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Hyperbranched Polyamine/Cu Nanoparticles for Epoxy Thermoset

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Copper nanoparticles have been synthesized in a colloidal solution of hyperbranched polyamine by a reductive technique. The formation of Cu nanoparticles was confirmed from UV, FT-IR, XRD and TEM studies. This colloidal solution of hyperbranched polyamine/Cu nanoparticles as well as hyperbranched polyamine alone have been used to cure commercially available bisphenol-A based epoxy resin at different dose levels (10–30 phr) with and without commercial poly(amido amine) hardener. The drying time, hardness, impact and chemical resistance of the cured epoxy resin have been investigated. The studies on morphology, thermostability and flame retardancy of cured films indicate the uniform distribution of different phases, high thermostability (up to 250°C) and self extinguishing characteristics respectively. Effective antifungal activity of the pure colloidal solution of hyperbranched polyamine/Cu-nanoparticles against *Candida albicans* fungus was observed.

Keywords: Nanoparticles, hyperbranched, epoxy, thermal properties, antifungal activity

1 Introduction

Nonlinear highly branched polymers such as dendrimers and hyperbranched polymers have attracted considerable interest during recent years due to their unique architecture and unusual properties, like low viscosity, high solubility, a large number of active functionalities, compact three dimensional non-entangled globular structures (1–4). Hyperbranched polymers are preferred over dendrimers because of their easy single step synthesis (5, 6), which helps in large scale production at a reasonable cost and thus make them more interesting for commercial production (7, 8).

As important industrial materials, epoxy resin is one of the most important thermosetting industrial materials. It has many excellent properties, such as high thermal stabilities, good adhesion, improved mechanical and electrical properties and is widely utilized in the field of coating, adhesives, casting, etc. (9–11). Despite such versatility, the applications are intended for demand as an increasingly high performance epoxy material. However, it is well known that the commonly used epoxy resin is generally quite brittle when cured with a large amount of common curing agents such as aliphatic or aromatic amine, amides, dicarboxilic acids or anhydrides, etc., because of its highly crosslinked structure, which rigidifies the molecular network, decrease deformability and increases process induced shrinkage (12). Hyperbranched polymers have a high potential as additives and modifiers in engineering materials. The chemical and physical structure of hyperbranched polymers induce unique properties that can solve the problems related to processability, property compromises and compatibility, and make them extensively suitable as crosslinker in low viscosity epoxy resins (13–15). The main drawback of epoxy resins like other organic polymers is their flammability, which limits their use in many applications like electronics, high performance adhesives, coatings, etc. (16,17). Considerable attention has been paid, therefore, to control the flammability of epoxy resins. The use of nitrogenous macromolecular hyperbranched polyamine flame retardant eliminates all the drawbacks of conventional small molecular flame-retardant additives, as well as acting as a reactive types additive, which is very effective as it may chemically attach with the resin system (16–20).

Advanced antifungal coating materials are very important innovations for a number of biotechnological applications. Metal-polymer nanocomposites can be a valid option for such purposes because of the highly dispersed nature of the metal releasing clusters and a large nanoparticalepolymer interface area that ensures high reactivity (21). It is already known that fungi can also be harmful pathogenic agents and copper has been used for decades as an effective fungicidal. All this calls for exploring alternative materials for efficient antifungal coatings, although the main

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concern in this strategy is to minimize their toxicity towards humans.

Thus, effort can be made to prepare stable nanoparticles of this metal with a control size in the suitable matrices. Hyperbranched polymers, particularly with polar terminal groups like amine, hydroxyl, amide, etc., are one of most useful classes of matrices (22–24). This is due to fact that these polymers fit perfectly with the definition of an ideal matrix, which stabilize the nanoparticles as it has large number of easily accessible terminal functional groups, high solubility in different solvents and low viscosity (25). Xu and his coworkers (24) already used a hyperbranched poly(amine-ester) to stabilize Cu-nanoparticles and Anyaogu et al. recently used Cu nanoparticles as antimicrobial agents (26).

Here, the authors, therefore, wish to report the use of hyperbranched polyamine/Cu nanoparticles as potential agents for high performance epoxy resin. The synthesis and characterization of Cu nanoparticles were also reported. The antifungal activity of copper nanoparticles in colloidal hyperbranched polyamine solution, as well as in cured epoxy resin, has also been studied.

2 Experimental

2.1 Materials

The hyperbranched polyamine (HBPA, Figure 1) was prepared according to the reported procedure (18). Bisphenol-A based epoxy resin (viscosity—450–650 mPas at 25°C, epoxy equivalent—182–192 g/eq. and density 1.15 g/cc at 25°C) and poly(amido amine) hardener, (ER-HD) (viscosity—10–25 Pas at 25°C, amine value – 6.6–7.5 eq/kg and density 0.98 g/cc at 25°C) were obtained from Hindustan Ciba Geigy Ltd., Mumbai and used as received. Copper acetate and sodium borohydrate (Merck, India) were used as received. N,N′-Dimethyl sulfoxide (DMSO, Merck,

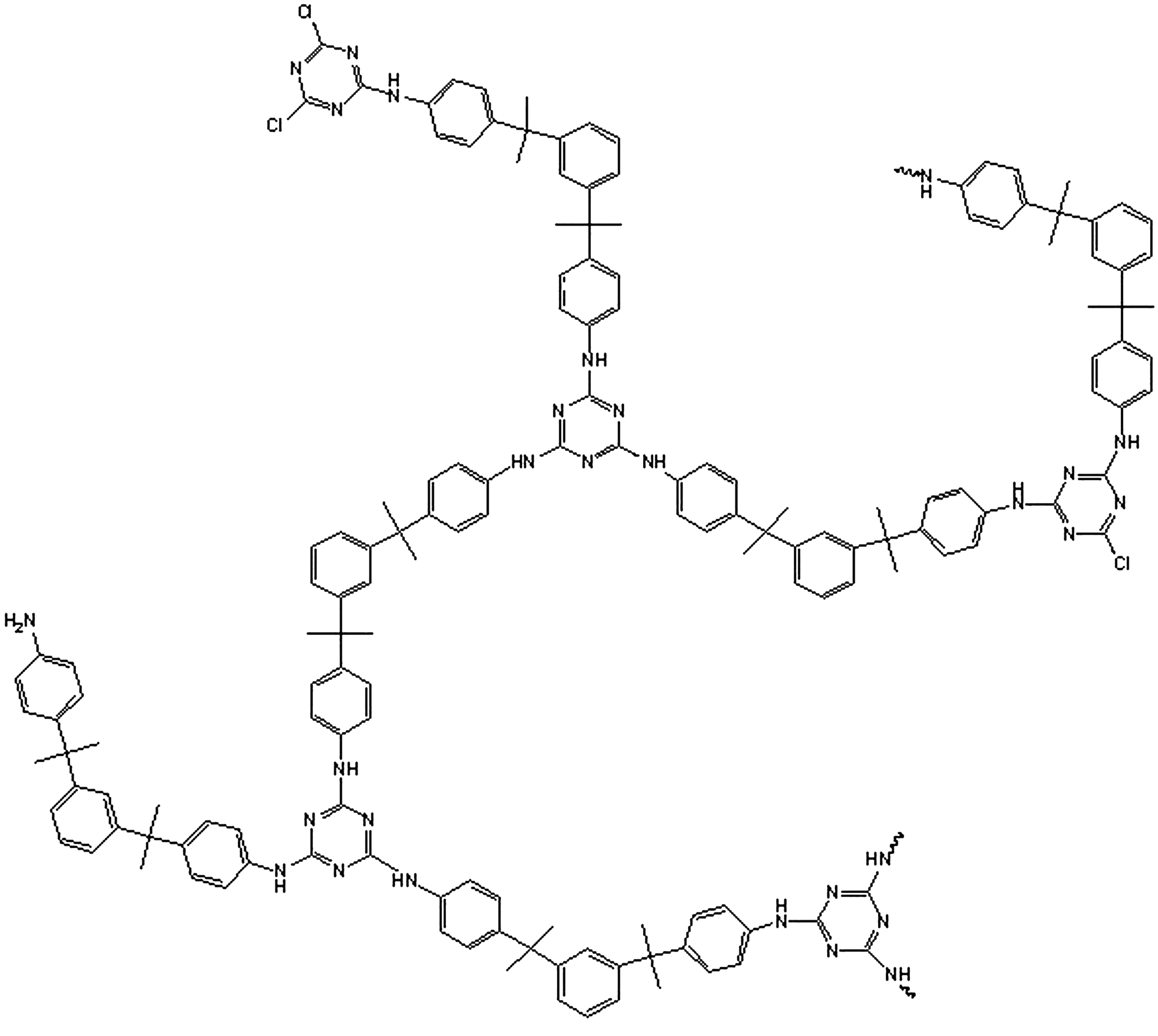

Fig. 1. Structure of hyperbranched polyamine, HBPA.

India) was used after purification by the conventional technique. Nutrient broth and nutrient agar (HIMEDIA, India) were used as received. *Candida albicans* (MTCC 227) was collected from the Department of Molecular Biology and Biotechnology, Tezpur University, India.

2.2 Preparation of Copper Nanoparticles

1 g of HBPA with 10 mL of DMSO was taken in a round bottom flask with constant stirring under N_2 purge. 5 mL solution of 0.1 g of copper acetate in water was added dropwise into the polymer solution with vigorous stirring in room temperature (ca 27°C). After completion of the addition, the reaction mixture was stirred for another 30 min. Then, 0.1 g of aqueous solution of $NaBH_4$ was added dropwise into the mixture. The reaction mixture was further stirred for another 30 min. The color of the resultant solution turns deep blue to golden brown. This solution was kept for further studies.

2.3 Curing of Epoxy Resin

A homogenous mixture of epoxy resin with 10, 15, 20 and 25 phr (phr = parts per hundred grams of resin) of hyperbranched polyamine (HBPA-Cu) with and without 50 phr of poly(amido amine) hardener was prepared separately in a glass beaker at room temperature by hand stirring for 5–7 min. Then, the mixtures were uniformly coated on mild steel plates (150 mm × 50 mm × 1.60 mm), tin plates (150 mm × 50 mm × 0.40 mm.) and glass plates (75 mm × 25 mm × 1.75 mm) and allowed to cure at specified temperatures for the different time period.

2.4 Preparation of Culture Media and Testing of Antibacterial Activity

100 ml of both potato dextrose broth and agar was prepared as described in the media container and sterilization was done. Plates were poured and the broths were inoculated in the laminar flow. The fungal broth was incubated for 2 days in the 30°C to get 1×10^6 population per ml of the media. Three grooves in each solidified plates were made by a sterilized crock borer (5 mm diameter) and that medium was removed from the dish by help of a disinfected wire loop. 40 μL of each test solution of different concentrations was poured in each groove in three dishes. Each dish contained polymer/copper nanoparticles, a pure polymer solution of same concentration and a 3rd dish was used for control study by taking DMSO:water (1:1) solvent only, without any test sample. Now, the plates were incubated in the oven at 30°C for 2 days and results were observed.

2.5 Measurements

UV spectra of samples were recorded on a Hitachi (U-2001, Tokyo, Japan) UV spectrophotometer by using 0.001% solution in DMSO:water (1:1). X-ray diffraction studies were made on the powder samples at room temperature (ca. 27°C) on a Rigaku X-ray diffractometer (Miniflex, UK). The scanning rate used was 5.0° min^{-1} over the range of $2\theta = 10$–$90°$ for the above study. The size and distribution of copper nanoparticles were studied by using a JEOL, model number JEMCXII transmission electron microscope (TEM) at an operating voltage of 80 kV. The distribution of copper nanoparticles and morphology of the cured resin were studied by using variable pressure digital scanning electron microscope (SEM, model LEO 1430VP). FT-IR spectra for the compounds were recorded in a Nicolet (Impact 410, Madison, USA) FT-IR spectrophotometer by using KBr pellets. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were carried out in Shimazdu TG 50 and DSC 60 thermal analyzers, respectively using the nitrogen flow rate of 30 mL/min and at the heat rate of 10°C/min. The flame retardancy test of all samples was carried out by measurement of the limiting oxygen index (LOI) value by a flammability tester (S.C. Dey Co., Kolkata) as per the standard ASTM D 2863–77 procedure. The coating performance of the cured films was evaluated by determination of pencil hardness using pencils of different grades ranging from 6B to 6H and adhesion (cross-cut) by using commercial cello tape.

3 Results and Discussion

3.1 Formation and Characterization of Copper Nanoparticles

The copper nanoparticle is formed *in situ* in the matrix of hyperbranched polyamine by the reduction of copper acetate in DMSO-water (1:1, v/v) mixed solvent. It is well known that Cu nanoparticles tend to aggregate very quickly in the medium (27). The extent of agglomeration can be effectively reduced by lowering the surface energy by adsorption of stabilizers such as polymers or surfactants present in the medium. Thus, hyperbranched polymer also supports the stabilization of metal colloidal solution, prevents agglomeration and precipitation of the particles. As the used hyperbranched polyamine has tertiary and secondary nitrogen in its structure along with a large number of free active surface primary amine groups, so the metal ions (Cu^{2+}) are formed stable complex and dispersed uniformly. Furthermore, at this ratio, it is believed that the copper nanoparticles formed are uniform in size and dispersion, which are most desirable for such preparation. The fact is supported by TEM studies. Hence, some of the challenging issues of nanoparticles formation were achieved to a certain extent through this technique. The excess amount of reducing agent was used to ensure complete reduction of Cu^{2+} to Cu(0), which is confirmed by the change reaction solution color from blue to golden brown and subsequent characterization of copper nanoparticles by different spectroscopic

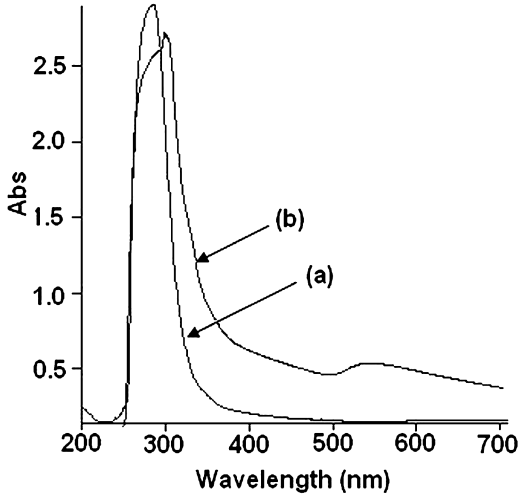

Fig. 2. UV spectra of (a) HBPA and (b) HBPA-Cu.

techniques. The colloidal copper nanoparticles have been stored for more than three months at room temperature and found to be stable in the absence of oxygen.

The formation of copper nanoparticles in hyperbranched polymer matrix is first observed by UV-visible absorption spectral studies. Chemical reduction of Cu^{2+}-loaded hyperbranched polyamine with excess of $NaBH_4$ results in intra-hyperbranched-Cu nanoparticles (28). Evidence for this comes from the immediate change in solution color from blue to golden brown. The absorbance band in UV spectrum shows a monotonic decrease from about 300 nm to 570 nm with a nearly exponential slope (Figure 2). The measured onset of this transition at 570 nm agrees with the accepted value [29], which strongly suggests that the presence of separated copper nanoparticles, which is further supported by TEM studies.

Figure 3 shows the infrared spectra for the pure hyperbranched polymer (HBPA) and polymer in the presence of copper nanoparticles (HBPA-Cu). The analysis showed that the spectral features of HBPA and HBPA-Cu samples are quite different. All the amines viz. primary, secondary and tertiary vibration frequencies showed a shift in the 3420 -3300 cm^{-1} range for stretching, 1585–1560 cm^{-1} and 1487–1472 cm^{-1} for bending vibration and a decrease in transmittance of the bands in the presence of copper nanoparticles compared to the pure polymer. The result indicates a strong interaction between amines and Cu nanoparticles.

TEM (Figure 4) studies confirmed that Cu-nanoparticles are not agglomerated, well-dispersed and almost spherical shape with particles size 3 nm to 15 nm. The size distribution of the particles is also found to be narrow (Figure 5).

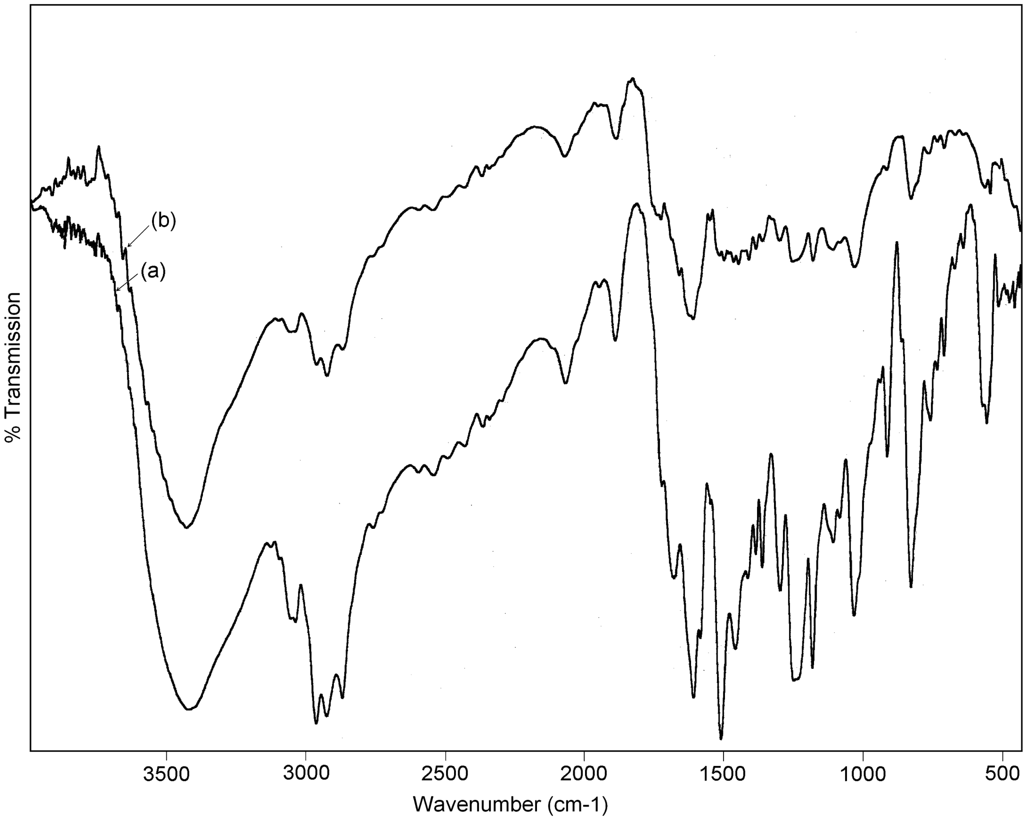

Fig. 3. FT-IR spectra of (a) HBPA and (b) HBPA-Cu.

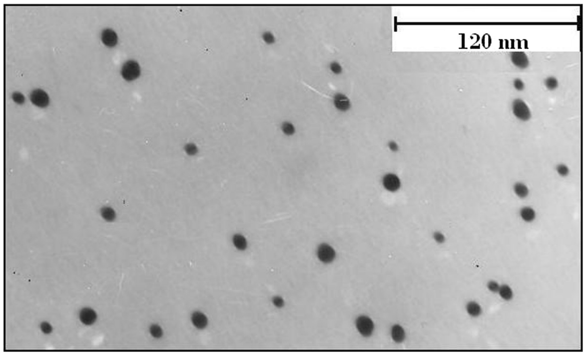

Fig. 4. TEM micrograph of copper nanoparticles.

The X-ray diffractrogram (Figure 6) of the powder sample is agreed well with the literature values (30). All the reflection peaks at 2θ values of about 43.5°, 50.7°, 70.2° are represent the 111, 200 and 220 Bragg's reflections of the cubic structure of copper. The Scherrer's equation was used to estimate the crystalline domain size (D):

$$D = k\lambda/\beta\cos\theta$$

Where $k = 0.9$ is for the Cu cubic structure, $\lambda = 1.541$ Å is the X-ray wavelength, β is the angular width and θ is the diffraction angle. The average crystalline domain size was found to be 8.5 nm and this result is in agreement with average diameter of Cu nanoparticles estimated by TEM.

3.2 Curing Study of the Epoxy Resin

The curing or crosslinking of epoxy resin is done through the epoxy/hydroxyl groups. The curing agents commonly used are diamines and polyamines or acids and anhydrides. The bisphenol A based epoxy resin was cured here by using a commercial poly(amido amine) hardener (50 phr) at 100°C for 30 min. However, the same was also cured by using a combination of the above hardener (25 phr) and HBPA (15 phr) at the same time and temperature. Also, the hyperbranched/Cu nonoparticles (HBPA-Cu) system with poly(amido amine) hardener can cure the resin at the same time and dose as hyperbranched polymer alone. However, when hyperbranched polyamine (HBPA) was used alone with the above resin, it has been found that the epoxy can be cured at 100°C for 40 to 20 min at a dose level of 10 to 30 phr (Table 1). This is due to the presence of a large numbers of free reactive surface primary and secondary amino groups in the structure of the hyperbranched polyamine, which may react with an epoxy group of the epoxy resin. The dose higher than 30 phr was not studied because of a commercial point of view, as well as due to the fact that the cured resin became rather brittle even at a dose level of 30 phr of hyperbranched polymer. This may be due to the presence of the rigid structure of the hyperbranched polymer.

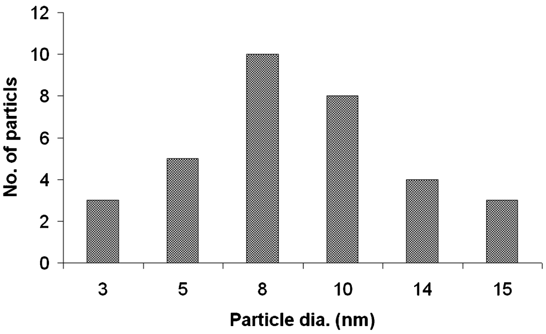

Fig. 5. Histogram for size distribution of copper nanoparticles.

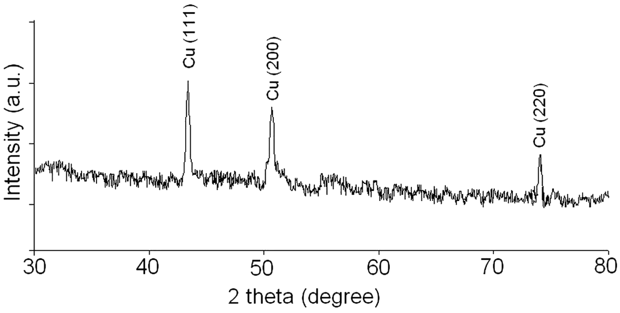

Fig. 6. X-ray diffractogram of HBPA-Cu.

3.3 Coating Performance of the Epoxy Resin

The performance of the epoxy resin was studied by the measurement of drying time, pencil hardness, adhesive strength, thermal stability, flame retardancy (LOI) and chemical resistance in different chemical media. The results were compared for the poly(amido amine) hardener (ER-HD) curing system to the combination system of ER-HD with 15 phr of hyperbranched polyamine/Cu-nanoparticles (ER-HD-15PA/Cu). The miscibility of the hyperbranched polymer with the resin system was studied by SEM (Figure 7) and it has been observed that there is no distinct phase separation in both cases.

Table 1. Drying time of epoxy resin

Resin code	*Curing system (phr)*	*Time (min)*
ER-HD	100:50:: Epoxy:Hardener	30
ER-15PA	100:15:: Epoxy: HBPA	45
ER-20PA	100:20:: Epoxy: HBPA	35
ER-30PA	100:30:: Epoxy: HBPA	25
ER-HD-10PA	100:25:10:: Epoxy:Hardener:HBPA	35
ER-HD-15PA	100:25:15:: Epoxy:Hardener:HBPA	30
ER-HD-20PA	100:25:20:: Epoxy:Hardener:HBPA	25
ER-HD-15PA/ Cu	100:25:15:: Epoxy:Hardener:HBPA-Cu	30

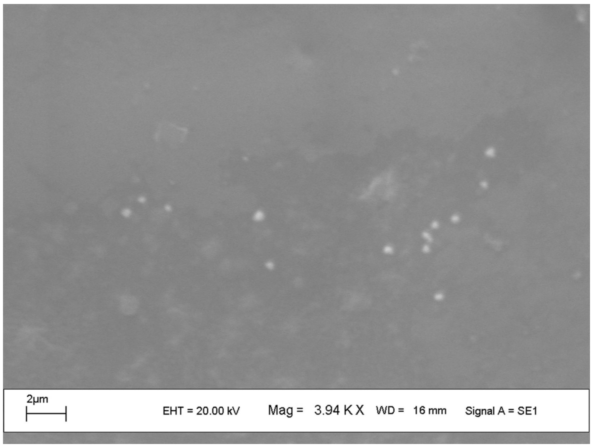

Fig. 7. SEM micrograph for ER-HD-15PA/Cu.

3.4 Physical Properties

The drying of resin results in the conversion from the liquid state to solid state by crosslinking reaction, which forms a three dimensional network structure. In this case, the crosslinking is mainly from the reaction of active hydrogen atoms of primary and secondary amine groups with epoxy groups. The aliphatic poly/diamines are highly reactive and offer fast curing even at room temperatures but they are toxic and skin sensitive. Furthermore, the aliphatic amine cured epoxy exhibits low heat deflection temperature compared to aromatic diamine cured epoxy, though aromatic diamines are well-known to be very hazardous and highly carcinogenic. Again, drying of resin with aromatic hyperbranched polyamine (expected no such problems) the time required is less (Table 1), which is due to the various crosslinking reactions with a large number of functional groups present in their structure (Figure 1). The pencil hardness (Table 2) value for the ER-HD-15PA/Cu is higher than the ER-HD and is due to higher crosslinking density, the presence of rigid aromatic and triazine moieties and a higher number of H-bonding in the former than the latter. The swelling test and FT-IR study also supports this fact. The FT-IR spectrum of ER-HD-15PA/Cu indicates the presence of broad band for extended H-bonded OH groups at 3333 cm^{-1}. The adhesion characteristic for both the resin systems is very good, which is due to the presence of different polar groups. These results indicated that ER-HD-15PA/Cu is a better material than ER-HD for surface coating applications.

Table 2. Coating properties of epoxy resin

Property	*ER-HD*	*ER-HD-15PA/Cu*
Drying time (min)	30	30
Pencil hardness	3H pass	4H pass
Adhesion (%)	100	100
Swelling (%)	10.71	3.69
LOI	21	26
Initial decomposition temperature (°C)	220	275

3.5 Flame Retardancy Study

As already stated in the introduction, the polymeric nature and hyperbranched architecture make these types of polymers very compatible with the other polymeric systems, so it is expected and also found from SEM studies that HBPA and epoxy resin formed a miscible system (Figure 7). This result also indicates that the hyperbranched polyamine has agood compatibility capability with the epoxy resin system.

It has already been reported (27) and found in this study that triazine based polymers have very good flame retardant behavior for their excellent char forming effect. This is mainly due to the presence of tertiary nitrogen in their ring structure. They also have other advantages like low toxicity, no corrosion, low smoke, good compatibility, etc. The LOI value may be used as an indicator to evaluate flame retardancy of a polymer. The hydrocarbon-based polymers with high hydrogen/carbon ratio like epoxy resins are highly susceptible to flame. Thus, the flame-retardant behavior of these resin systems was examined by the LOI test. The results are tabulated in Table 2. From the table, it has been observed that the LOI value of epoxy resin of ER-HD cured system is lower than that with 15 phr of hyperbranched polyamine/Cu nanoparticle system. This increment of LOI value is due to the flame retardant characteristic of HBPA, as it has nitrogen and chlorine as the special elements in its structure.

3.6 Thermal Study

From the thermogravimetric (TG) analysis of the resin systems, it has been found that the thermostability of the resin was enhanced by the presence of hyperbranched polyamine (Figure 8). The initial decomposition temperature with the HBPA is much higher than that without hyperbranched polymer under the nitrogen atmosphere (Table 2). However, thermostability of the resin was further enhanced a little in the presence of Cu nanoparticles. These findings suggest that hyperbranched polyamine not only promotes some amounts of char formation (where heterocyclic moiety is mainly responsible) in the solid polymers, but it also helps the thermostability of the resin, which is due to chemical crosslinking, formation of H-bonding, enhanced compatibility, etc.

3.7 Chemical Resistance

The results for the cured thermoset systems indicate that they have excellent chemical resistance in all tested media except a dilute aqueous NaOH solution. In an alkali solution, the loss of adhesion was observed in both cases, though the loss of weight in the case of EP-HD is a little

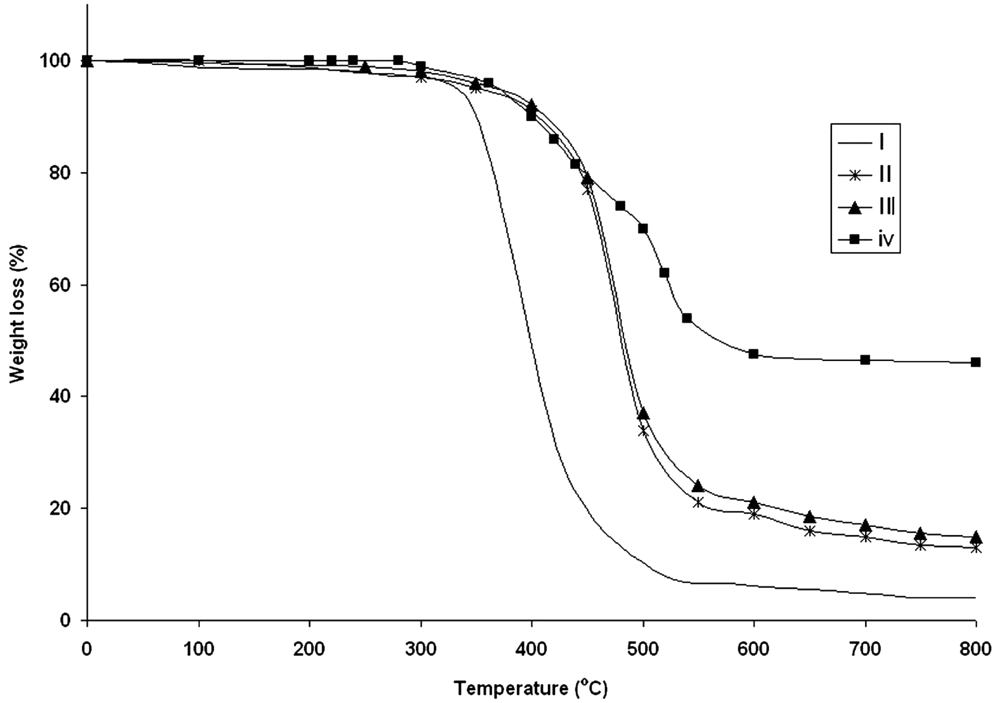

Fig. 8. TG thermograms for I = EP-HD, II = EP-HD-15PA, III = ER-HD-15PA/Cu and IV = HBPA.

higher than the ER-HD-15PA/Cu system. This improvement of alkali resistance may be due to the higher crosslinking density, the presence of rigid aromatic moieties and greater H-bonding in the former than the latter.

3.8 Biological Activity

In the field of biomedical polymeric materials, infections associated with the biomaterials represent a significant challenge to develop antimicrobial surfaces for more wide spread applications of medical implants. In this context, Cu nanomaterials exhibit effective antifungal properties (21). In this report, the results of antifungal studies clearly demonstrated (Figure 9) that the colloidal copper nanoparticles inhibited the growth of the tested fungus viz. *Candida albicans* even at very low total concentrations of copper (1.4 g/100 L). The anitimicrobial activity of the free HBPA is also tested and no antimicrobial activity was observed in the tested microorganism, so, the activity is due to Cu-nano particles. However, the influence of hyperbranched polyamine is not known in this case. Further, the mechanism of the bactericidal effect of copper colloid particles against the bacteria is not very well understood. However, copper nanoparticles may attach to the surface of the cell membrane and disturb its power function such as permeability and respiration. It is reasonable to state that the binding of the active agent to the bacteria depends on the surface area available for such interactions. The extremely small size of copper nanoparticles means they exhibit enhanced properties when compared with bulk copper. Because smaller particles, having the larger surface area and hence, interactions, will be more than the larger particles active agent. This allows them to easily interact with other particles and increases their antifungal efficiency. Thus, the development of new antibacterial substances is very significant.

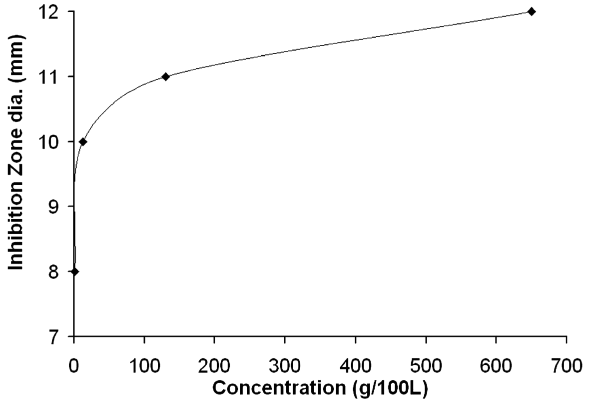

Fig. 9. Variation of inhibition zone diameter with concentration of HBPA-Cu solution for *Candida albicans* fungus.

4 Conclusions

From this study, it can be concluded that well-dispersed and stable copper nanoparticles have been prepared by using hyperbranched polyamine containing s-triazine ring as the matrix. This hyperbranched polyamine/Cu nanoparticles colloidal solution was used successfully as a high performance curing agent for epoxy resin. The performance characteristics like curing time, hardness, thermostability, flame retardancy, chemical resistance, etc. of the resin are improved by the addition of the hyperbranched polyamine/Cu nanoparticles at a relatively low dose level. This hyperbranched polyamine/Cu nanoparticles colloidal solution acts as effective antifungal activity against *Candida albicans* fungus.

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