

Rheological Characterization of UV-Curable Epoxy Systems: Effects of *o*-Boehmite Nanofillers and a Hyperbranched Polymeric Modifier

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ABSTRACT: An organo-modified Boehmite (*o*-Boehmite) was used to prepare nanocomposite UV-curing coatings, based on a cycloaliphatic epoxy resin (3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate). A hyperbranched polymer (HBP) based on highly branched polyester, was also added to the resin, with the aim to modify its reactivity, such as a possible route to increase the toughness of the resin. Different amounts of the nanofiller and the HBP, ranging from 5 up to 20 wt % of resin, were dispersed into the resin in the presence of triarylsulfonium hexafluoroantimonate, as a photoinitiator for the UV curing of the resin. The rheological behavior of the formulations produced was studied as function of the shear rate and of the content of each filler using a cone and plate rheometer. A general increase in viscosity was observed

with increasing the volume fraction of each filler and a moderate pseudoplastic behavior was observed when *o*-Boehmite filler was added. A non-Newtonian behavior was observed with the incorporation of the HBP. The viscosity of the epoxy/boehmite resin mixtures was analyzed as function of the nanofiller volume fraction. In the case of epoxy/hyperbranched resin mixtures, the Cross equation was used to predict the viscosity of each formulation as a function of the shear rate and an appropriate relationship to predict the viscosity of each formulation as a function of the filler volume fraction, was determined. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1302–1310, 2009

Key words: epoxy resins; photopolymerization; rheology; boehmite; HBPs

INTRODUCTION

Over the last several years, new radiation curing technologies have been used industrially, including ultraviolet (UV) and electron beam sources, for the production of coatings, graphic arts, inks, adhesives and microelectronics, encapsulations, which have traditionally being cured thermally from solvent containing formulations.¹ The first application of UV technology was in the graphic arts, as witnessed by the first patent on UV printing inks technology granted in 1946. Nowadays, over 20,000 tons of UV cured inks and overprint varnishes are used in the European printing industry. Nevertheless, in comparison with the total volume of inks used for printing, UV curable inks represent only a small portion. The recent high growth rate of the UV printing technology is especially remarkable in lithography and flexography; the latter, in particular, is the fastest growing segment. A flexographic printer that use UV technology can reach the print quality of the conventional litho or even gravure processes.¹

In the field of UV curable resins there are two main types, which differ from each other only with respect to polymerization mechanism. Acrylate resins and unsaturated polyesters are polymerized by a free radical mechanism, while epoxy and vinyl ester resins are mainly cured by a cationic polymerization mechanism.²

The recent growing interest in cationic photopolymerization is related to the development of very efficient photoinitiators and to the distinct advantages in different applications of this radiation curing method.² As in any other UV curing process, cationic photopolymerization is performed in bulk without the use of solvents and it can be regarded, therefore, as an environmental-friendly process.³ The cationic UV-curable monomers, in fact, usually show low toxicity and irritation potential.⁴ Furthermore, cationic photopolymerization is oxygen insensitive to so that the use of an inert atmosphere as in radical polymerization is not more required.⁵ For this reason the process is finding applications in a variety of areas, including coatings, inks, adhesives, rapid prototyping and electronics.⁴ In addition to these, cationic polymerization is used in stereolithography laser induced. Stereolithography is the most used rapid prototyping process for the fabrication of solid objects starting from three dimensional CAD

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models. Cationic photopolymerization, finally, plays an important role also in the production of dentistry materials and in the preparation of foils used for the removal of nonionic and anionic pollutants, leachates from agricultural lands and landfills.⁴

In previous works, a cycloaliphatic epoxy resin was chosen for a UV-curing, using triarylsulfonium hexafluoroantimonate salt as photoinitiator.⁶

In a previous communication, the possibility of preparing nanocomposite coatings by using photochemically initiated cationic polymerization in presence of Boehmite (γ -Al₂O₃) nanoparticles, modified with alkylbenzenesulfonic acid, was explored.⁶

Nanocomposites, based on polymeric matrices and reinforced with inorganic clay minerals, producing particles of dimensions in the nanometer range, have improved mechanical and barrier properties, compared to conventional microcomposites. Their unique phase morphology, derived by layer intercalation or exfoliation, is able, in fact, to maximize the interfacial area between the organic and inorganic phases and to enhance the bulk properties.⁷ Only few examples related to the incorporation of Boehmite into polymers to prepare nanocomposite materials have been reported in the literature.^{8–11} The Boehmite particles are colloidal plate-like crystals with a high anisotropy. They consist of double layers of oxygen octahedra partially filled with Al cations.¹² Their aqueous dispersions exhibit flow birefringence, thixotropy and elasticity.¹³ A valuable advantage of Boehmite nanoparticles is their availability on a large industrial scale coupled with a tailorable interface (either hydrophobic, hydrophilic or silane treated) able to promote their dispersion in a large number of resins. A proper surface modification is required, in particular, to obtain a good compatibility with different matrices still using the conventional preparation techniques for nanocomposites.¹³

In a second contribution, the use of a hydroxyl-functionalized hyperbranched polymer (HBP) was analyzed as a mean to modify the rate of reaction of the cycloaliphatic epoxy resin (Esposito Corcione et al., submitted). HBPs, belonging to novel dendritic molecules, have recently gained considerable attention, due to their peculiar structure and unique properties. They are characterized by highly branched backbone with a large number of reactive groups, which provide them with excellent flow and processing properties.^{14–17} Hyperbranched polyesters with different terminations have been successfully employed as multifunctional crosslinkers in coatings and in thermosets, with thermal and UV curing methods. Their addition to resin formulation has been explored to improve the thermal properties and modulus, to change the rheology and to

improve the flow, the viscosity and the surface properties.

In our previous papers, kinetics of photopolymerization were studied on modified and unmodified systems, by means of Photocalorimetry and Real-Time FTIR Spectroscopy. A good knowledge of the conversion profiles within the material during photopolymerization is essential to ensure the effectiveness of photocurable systems and to tailor them to specific application.

To obtain a wide knowledge of the systems, rheological characterization was performed on each formulation produced. The use of these systems in the mentioned applications, in fact, requires accurate information on their viscosity. The monomers most commonly used in UV-curable processes generally show a Newtonian rheological behavior, with a viscosity at room temperature being usually lower than 0.5 Pa s.¹⁸ As an example, a phototoactivated resin used for stereolithography processes, commercialized from 3D System, possesses viscosities ranging from 0.15 to 0.2 Pa s, whereas epoxy cycloaliphatic resins used for coatings, commercialized by Dow Corning, do not exceed 0.45 Pa s. In this paper, the rheological behavior of the systems was studied as a function of the shear rate and the content of each filler added in a cone-plate configuration rheometer. Appropriate theoretical models were used to fit the experimental data for each system produced.

EXPERIMENTAL

Materials

3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (CE) was chosen as precursor of a polymeric matrix. The chemical formula of CE is shown in Figure 1. Two different fillers were added to the CE resin, respectively, an organo-modified Boehmite nanofiller, to produce a nanocomposite structure, and a hyperbranched aliphatic polyester.

An organo-modified Boehmite (*o*-Boehmite), supplied by Sasol (Brunsbüttel, Germany), was chosen, commercially known as Disperal[®] OS1. The surface modification of the particles of Boehmite was required to achieve a good compatibility with the matrix resin using conventional nanocomposite preparation techniques. Some of the physical-chemical properties of the nanoclay are summarized in

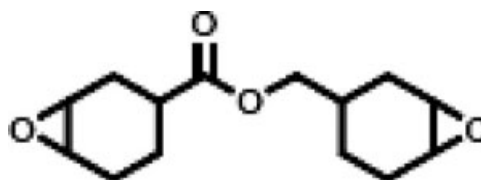


Figure 1 Chemical formula of the epoxy resin CE.

TABLE I
Physic-Chemical Properties of the Used Nanoclay, OS1

Typical chemical and physical properties	OS1
PTSA or ASA	7
Miscible with	Medium polar matrix
Loose bulk density [g/L]	400–600
Dispersed particle size ³ [nm]	100

Table I. The projection of the crystalline structure of the neat Boehmite is shown in Figure 2.

The OH-terminated hyperbranched aliphatic polyester used is produced by Perstop and sold with the trademark Boltorn H 20. The molecular weight of H 20 (M_w), as reported on data sheet, is about 2100 g/mol, the theoretical number of OH groups is 16 per molecule and its viscosity, measured at 110°C is 7 Pa s at shear rate of 30 s⁻¹. Finally, its T_g , measured by dynamic mechanical analysis (DMA), is 30°C. The chemical formula of H 20 is shown in Figure 3.

Different amounts of *o*-Boehmite or HPB (ranging from 5 up to 20 wt % of resin) were added to the CE resin. A commercially available mixture of antimonate sulfonium salts, used as photoinitiator for the CE resin, was used at a fixed 5 wt % level. The trademark of the photoinitiator is UVI 6976, obtained from Dow, supplied as a solution [50 wt %] in propylene carbonate.

Preparation of mixtures

The preparation of the mixtures containing *o*-Boehmite was performed by the solvent dispersion method, able to improve the dispersion of the nanofiller in the epoxy matrix.¹⁹ Following this procedure,

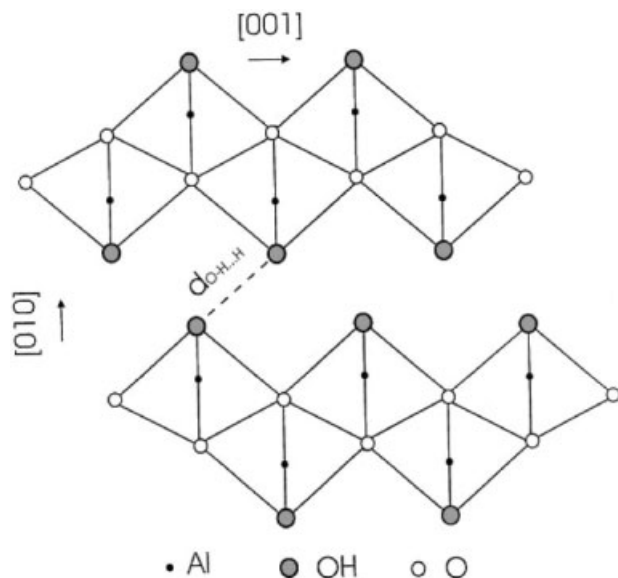


Figure 2 Projection of neat Boehmite crystalline structure.

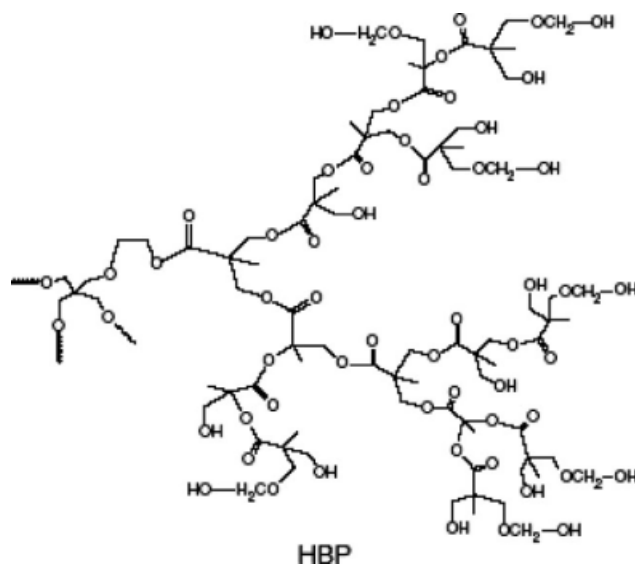


Figure 3 Chemical formula of the aliphatic polyester hyperbranched H 20.

the *o*-Boehmite was dispersed in a polar organic solvent. Acetone was used as solvent due to its high compatibility with *o*-Boehmite and the epoxy resin.⁶

The procedure employed to add the nanosized particles of *o*-Boehmite to the CE resin is as follows:

1. Sonification of *o*-Boehmite in acetone for 1 h.
2. Addition of *o*-Boehmite-solvent dispersion to the epoxy resin CE.
3. Mechanical stirring of the final dispersion for 5–7 h at 80°C.
4. Addition of the photoinitiator to the dispersion.

The amounts of *o*-Boehmite used were respectively, 3, 5, and 10% wt of resin.

The procedure employed to add the OH-terminated hyperbranched H 20 to the CE resin is as follows:

1. The H 20 was first finely ground.
2. It was dissolved at 50°C in methanol using a magnetic stirrer for 20 min.
3. This alcoholic solution was added to the epoxy resin CE.
4. After the evaporation of the solvent, in oven at 70°C, the photoinitiator was added to the dispersion and mixed.

Two compositions were examined at 10 and 20% wt resin. In the previous study, the complete solubility between H 20 and the epoxy resin has been verified (Esposito Corcione et al., submitted).

In Table II the composition of all the mixtures with *o*-Boehmite and H20, are reported. Referring to

TABLE II
Weight and Volumetric Composition of Mixtures Realized with *o*-Boehmite and H 20

Sample	Weight composition	Volumetric composition
CE	100% Epoxy resin and photoinitiator	100 % Epoxy resin and photoinitiator
3 OS1	97% wt Epoxy resin and photoinitiator + 3% wt OS1	99.57 % vol Epoxy resin and photoinitiator + 0.43 % vol Boehmite
5 OS1	95% wt Epoxy resin and photoinitiator + 5% wt OS1	99.28 % vol Epoxy resin and photoinitiator + 0.72 % vol Boehmite
10 OS1	90% wt Epoxy resin and photoinitiator + 10% wt OS1	98.49 % vol Epoxy resin and photoinitiator + 1.51 % vol Boehmite
10 H 20	90% wt Epoxy resin and photoinitiator + 10% wt H ₂ O	91.86 % vol Epoxy resin and photoinitiator + 8.14 % vol H ₂ O
20 H 20	80% wt Epoxy resin and photoinitiator + 20% wt H ₂ O	83.39 % vol Epoxy resin and photoinitiator + 16.61 % vol H ₂ O

the volumetric compositions of the mixtures containing *o*-Boehmite, they were calculated in a previous work, starting from the data of the thermogravimetric analysis.⁶ For the mixtures containing H 20, the volumetric compositions were calculated from the density value of H 20 and CE resin reported on its data sheet.

Rheological characterization

The rheological characterization of all the formulation realized was carried out in a strain controlled rheometer (Ares Rheometric Scientific). The tests were performed with a cone and plate flow geometry (radius of the plate 12.5 mm) in steady state mode. The experimental parameters were chosen to simulate the possible operative conditions. To this end, the tests were conducted at room temperature (30°C) using a shear rate range of 0.05 s⁻¹ and 100 s⁻¹. A first sweep experiment was always followed by a second experiment performed on the same sample and using the same conditions. The rheological

experiments were repeated at least three time to check the repeatability of results.

At the end of the rheological characterization, for each system an appropriate theoretical equation was identified to fit the experimental data. The viscosity of epoxy/*o*-Boehmite formulations was considered as function of the nanofiller volume fraction, while the viscosity of the epoxy/H 20 systems as a function of shear rate using Cross equation and of the H 20 volume fraction using a different equation.

RESULTS AND DISCUSSION

CE/*o*-Boehmite mixtures

In Figure 4, the viscosity of the CE resin is reported as a function of the shear rate. The resin displays a Newtonian behavior and an average viscosity value of 0.23 Pa s. No differences is apparent between the curves from the two consecutive steps.

In Figure 5, are shown the viscosity of the CE resin filled with 5% wt OS1 as a function of shear rate for the first and second sweep experiments. In

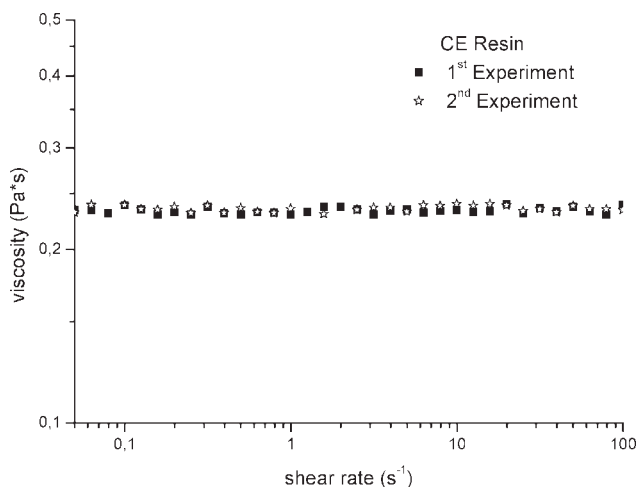


Figure 4 Viscosity of CE resin, from the first and the second sweep experiments, as a function of shear rate.

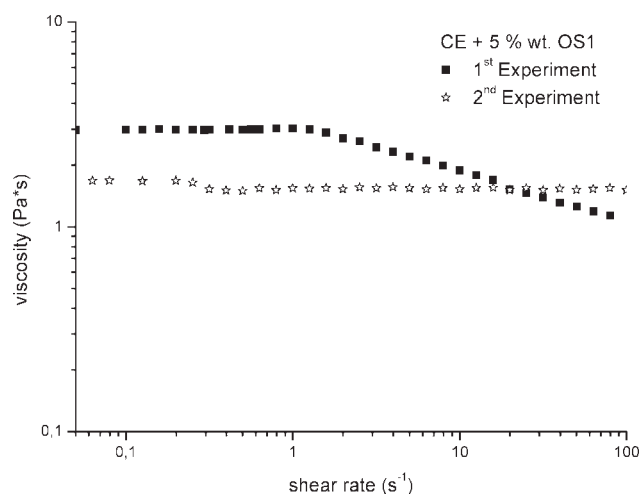


Figure 5 Viscosity of CE resin filled with 5% wt of OS1, from the first and the second sweep experiments, as a function of shear rate.

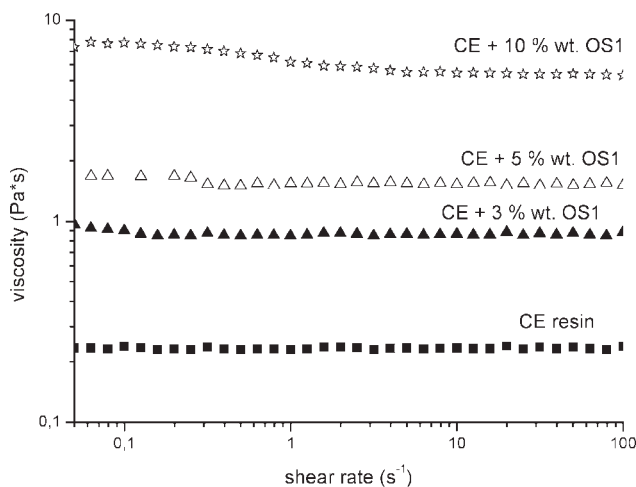


Figure 6 Viscosity of unfilled CE compared with those of CE filled with 5% wt and 10% wt of OS1 *o*-Boehmite (second sweep experiments).

this case the viscosity curves found from the two successive experiments are markedly different and, in particular, the viscosity calculated from the first sweep experiment is higher than that obtained in the second run. Moreover, while in the first experiment was observed a non Newtonian behavior, the viscosity appears to be fairly Newtonian in the subsequent experiment. These observations suggest that there is a possible aggregation effect of the solid inorganic nanofiller. Accordingly, a first sweep experiment (preshear step) was always performed on all mixtures containing the *o*-Boehmite before the actual rheological measurements were made.

In Figure 6, the viscosity of unfilled CE is compared with that of CE filled with 3, 5, and 10% wt of OS1. These show the classical behavior of filled resins. The viscosity of the mixtures increases with increasing the volume fraction of OS1. The viscosity of all the mixtures containing the OS1 filler shows a moderate pseudoplastic behavior, assuming a value approximately independent of the shear rate beyond one s^{-1} , irrespective to the amount of the nanofillers present in the resin. This behavior has already been reported for mixtures of liquids containing nanofillers, such as montmorillonite, which is attributed to the shape of the filler exhibiting a certain amount of orientation with increasing the shear rate.²⁰

The dependence of the viscosity on the nanofiller volume fraction was analyzed on the CE resin and its mixtures. The shear rate range used varied from 1 to 100 s^{-1} , which corresponds to the range of shear rate in most UV radiation processes. In particular, in the case of stereolithography, a shear rate of 30 s^{-1} has been recommended.¹⁸ In the case of UV-printing of thin films (thickness $<20 \mu\text{m}$), high printing speed ($>250 \text{ m/min}$) are required. Since the shear rate is

related to the printing speed, v , and to the film thickness, d , through the following relationship:

$$\text{Shear rate} = v/d$$

The shear rate in this case is much higher than 100 s^{-1} .²¹

The rheology of multiphase systems, and, more specifically, of solid-liquid suspensions, has been the object of numerous investigations, both theoretical and experimental, starting from the work of Einstein.^{22,23} The Einstein equation, in particular, can be applied to very dilute suspensions (solid volume fraction, Φ , lower than 0.02) of solid rigid spheres in a Newtonian field,²⁴ as following:

$$\eta_r = 1 + 2.5 \Phi \quad (1)$$

where: η_r is the relative viscosity of the suspension, calculated as the ratio between the viscosity of the filled suspension, η , and the viscosity of the suspending medium, η_s .

The classical equation of Einstein was generalized to include a) the effect of viscoelasticity of the particles;²⁵ b) the non zero Reynolds number corrections;²⁶ c) the deformability of the solid particles;²⁷ d) the non spherical shape of the solid particles;²⁸ e) the sedimentation process of the filler.²⁹ Numerous relationships between relative viscosity, η_r , and the volume fraction of the solid particles, Φ , have been proposed.³⁰ These theoretical models start from three assumptions: (1) the diameter of rigid particles is large compared to the size of the suspending medium molecules, but small compared to dimensions of the gap in which the liquid mixture flows in a particular rheometer; (2) the flow is at steady state without inertial, concentration gradient or wall slip effects; and (3) the suspending medium adheres perfectly to particles.³¹

There could be also a fourth assumption to take into account the interparticle interaction, depending on the theoretical model used.

All the proposed equations assume that the diameter of the solid particles does not affect the viscosity of the suspension. In practice, it has been found that the relative viscosity of suspensions with very small particles (with diameter $\ll 1 \mu\text{m}$) is higher than that theoretically predicted by the aforementioned equations.

Three are the possible reasons for this:³¹

1. The low mobility of the molecules of the suspending medium adsorbed on the surface of the solid particles, due to the high surface area of the latter.
2. A substantial contribution from Brownian motion.

3. Colloidal aggregation of very small particles producing a weak lace configuration.

Form the analysis of the rheological data found in 16 different laboratories for suspensions of particles with micrometric dimensions, Thomas in 1965 obtained a good superposition of data with the following empirical equation:³¹

$$\eta_r = 1 + k_1 \Phi + k_2 \Phi^2 + k_3 \exp(k_4 \Phi) \quad (2)$$

with: $k_1 = 2.5$, $k_2 = 10.05$, $k_3 = 0.00273$, $k_4 = 16.6$.

Equation (2) was developed starting from the classical Einstein model, eq. (1), and operating a correction that takes into account for the micrometric diameters of particles possessing spherical shape. In particular, referring to the physical significance of the parameters introduced in eq. (2), k_1 takes into account the shape of the particles in suspension. The value of k_1 is 2.5 for spherical particles in the Einstein equation. Guth found that, in the case of non spherical particles, k_1 depends on the aspect ratio, p , according to eq. (3):³¹

$$k_1 = \frac{p}{2 \ln(2p) - 3} + 2 \quad (3)$$

The parameter k_2 was first introduced by Bachtelor to consider the increase in viscosity taking place in more concentrated suspensions (solid volume fraction $\Phi > 0.02$).³¹ Other authors have reported k_2 values ranging from 7 to 14.³¹ Finally, k_3 and k_4 were introduced by Thomas in the case of suspensions containing very small particles, as already mentioned.

To the best of our knowledge, the dependency of the relative viscosity on the volume fraction of solid particles possessing nanometric dimensions and not necessarily spherical has not yet been considered in depth. The *o*-Boehmite particles, used in the present study, have dimension of about 100 nm when dispersed in an epoxy matrix (as reported on the data sheet). The hypothesis for validity of Thomas equation in relation to the dimension of particles is, therefore, satisfied in this case. However, the shape of the particles is not exactly spherical, as reported in a previous work.¹⁹ In that study an aspect ratio for *o*-Boehmite particles dispersed in a thermally cured epoxy resin was found to be approximately three. By substituting this value in eq. (3), the resulting value for k_1 becomes 3.14. Moreover, the k_2 parameter in Thomas equation was set in our case equal to 0, since the solid volume fraction in the suspensions used was lower than 0.02. In other words, we have neglected a possible further increase in viscosity for higher concentrations than the dilute suspensions. Thomas eq. (2) modified to satisfy our requirements is, therefore:

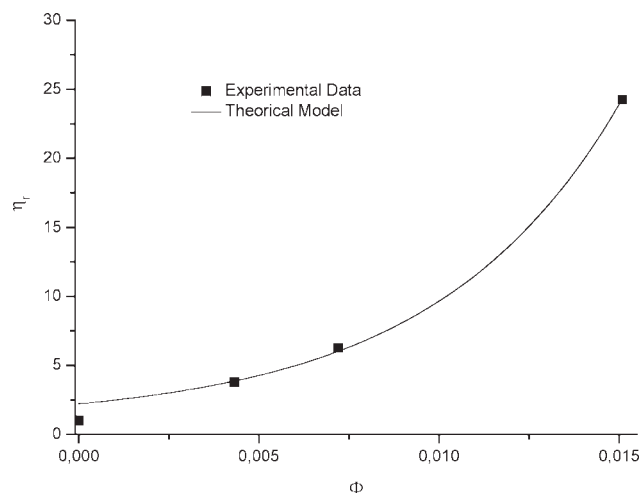


Figure 7 Comparison between the experimental relative viscosity and the prediction from modified Thomas model [eq. (4)].

$$\eta_r = 1 + 3.14 \Phi + k_3 \exp(k_4 \Phi) \quad (4)$$

This modified model applied to the experimental rheological data calculated for the mixtures used gives a good fit using the following numerical values for the parameters reported in eq. (4):

$$k_3 = 1.23$$

$$k_4 = 194.8$$

The comparison between the experimental viscosity data and the prediction of the model is shown in Figure 7.

CE/H 20 mixtures

The change of rheological behavior of the formulations based on the resin CE and HBP H 20 was examined as a function of the shear rate and filler content in a cone and plate rheometer. In Figure 8, the viscosity of the CE resin containing a 10% wt of H 20, measured in two subsequent sweep experiments, is plotted as a function of the shear rate. This formulation displays a pseudoplastic behavior with no differences between the two rheological curves, which indicates the absence of any possible effect of aggregation of the HBP on the rheology of the mixture. It has to be borne in mind, however, that a pre-shear step was always performed on the mixtures before the actual rheological measurements.

In Figure 9, the viscosity of unfilled CE resin as a function of the shear rate is compared with that of CE filled with 10 and 20% wt of H 20. A general increase in viscosity is observed with increasing the content of H 20. Furthermore, both systems containing H 20 show a pseudoplastic rheological behavior.

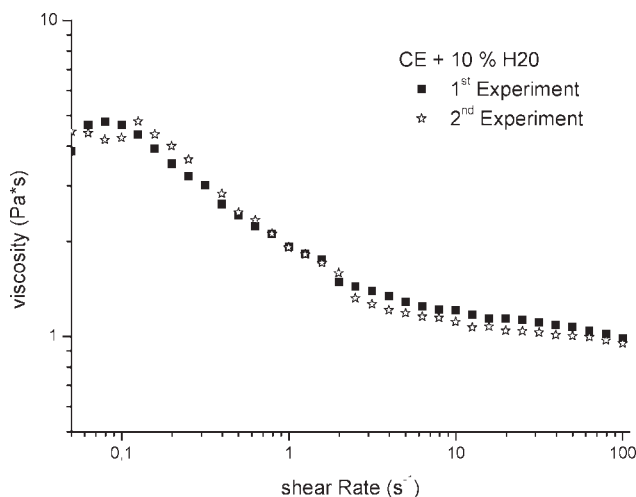


Figure 8 Viscosity of CE resin containing 10% wt of H 20, from the first and the second sweep experiments, as a function of shear rate.

This pseudoplastic behavior can be explained by a possible increase in M_w of mixtures based on the CE resin and containing the HBP, which behave as larger and more entangled polymeric molecules. It has been reported that OH-terminated hyperbranched aliphatic polyesters possess a strongly interactive structure at the end of the branches which attracts and immobilizes the reacting molecules of the epoxy resin.³² A similar behavior was found in another study, performed on a trifunctional triglycidyl-*p*-aminophenol (TGAP) epoxy resin containing similar OH-terminated hyperbranched aliphatic polyester, i.e., H 30.³² While the viscosity of TGAP resin was low with a Newtonian behavior, when the OH-terminated hyperbranched aliphatic polyester H 30 was added even in small percentages, around 5 wt %, the viscosity of the mixtures was

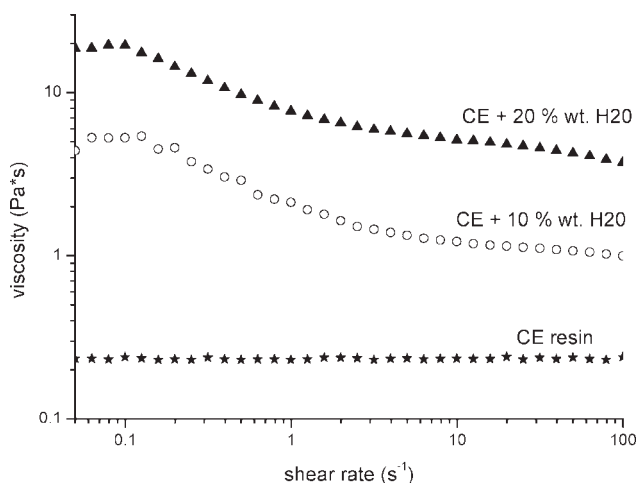


Figure 9 Viscosity of unfilled CE compared with those of CE containing 10% and 20 wt of H 20 (second sweep experiments).

considerably higher and exhibited a pseudoplastic behavior. This was explained in terms of a dominance of the shear-thinning behavior of the hyperbranched aliphatic polyester H 30, derived from the interactions between the functional groups on the molecular periphery.³³

In the context of the pseudoplastic rheological behavior of polymers and resins, the “zero shear viscosity” is an important scaling parameter. However, it may be difficult to reach sufficiently low values of the shear rate for many commercial resins using the available rheometers. Since the empirical “power law equation,” i.e.:

$$\eta = K\dot{\gamma}^{(n-1)} \quad (5)$$

(where K and n are model parameters, generally called consistency and flow index, respectively; and $\dot{\gamma}$ is the shear rate) does not allow to determine the zero shear viscosity, variations of this equation have been proposed. Cross proposed a model able to predict the plateau values for lower and upper Newtonian viscosities, indicated as η_0 and η_∞ , respectively:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\lambda\dot{\gamma})^m} \quad (6)$$

where λ and m are model parameters; $\dot{\gamma}$ is the shear rate. In particular, λ is the reciprocal of the shear rate at which the calculated value of η equals η_0 , while the parameter m is related to the power law index, n, by the expression:²⁴

$$m = 1 - n \quad (7)$$

The viscosity of epoxy/hyperbranched systems, η , was first calculated as a function of the shear rate using Cross equation.²⁴ Even though the shear rate range of interest for the UV applications is from 1 to 100 s^{-1} , the strong pseudoplastic trend of the mixtures containing the hyperbranched H 20 required the analysis of the whole shear rate range investigated. The values of the parameters in eq. (6), calculated by a non linear fitting of the experimental data shown in Figure 9, are reported in Table III. The resin CE displays a Newtonian behavior, therefore a zero value was set for both λ and m parameters. Referring to the mixtures containing H 20, at very low shear rates their viscosity is considerably higher than that of pure CE, as already pointed out. From the

TABLE III
Parameters of Cross Equation

Sample	η_0 (Pa s)	η_∞ (Pa s)	λ (s)	M
CE	0.23	0.23	0	0
10 H 20	7.45	0.87	5.53 ± 0.42	0.78 ± 0.042
20 H 20	26.24	4.05	5.89 ± 0.24	0.86 ± 0.032

calculation based on the Cross equation, the viscosity of both mixtures at very high shear rate values (i.e., η_∞) is also higher than that of the resin CE, especially for the 20% wt composition. The values of the parameter m calculated for the mixtures possessing 10 and 20% wt of H 20 are very similar, as witnessed by the similar behavior of their rheological curves. The values of λ found for both mixtures are also similar, showing a small increase by increasing the content of the HBP. This indicates that the pseudoplastic behavior starts at slightly lower shear rate values.

Finally, an appropriate relationship to predict the viscosity of each formulation as a function of the filler volume fraction, was derived. In this case, the additive rule generally employed to calculate the viscosity of mixtures composed by two or more fluid polymers cannot be used, since the viscosity was measured at ambient temperature, i.e., a condition in which the HBP is in the solid state. The Einstein equation cannot be either used, since the mixtures with the hyperbranched aliphatic polyester H 20 are not suspensions but polymeric solutions.

The relative viscosity (η_r) of each mixture, as well as of the pure CE resin, was, therefore, reported as a function of the volume fraction of the HBP H 20 (Φ), by varying the shear rate values, from 0 to 100 s^{-1} . The zero shear viscosity values in Table III were used to fit the experimental data, i.e.:

$$\eta_r = \exp(P\Phi) \quad (8)$$

The fitting with the experimental data is reported for several shear rate values in Figure 10. The parameter P decreases with increasing the shear rate, as reported in Table IV. It is interesting to note that in lower and upper Newtonian regions, the parameter P is almost independent from shear rate, but

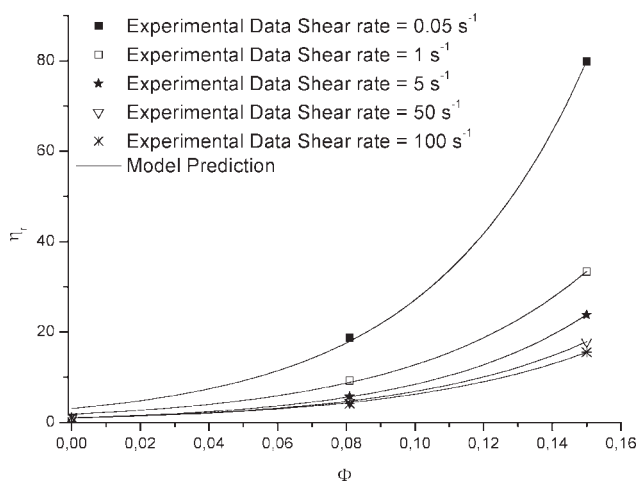


Figure 10 Comparison between the experimental relative viscosity and the prediction from eq. (8) of mixtures containing 10% and 20 wt of H 20 by varying the shear rate.

TABLE IV
Parameter P of Equation (8) as a Function of the Shear Rate

γ (s^{-1})	P
0	29.9 ± 0.42
0.05	29.2 ± 0.42
0.1	29.4 ± 0.64
0.3	26.1 ± 0.56
0.5	25.0 ± 0.55
1	23.4 ± 0.35
5	21.1 ± 0.03
10	20.5 ± 0.02
50	19.2 ± 0.06
80	18.8 ± 0.04
100	18.3 ± 0.06

decreases appreciably in the intermediate pseudoplastic region.

Further studies are in progress to verify the validity of eq. (8) to other mixtures based on an epoxy resin containing an HBP.

CONCLUSIONS

The rheological behavior of several formulations based on a cycloaliphatic epoxy resin for use in UV-curable products, containing an organo-modified Boehmite, OS1, or a hyperbranched aliphatic polyester, H 20, was analyzed as a function of the shear rate and of the content of each filler in a cone and plate rheometer.

A general increase in viscosity was observed with increasing the volume fraction of either fillers. A quasiNewtonian behavior was found at relatively high shear rates when *o*-Boehmite was added. A nonNewtonian behavior, over the entire range of shear rates, was always observed when the HBP was used, irrespective to the composition used.

Using the Thomas model for the viscosity of the suspensions, a modified equation was developed able to predict the values of viscosity of the mixtures containing the *o*-Boehmite as a function of the fraction volume content of the inorganic filler.

The viscosity data of the epoxy/hyperbranched systems were fitted using the Cross equation. The zero shear viscosity was determined for the mixtures studied. Finally, a suitable relationship able to predict the viscosity of formulations containing the HBP as a function of its filler volume fraction, was determined.

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