therefore, this work was devoted to explore the application of hyperbranched polymers as alternative for low molecular weight commercial amine hardeners and as modifying agents to improve toughness properties of epoxy resins. Accordingly, amino-terminated hyperbranched poly(ester-amine) (HP) was prepared in one pot reaction based on Michael addition of poly(ethylene glycol) diacrylate (PEODA) to *N*-methyl-1,3-propanediamine (NPA).

The prepared HP was tested as toughening agent for the epoxy resin (Epon-828). In addition, HP was also tested as alternative or as co-curing agent with the commercial amine hardener Ancamine (A) of epoxy resin (Epon-828), in presence of Montmorillonite organoclay (OMMT) nanoparticles as reinforcing filler. The effect of HP and OMMT contents on the physico-mechanical and thermal properties of the cured epoxy/OMMT composites was investigated. Furthermore, degree of intercalation/exfoliation and degree of dispersion OMMT within the epoxy resin and their effect on the final properties of the cured epoxy/OMMT composites were also studied in terms of XRD, TEM and TGA measurements.

EXPERIMENTAL

Materials

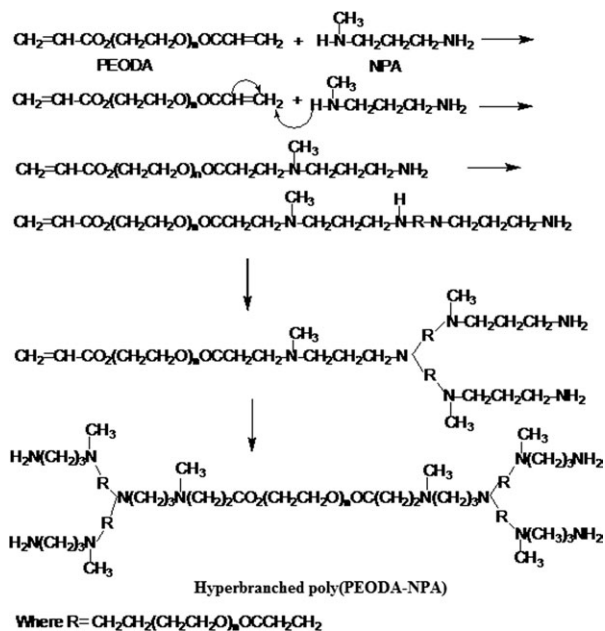
Poly(ethylene glycol) diacrylate [PEODA] of M_w 700 g mol⁻¹ (Aldrich) and *N*-methyl-1,3-propane diamine (NPA) (Aldrich), were used. The epoxy resin (Epon-828), a prepolymer of diglycidyl ether of bisphenol A (DGEBA), and its commercial amine hardener (Ancamine[®] 1618) were kindly supplied from Yasmis-Misr Company for Construction Chemicals, Cairo, Egypt. Ancamine[®] 1618 is a modified cycloaliphatic amine hardener produced by Air Products Company. The mixing ratio by weight of Epon-828:Ancamine[®] 1618 is 100:60. Montmorillonite clay (Na⁺MMT) (Sigma-Aldrich), with cationic exchange capacity (CEC = 88 meq/100 g) was used. The cationic emulsifier cetyl trimethyl ammonium bromide (CTAB) (Aldrich) was used as treating agent for montmorillonite (MMT) clay to prepare the organoclay (OMMT). All other chemicals used were of pure grade and they were used as received.

Preparation of Hyperbranched Poly(PEODA-NPA)

Hyperbranched poly(PEODA-NPA) (HP) was prepared by the reaction of equimolar amounts of poly(ethylene glycol) diacrylate (PEODA) and *N*-methyl-1,3-propanediamine (NPA) as described before [57]. Briefly, 14 g (20 mmol) of PEODA in 15 mL chloroform were added drop wise to a solution of NPA, 1.763g (20 mmol) in 15 mL chloroform under continuous stirring. This mixture was kept at 35°C for 150 h, followed by pouring into a mixture of 600 mL acetone and 20 mL HCl (8M) solution. The pale yellow precipitate formed was washed several times with acetone, collected and dried under vacuum for further characterization. Synthesis route of the hyperbranched poly(PEODA-NPA) is represented in Scheme 1.

Preparation of Organoclay (OMMT)

Based on the cationic exchange capacity (CEC) of the Montmorillonite (Na⁺MMT) clay, an excess amount of cetyl trimethyl ammonium bromide (CTAB) was estimated, according to Eq. 1, and dissolved in 10 ml



SCHEME 1. Synthesis route of the hyperbranched poly(PEODA-NPA) (HP).

distilled water. Afterward, CTAB solution was added to another solution containing MMT clay dispersed in distilled water, at room temperature [58]. Then, the mixed solutions were heated up to 80°C under vigorous stirring for 6–8 h, followed by cooling at room temperature. The modified clay (OMMT) was separated by filtration and washed several times with distilled water to get rid of the unreacted CTAB. The filtrate was tested against AgNO₃ solution (1 g AgNO₃ in 100 ml distilled H₂O) to obtain a modified clay without CTAB residuals. Then, OMMT clay was dried at 60°C under vacuum for 24 h. Finally, the clay was grinded in a mortar using a pestle into fine powder for further investigation.

$$\text{CTAB (g)} = 88(\text{meq}) \times \text{Clay(g)} \times 1.5 \times \text{Mwt of CTAB} / 10^5 \quad (1)$$

Where 88 meq/100 g represents the CEC value per 100 g of clay, and 1.5 (>1) indicates the excess amount of CTAB (intercalating agent).

Preparation of Epoxy/OMMT Nanocomposites

Epoxy/OMMT nanocomposites with different OMMT clay content (1–5 wt%) were prepared by mixing the organoclay with the epoxy resin at room temperature, using a high-speed shear mixer (3000 rpm) for 30 min. The mixture was subsequently sonicated for 1 h for further dispersion of clay in the epoxy matrix. Afterward and based on the weight of the epoxy resin, HP and/or the commercial amine (Ancamine) hardener was added to the epoxy/OMMT mixture, and then mixed for 5 min at room temperature using a high-speed shear mixer. The

produced mixture was degassed and applied on different metal and glass substrates using film applicator of wet film thickness of 100 μm to obtain epoxy/OMMT nanocomposite coating films with uniform film thickness. Then, the coating films were left to dry in air for 24 h, followed by accelerated curing in an air circulated oven at 60°C for 24 h. After that, the coating films were left for 24 h at ambient temperature, followed by physico-mechanical measurements.

Characterization

Chemical Composition Using FTIR Measurements. The chemical composition of the prepared hyperbranched polymer (HP) was assessed using Infrared spectroscopic technique [FTIR, 6100 Jasco, Japan]. In addition, FTIR was also used to investigate the modification of the virgin clay (MMT) to form the organoclay (OMMT). The spectra were recorded on KBr disc, at 4 cm⁻¹ resolution, from 4000 to 400 cm⁻¹.

Gel Permeation Chromatography (GPC) Measurements. Weight average molecular weight (*M_w*), number average molecular weight (*M_n*) and polydispersity index (PDI) of the prepared HP were determined by gel permeation chromatography [Agilent 1100 series, Germany] using linear polystyrene as a standard for calibration, and *N,N*-dimethylformamide (DMF) as the eluent at a flow rate of 1 ml min⁻¹. The refractive index detector was G-1362A with 100-10⁴-10⁵ Å ultrastyrigel columns connected in series.

Thermal Gravimetric Analysis. Thermal stability of the epoxy/OMMT nanocomposites was investigated using thermogravimetric and differential thermal analyses (TGA/DTA) using thermal analyzer (Shimadzu DTG - 60H, Japan) at 10°C min⁻¹ heating rate, from room temperature up to 700°C, under inert N₂ atmosphere.

X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) Measurements. The degree of intercalation/exfoliation of the organoclay was evaluated using X-ray diffractometer [Bruker D8 Advance, USA] with Cu Kα radiation (λ = 1.54) at K_v = 40 and mA = 40. On the other hand, the degree of organoclay dispersion within the epoxy matrix was investigated using transmission electron microscope [JEOL TEM microscope, Japan].

Physico-mechanical Properties of Epoxy/OMMT Nanocomposites. Physico-mechanical properties of the epoxy cured films were examined according to international standards methods. Briefly, neat epoxy and epoxy/OMMT nanocomposite films were applied to glass substrates to determine their hardness and gloss, while coating films were applied to steel substrates to determine their mechanical properties (cupping, impact and adhesion tests) after curing. Gloss test of the cured epoxy films

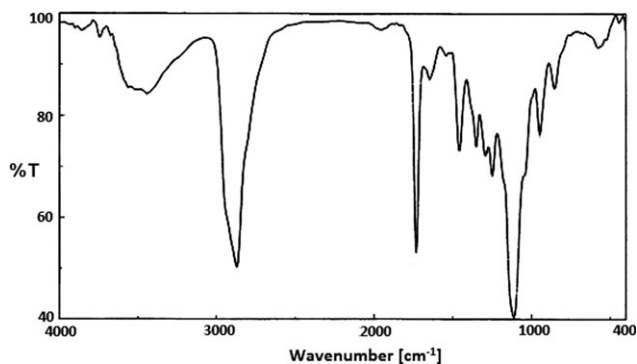


FIG. 1. IR spectrum of the hyperbranched poly(PEODA-NPA) (HP).

was carried out using Eriechsen gloss meter 20–60–85° (Germany) at 60° angle of incident light [59]. Hardness was determined by using standard König pendulum hardness tester (Eriechsen, Model 299/300, Germany) [60]. Ductility or cupping test was performed to measure the flexibility and adhesive quality of epoxy cured films on the metal substrate using Eriechsen cupping instrument (Germany) [61]. This test determines the depth (in mm) of a hemispherical indenter, which applied under uniform pressure to the uncoated side of the test panel, until the coating film tears or flakes. In addition, the resistance of epoxy cured films to the effects of rapid deformation (impact) was measured using Eriechsen impact tester (Germany) [62]. In this test, the epoxy cured film was subjected to rapid impact of 1 kg weight falling from a specific height (60 cm), and then the impacted area was checked for any cracks around the impact point using a magnifying lens (10×). Adhesion of the cured epoxy films on the metal substrate was determined using cross-cut tester (Sheen Company, UK) [63]. This test is carried out by making cutting through the paint film penetrating down to the substrate surface in one steady motion using a multicross cutter with 11 blades in cutting distance of 1 mm, followed by a further sectional strip in a right angle with the preceding sectional strip resulting in a grid of 100 squares (cross-cut). The rate of adhesion was determined according to the percent of detached or chipped off area of the coating cut sections, using a special adhesive tape. All physico-mechanical records were the average of three replicates.

RESULTS AND DISCUSSION

Preparation and Characterization of Hyperbranched Poly(PEODA-NPA)

The hyperbranched poly(PEODA-NPA) (HP) was prepared by one pot reaction during direct polyaddition of polyethylene glycol diacrylate (PEODA) to *N*-methyl-1,3-propane diamine (NPA). The chemical structure of the prepared HP was verified using FTIR technique. As indicated in the infrared spectrum of HP in Fig. 1, the characteristic peaks appeared at 1732 and 1647 cm^{-1} are related to the vibration

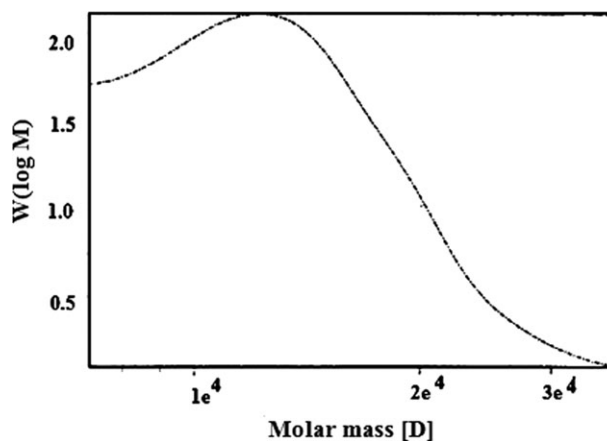


FIG. 2. GPC chart of the hyperbranched poly(PEODA-NPA) (HP).

bands of carbonyl group (C=O) and C=C, respectively. The broad splitted band at 3446 cm^{-1} refers to N—H stretching of the primary (terminal) amino groups. The sharp peaks at 2871 and 1111 cm^{-1} are related to CH_2 and C—N stretching bands, respectively.

Molecular weight measurements of the prepared HP were determined using GPC technique, as shown in Fig. 2. The weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PDI) = M_w/M_n of the prepared HP were found to be 14,000 g mol^{-1} , 12,249 g mol^{-1} , and 1.14, respectively. The low PDI value refers to the narrow size distribution of the prepared HP, i.e., it seems to be monodisperse.

Preparation and Characterization of the Organoclay (OMMT)

The organoclay (OMMT) was successfully prepared by treatment of the virgin Montmorillonite (Na^+MMT) clay with the cationic CTAB surfactant. IR spectra of the virgin MMT clay and the organo-modified clay (OMMT) with CTAB are shown in Fig. 3. The emergence of

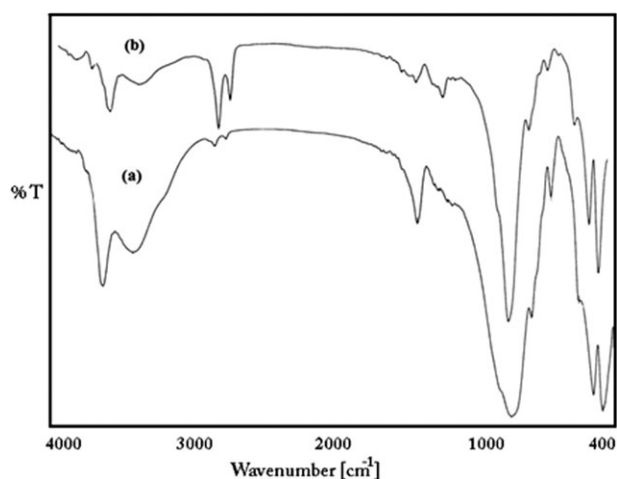


FIG. 3. IR spectra of Montmorillonit clay (a) before and (b) after modification with CTAB.

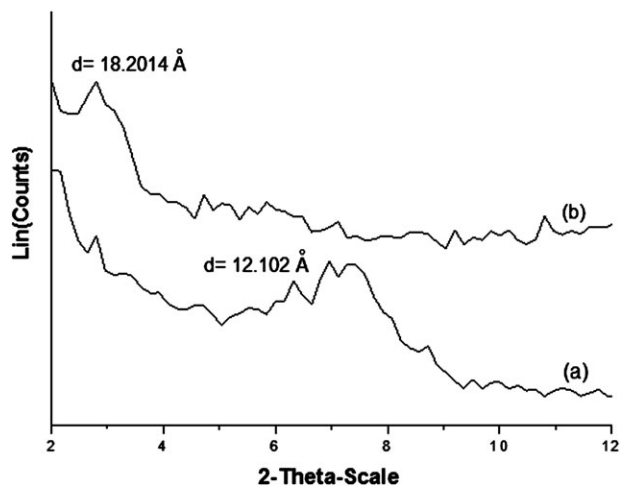


FIG. 4. XRD chart of Montmorillonite clay (a) before and (b) after modification with CTAB.

characteristic peaks at 2850 and 2950 cm^{-1} , which belongs to stretching vibration of CH_2 of the long hydrocarbon chain of CTAB, indicates to the successful treatment of MMT with CTAB. Furthermore, as shown in the XRD chart (Fig. 4), the shifting of 2θ peak of the virgin MMT clay ($d = 12.102 \text{ \AA}$) to a lower value ($d = 18.298 \text{ \AA}$) gives an evidence for increasing the intergallery space (d) between layers of the organoclay, which means the intercalation of CTAB between the platelets of Montmorillonite (Na^+MMT) clay.

Curing of Epoxy Resin With the Hyperbranched Poly(PEODA-NPA)

A comparison study was carried out between physico-mechanical properties of the cured films of the commercial epoxy resin (Epon-828/Ancamine) system (blank sample EA) and those (Epon-828/HP) cured with the prepared hyperbranched poly(PEODA-NPA) (HP) as alternative for the main hardener Ancamine, at different HP content, as shown in Table 1. It is clear from Table 1 and Fig. 5a that the pendulum hardness (320 s) of the epoxy

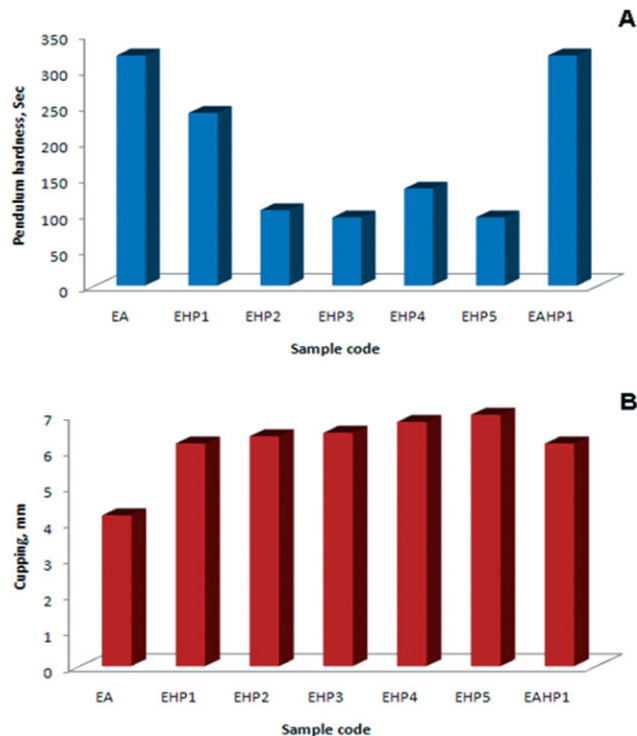


FIG. 5. Pendulum hardness (A), and cupping (B) of epoxy cured films at different epoxy:HP weight ratios, (EHP1, 100:20), (EHP2, 100:40), (EHP3, 100:60), (EHP4, 100:80), (EHP5, 100:100). EA blank sample is cured with Ancamine hardener at epoxy: hardener weight ratio (100:60) and EAHP6 is epoxy resin cured with Ancamine in combination with HP at epoxy:A:HP weight ratio 100:20:20. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cured films (blank sample EA) decreases to be 240 s (sample EHP1) upon using HP as an alternative for the main hardener Ancamine (A). The consecutive increase in HP content, from 20 to 100 wt%, led to further decrease in hardness of the cured epoxy films. On the other hand, impact strength and flexibility (cupping) of the cured epoxy coating films increased in parallel with HP content, as compared with the blank sample (EA) (Fig. 5b). This behavior could be attributed to the presence of long ethylene oxide ($\text{CH}_2-\text{CH}_2-\text{O}-$)— chain of PEODA in the

TABLE 1. Formulation and physico-mechanical properties of epoxy resin/HP cured films.

Sample code	EA	EHP1	EHP2	EHP3	EHP4	EHP5	EAHP1
Composition							
Epon-828 (epoxy resin) (g)	100	100	100	100	100	100	100
Ancamine (Hardener) (g)	60	—	—	—	—	—	20
Poly(PEODA-NPA) (HP) (g)	—	20	40	60	80	100	20
Physico-mechanical properties							
Hardness (pendulum) (s)	320	240	105	95	135	95	320
Impact test at 60 cm height	Fail	Pass	Pass	Pass	Pass	Pass	Pass
Cupping test (mm)	4.2	6.2	6.4	6.5	6.8	7	6.2
Gloss at 60°, GU ^a	125	130	131	130	125	120	130
Adhesion to metal ^b	5B	5B	5B	5B	5B	5B	5B

^a GU: gloss unit.

^b Rate of adhesion: **5B** means that the percent of detached or chipped off area of the coating cut sections is 0%.

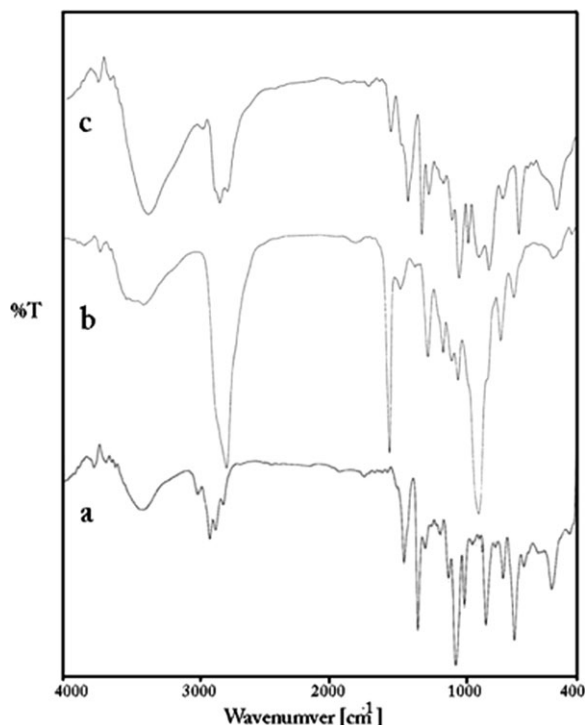


FIG. 6. FTIR spectra of (a) neat epoxy resin (Epon-828), (b) hyperbranched polymer (HP) and (c) epoxy /HP (100:20) cured film.

structure of HP, which confers flexibility to the epoxy cured films. Surprisingly, no significant change in gloss was observed, and adhesion of the cured epoxy films on the metal surface was also not affected by using HP in all epoxy formulations, as compared with that cured with the commercial amine hardener (A). Based on these results, it was interesting to make a combination between hardness and flexibility of the cured epoxy resin to improve its toughness. To achieve this target, the epoxy formulation (EAHP1) containing 20 wt% of the main hardener (Ancamine) in combination with 20 wt% of the hyperbranched polymer was prepared, as shown in Table 1. It is obvious that the epoxy cured films of EAHP1 sample has remarkable improvement

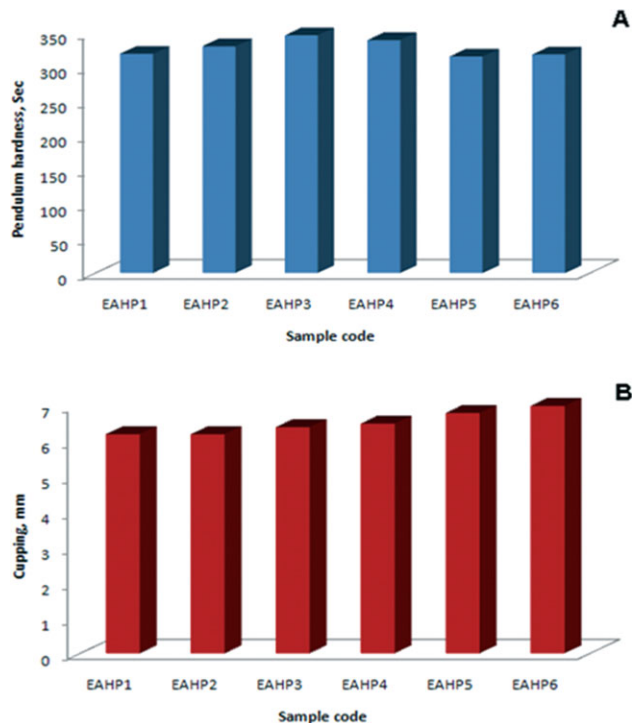


FIG. 7. Pendulum hardness (A), and cupping (B) of epoxy/OMMT nanocomposites films cured with Ancamine hardener in combination with HP at epoxy:A:HP weight ratio 100:20:20, at different OMMT loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in hardness (320 s) with maintained and acceptable flexibility (cupping = 6.2 mm), without affecting on the other mechanical properties. These promising results provide an evidence for the successful use and the high efficiency of hyperbranched polymer (HP) as toughening and co-curing agent in combination with the commercial Ancamine hardener (A). More interestingly, the use of HP led to reducing the content of Ancamin (solvent soluble) hardener required for curing of epoxy resin (from 60 to 20 wt% of the neat epoxy resin). From the environmental point of view, this is

TABLE 2. Formulation and physico-mechanical properties of epoxy/OMMT clay nanocomposites cured with Ancamine hardener in presence of HP as toughening and co-curing agent at different OMMT loadings.

Sample code						
Composition	EAHP1	EAHP2	EAHP3	EAHP4	EAHP5	EAHP6
Epon-828 (epoxy resin) (g)	100	100	100	100	100	100
Ancamine (Hardener) (g)	20	20	20	20	20	20
Poly(PEODA-NPA) (HP) (g)	20	20	20	20	20	20
Organoclay (OMMT), wt%	—	1	2	3	4	5
Physico-mechanical properties						
Hardness (pendulum) (s)	320	331	347	340	316	319
Impact test at 60 cm height	Pass	Pass	Pass	Pass	Pass	Pass
Cupping test (mm)	6.2	6.2	6.4	6.5	6.8	7
Gloss at 60°, GU ^a	130	130	131	130	125	120
Adhesion to metal ^b	5B	5B	5B	5B	5B	5B

^a GU: gloss unit.

^b Rate of adhesion: **5B** means that the percent of detached or chipped off area of the coating cut sections is 0%.

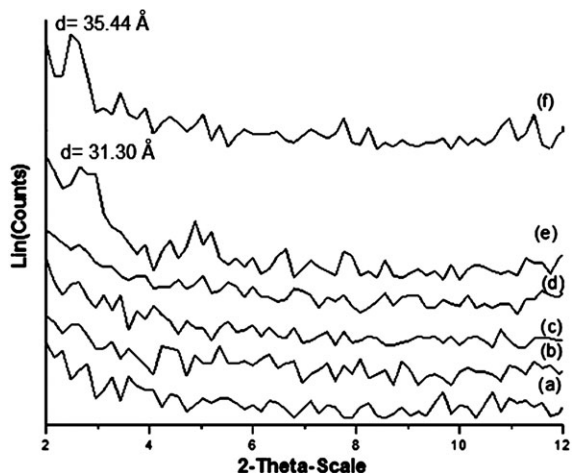


FIG. 8. XRD charts of neat epoxy resin (a), and epoxy resin/OMMT/A/HP nanocomposites at different OMMT loadings; 1 wt% (b), 2 wt% (c), 3 wt% (d), 4 wt% (e), and 5 wt% (f).

considered a great advantage in reducing the volatile organic content (VOC) during the curing of epoxy resin, and consequently less pollution.

The interaction between epoxy resin and the amino-terminated hyperbranched polymer (HP) was proved by FTIR technique. Figure 6 shows IR spectra of epoxy (Epon-828) resin (a), HP (b), and epoxy/HP cured film (c). The characteristic IR bands of the epoxy resin (Epon-828), as shown in Fig. 6a, are as follow: a broad band of O—H stretching at $3200\text{--}3650\text{ cm}^{-1}$, C—H (aliphatic) stretching bands at $2860\text{--}3060\text{ cm}^{-1}$, aromatic C=C of phenyl ring stretching bands at 1620 and 1462 cm^{-1} , symmetric stretching band of epoxy ring at 1250 cm^{-1} , asymmetric epoxy ring stretching band at 922 cm^{-1} and out-of-plane bending band of *p*-substituted phenyl ring at 825 cm^{-1} . After curing of epoxy resin with HP, the splitting in the broad peak of the terminal primary NH_2 groups (3446 cm^{-1}) of HP disappeared, as shown in Fig. 6b. In addition, the characteristic peak of the epoxy ring at 922 cm^{-1} vanished (Fig. 6c), proving the interaction between epoxy resin and HP via nucleophilic addition of the terminal primary amino groups of HP to the oxirane ring of the epoxy resin.

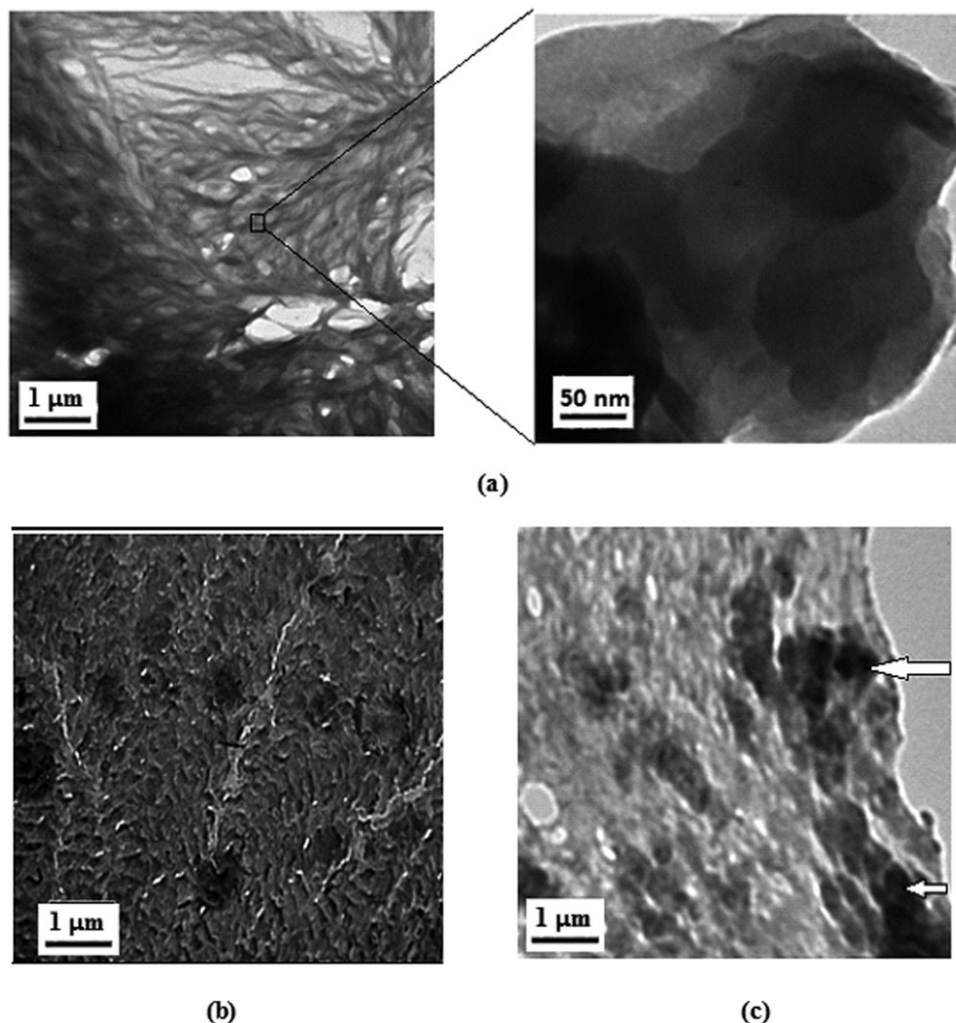


FIG. 9. TEM photos of epoxy resin/OMMT/A/HP nanocomposites at different OMMT loadings, 1 wt% (a), 3 wt% (b), and 5 wt% (c). Arrows in the photo (c) refer to organoclay (OMMT) aggregates.

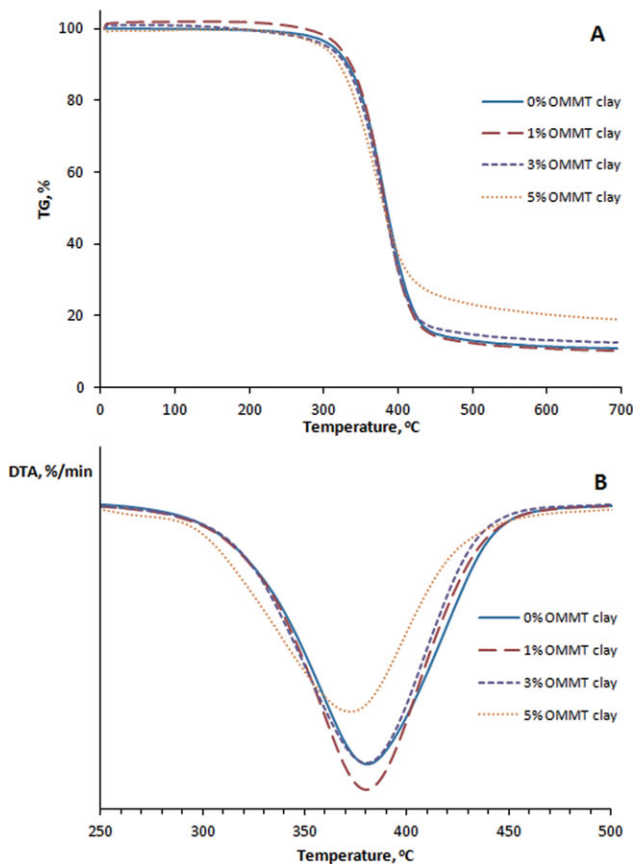


FIG. 10. TGA (a) and DTA (b) thermograms of epoxy/OMMT/A/HP nanocomposites at different OMMT loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Epoxy/Organoclay Nanocomposites Cured With Ancamine Hardener in Combination With Hyperbranched Poly(PEODA-NPA)

To study the effect of organoclay (OMMT) on physico-mechanical properties of the epoxy composite, the sample EAHP1 was used for further investigation, in presence of the reinforcing OMMT clay nanofiller at various loadings (1–5 wt%). Table 2 represents coating formulations of the epoxy/OMMT nanocomposites at various organoclay loadings. The epoxy/OMMT nanocomposites were cured using Ancamine hardener (A) at low loading (20 wt%) in combination with the prepared hyperbranched polymer (HP) as toughening and co-curing agent. As clearly seen from Table 2 and Fig. 7, the hardness of the cured films of the epoxy/OMMT nanocomposites increases by increasing OMMT content up to 3 wt% (sample EAHP4), and then started to decrease by the consecutive increase of OMMT content up to 5 wt%. On the other hand, the flexibility (cupping) of the epoxy/OMMT cured films slightly increases by increasing OMMT content up to 5wt%. This can be attributed to the lubrication effect of organoclay nanoparticles at high concentration [64]. Furthermore; the other physico-mechanical properties of the cured epoxy/OMMT nanocomposites were not

affected. The degree of intercalation/exfoliation and degree of dispersion of organoclay, within the epoxy cured matrix, were assessed using XRD and TEM techniques. Figure 8 shows XRD spectra of the neat epoxy cured with A and HP (Fig. 8a) and epoxy/OMMT/A/HP nanocomposites at various OMMT loadings (1–5wt%) (Fig. 8b–f). It is clear that at low OMMT loading (1–3 wt%) (Fig. 8b–d), no peaks were detected. This suggests that the platelets of OMMT intercalated by CTAB ($d = 18.298 \text{ \AA}$) (Fig. 4b) were completely exfoliated upon mixing with epoxy resin in presence of HP and Ancamine hardener. The consecutive increase in OMMT content (<3wt%) led to the emergence of peaks at 2θ values corresponding to d -spacing of 31.3 and 35.44 \AA for the samples EAHP5 and EAHP6, which contain 4 and 5 wt% OMMT, respectively. These peaks refer to the presence of intercalated or intercalated/exfoliated structure of OMMT in the epoxy cured films (Fig. 8e and f). This may be attributed to the presence of aggregated organoclay particles (tactoids) within the cured epoxy matrix. The same results were obtained by Isik et al. [65]. This means that the optimum OMMT content is 3 wt%.

On the other hand, transmission electron microscopic photos (Fig. 9) showed the homogeneous distribution of the exfoliated organoclay platelets in the epoxy matrix at low OMMT loading (1–3 wt%) (Fig. 9a and b). This result is in agreement with that obtained by XRD examination. More interestingly, at 1 wt% OMMT loading (Fig. 9a), the exfoliated organoclay platelets are homogeneously distributed taken the tree shape of the hyperbranched polymer, which promotes the exfoliation of the organoclay platelets during epoxy resin curing preventing their aggregation [40–43].

On the other hand, at high OMMT loading (5 wt%), relatively high amount of OMMT agglomerates were formed leading to inhomogeneous dispersion of OMMT clay within the epoxy resin (Fig. 9c). Here, it is worth to mention that the mixing of OMMT with epoxy resin for all samples was carried out at the same shear rate (3000 rpm) for 30 min, followed by sonication for 1 h. Accordingly, by increasing OMMT content (>3 wt%), the viscosity of the epoxy resin was highly increased, which may prevent the penetration of epoxy resin into the galleries between the organoclay layers that cause a decrease in OMMT/epoxy surface interaction. Accordingly, as the amount of the OMMT content increases, the intercalated structure of OMMT clay within the epoxy cured film was predominant [65].

Thermal Gravimetric Analysis (TGA/DTA)

Thermal stability of the prepared epoxy/OMMT/A/HP nanocomposites was investigated using TGA and DTA analyses at different OMMT loadings (1–5 wt%), as shown in Fig. 10. After thermal decomposition of neat epoxy and epoxy/OMMT nanocomposites, the residual mass of the epoxy resin increased in parallel with OMMT

content within the epoxy resin (Fig. 10A). In addition, a slight increase in decomposition temperature of the epoxy/OMMT nanocomposites was observed by incorporation of OMMT at low content. DTA thermogram (Fig. 10B) shows that the decomposition temperature of the cured epoxy containing 1 wt% of OMMT shifted to a higher temperature than that containing 5 wt% OMMT clay. This observation suggests the better dispersion of exfoliated OMMT platelets within the epoxy matrix at relatively low contents, and consequently, it reflects the higher interaction between exfoliated structure of OMMT clay and the epoxy matrix. This observation is in conformity with that obtained by X-ray and TEM measurements.

CONCLUSIONS

Amino-terminated hyperbranched poly(PEODA-NPA) (HP) was successfully synthesized in one pot reaction via Michael addition of poly(ethylene glycol) diacrylate (PEODA) to *N*-methyl-1,3-propanediamine (NPA). Epoxy resin (Epon-828) with marked improved toughness were prepared by using HP as toughening and co-curing agent in presence of Montmorillonite organoclay (OMMT) nanoparticles as reinforcing filler, without affecting the other properties of the cured epoxy films. In addition, further improvement in thermal stability was noticed upon using OMMT as reinforcing filler and particularly at relatively low OMMT loading (1 wt%). More interestingly, the use of HP as co-curing agent led to reduction in the content of the commercial Ancamin hardener (solvent soluble) required for hardening of epoxy resin. Consequently, epoxy resin with low volatile organic content (VOC) was obtained (less pollution), which is a highly favorable from the environmental perspective.

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REFERENCES

- O. Zabihi, A. Hooshafza, F. Moztarzadeh, H. Payravand, A. Afshar, and R. Alizadeh, *Thermochim. Acta*, **527**, 190 (2012).
- P. Khurana, S. Aggarwal, A.K. Narula, and V. Choudhary, *Polym. Int.*, **52**, 908 (2003).
- S. Ahmed, S.M. Ashraf, A. Hasnat, and A. Noor, *Indian J. Chem. Technol.*, **8**, 176 (2001).
- T.V.T. Velan and I.M. Bilal, *Bull. Mater. Sci.*, **23**, 425 (2000).
- T.H. Ho and C.S. Wang, *Polymer*, **37**, 2733 (1996).
- S.T. Lin and S.K. Huang, *Eur. Polym. J.*, **33**, 365 (1997).
- P.H. Sung and C.Y. Lin, *Eur. Polym. J.*, **33**, 903 (1997).
- H. Deligoz, T. Yalcinyuva, and S. Ozgumus, *Polym. J.*, **41**, 771 (2005).
- U. Lauter, S.W. Kantor, K. Schmidt-Rohr, and W.J. MacKnight, *Macromolecules*, **32**, 3426 (1999).
- P.R. Dvornic, H.J. Perpall, P.C. Uden, and R.W.J. Lenz, *J. Polym. Sci. Part A: Polym. Chem.*, **27**, 3503 (1989).
- S. Bhuniya and B. Adhikari, *J. Appl. Polym. Sci.*, **90**, 1497 (2003).
- A.A. Kumar, M. Alagar, and R.M.V.G.K. Rao, *J. Appl. Polym. Sci.*, **81**, 38 (2001).
- S.S. Ray and M. Okamoto, *Prog. Polym. Sci.*, **28**, 1539 (2003).
- A. Okada, M. Kawasumi, T. Kurauchi, and O. Kamigaito, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)*, **28**, 447 (1987).
- A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.*, **8**, 1179 (1993).
- A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, and O. Kamigaito, *Mater. Res. Soc. Symp. Proc.*, **171**, 45 (1990).
- K. Yano, A. Usuki, A. Okada, T. Kurauchi, and O. Kamigaito, *J. Polym. Sci. Part A: Polym. Chem.*, **31**, 2493 (1993).
- E.P. Giannelis, R. Krishnamoorti, and E. Manias, *Adv. Polym. Sci.*, **138**, 107 (1999).
- P.C. LeBaron, Z. Wang, and T.J. Pinnavaia, *Appl. Clay Sci.*, **15**, 11 (1999).
- E.P. Giannelis, *Adv. Mater.*, **8**, 29 (1996).
- R.A. Vaia, G. Price, P.N. Ruth, H.T. Nguyen, and J. Lichtenhan, *Appl. Clay Sci.*, **15**, 67 (1999).
- X. Kormmann, R. Thomann, R. Mulhaupt, J. Finter, and L.A. Berglund, *Polym. Eng. Sci.*, **42**, 1815 (2002).
- H.-S. Lee, P.D. Fasulo, W.R. Rodgers, and D.R. Paul, *Polymer*, **46**, 11673 (2005).
- Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, and O. Kamigaito, *J. Appl. Polym. Sci.*, **49**, 1259 (1999).
- T. Lan and T.J. Pinnavaia, *Chem. Mater.*, **6**, 2216 (1994).
- E.M. Petrie, *Epoxy Adhesive Formulations*, McGraw-Hill Publisher, New York (2006).
- T. Satoh, *Inter. J. Polym. Sci.*, (2012); doi:10.1155/2012/816163.
- J. M. J. Frechet, *Science*, **263**, 1710 (1994).
- M. Jikei and M.A. Kakimoto, *Prog. Polym. Sci.*, **26**, 1233 (2001).
- S. Peleshanko and V.V. Tsukruk, *Prog. Polym. Sci.*, **33**, 523 (2008).
- B.I. Voit and A. Lederer, *Chem. Rev.*, **109**, 5924 (2009).
- Y.H. Kim and R. Beckerbauer, *Macromolecules*, **27**, 1968 (1999).
- T.M. Miller, T.X. Neenan, E.W. Kwock, and S.M. Stein, *J. Am. Chem. Soc.*, **115**, 356 (1993).
- E. Malmström, M. Johansson, and A. Hult, *Macromolecules*, **28**, 1698 (1995).
- G. Yang, M. Jikei, and M. Kakimoto, *Macromolecules*, **32**, 2215 (1999).
- D.H. Bolton and K.L. Wooley, *Macromolecules*, **30**, 1890 (1997).

37. A. Morikawa, *Macromolecules*, **31**, 5999 (1998).
38. A. Kumar and S. Ramakrishnan, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 839 (1996).
39. D. Foix, X. Ramis, A. Serra, and M. Sangermano, *React. Funct. Polym.*, **71**, 417 (2011).
40. V.V. Tsukruk, *Prog Polym Sci.*, **22**, 247 (1997).
41. J.H. Zou, W.F. Shi, J. Wang, and J. Bo, *Macromol. Biosci.*, **5**, 662 (2005).
42. J. Xu, H. Wu, O.P. Mills, and P.A. Heiden, *J. Appl. Polym. Sci.*, **72**, 1065 (1999).
43. Y. Zhang, L. Wang, T. Wada, and H. Sasabe, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 1359 (1996).
44. J.S. Kim, H.C. Kim, B. Lee, and M. Ree, *Polymer*, **46**, 7394 (2005).
45. K. Fang, Z. Xu, X. Jiang, S. Fu, *Polym. Bull.*, **61**, 63 (2008).
46. L.J. Hobson, A.M. Kenwright, and W.J. Feast, *Chem. Commun.*, **19**, 1877 (1997).
47. L.J. Hobson and W.J. Feast, *Polymer*, **40**, 1279 (1990).
48. M. Sangermano, H. El Sayed, and B. Voit, *Polymer*, **52**, 2103 (2011).
49. X. Zhang, X. Zhang, Z. Wu, X. Gao, C. Cheng, Z. Wang, and C. Li, *Acta Biomater.*, **7**, 585 (2011).
50. D. Ratna, O. Becker, R. Krishnamurthy, G.P. Simon, and R.J. Varlet, *Polymer*, **44**, 7449 (2003).
51. L. Fogelström, E. Malmström, M. Johansson, and A. Hul, *ULACS Appl. Mater. Interfaces*, **2**, 1679 (2010).
52. C.J.G. Plummer, L. Garamszegi, Y. Leterrier, M. Rodlert, and J.A.E. Manson, *Chem. Mater.*, **14**, 486 (2002).
53. M. Rodlert, C.J.G. Plummer, L. Garamszegi, Y. Leterrier, H.J.M. Grunbauer, and J.A.E. Manson, *Polymer*, **45**, 949 (2004).
54. L. Fogelström, P. Antoni, E. Malmström, and A. ULHult, *Prog. Org. Coat.*, **55**, 284 (2006).
55. M. Rodlert, C.J.G. Plummer, Y. Leterrier, J.A.E. Manson, and H.J.M. Grunbauer, *J. Rheol.*, **48**, 1049 (2004).
56. Q. Wang, J.L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K. Kinbara, and T. Aida, *Nature*, **463**, 339 (2010).
57. C. Gao, W. Tang, and D. Yan, *J. Polym. Sci. Part A: Polym. Chem.*, **40**, 2340 (2002).
58. C.F. Dai, P.R. Li, and J.M. Yeh, *Eur. Polym. J.*, **44**, 2439 (2008).
59. ASTM D523, *Standard Test Method for Specular Gloss* (2008). www.astm.org/Standards/D523.htm.
60. ASTM D4366–95, *Standard Test Methods for Hardness of Organic Coatings by Pendulum Damping Tests* (2003). www.astm.org/Standards/D4366.htm.
61. ISO 1520, *Paints and Varnishes—Cupping Test* (2006). http://www.iso.org/iso/home/store/catalogue_tc/catalogue_detail.htm?csnumber=40923.
62. ASTM D2794–93, *Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact)* (2010). www.astm.org/Standards/D2794.htm.
63. ASTM D3359, *Standard Test Method for Measuring Adhesion by Tap Test* (2009). www.astm.org/Standards/D3359.htm.
64. M.Z. Myskova, J. Zelenka, V. Spacek, and F. Socha, *Mech. Compos. Mater.*, **39**, 1 (2003).
65. I. Isik, U. Yilmazer, and G. Bayram, *Polymer*, **44**, 6371 (2003).