Macromol. Symp. **2007**, 254, 9–15 DOI: 10.1002/masy.200750802

Hyperbranched Polymers in Cationic UV Curing

M. Sangermano,[*1] *E. Amerio,*[1] *A. Di Gianni,*[1] *A. Priola,*[1] *D. Pospiech,*[2] *B. Voit*[2]

Summary: A wide range of hyperbranched polymers (HBP) was synthesized and investigated as additives in cationic photopolymerization of epoxy systems. The HBP were inserted into the polymeric network either by a copolymerization or through a chain transfer reaction involving the phenolic hydroxyl groups. By varying the type and concentration of HBP a modification of the bulk properties of photocured films was induced. An increase of toughness properties together with a flexibilization was obtained without affecting the processability and the viscosity of the photocurable mixture. In the presence of fluorine-containing HBP, a surface modification was induced.

Keywords: cationic photopolymerization; epoxy resin; fluorinated additives; hyperbranched polymers; surface properties

1. Introduction

Hyperbranched polymers belong to a group of macromolecules known as dendritic polymers;[1–4] they are characterized by a highly branched backbone and by a large number of functional groups which can be further modified.[5,6] The dense branched structure, which results in a low amount of intra- and intermolecular entanglements, allows good flow and processing properties, which is very important for coating applications. Moreover their synthesis is relatively easy and, in many cases, they can be obtained by only one synthetic step.[7] These characteristics render HBPs very attractive structures for academia and for industry.

HBP with acrylate, vinyl ether, allyl ether or epoxy functions were studied as multifunctional crosslinker[8–10] in coatings and in thermosets.[11,12]

The use of hyperbranched polymers was also reported in sensorics,[13,14] as non linear optic material,[15] in molecular imprinting[16] and also soluble functional supports.[17] We can also recall their use as processing-promoting agents,[18] toughening[19] and reinforcing agents.[20] These examples demonstrate the very broad perspectives of hyperbranched polymers in all areas of modern polymer science.

The presence of a large number of functional end groups and the peculiar shape of the HBP's can also be exploited in the synthesis of organic-inorganic hybrid nanocomposites, as they can allow a better interaction of the organic phase with the inorganic particles.[21]

Considering their characteristics we were interested to employ HBP in UV curable formulations; in fact the UV curing process is getting an increasing importance in different fields such as inks, adhesives and coatings on a variety of substrates, including paper, metal, plastic and wood.[22] Moreover, a multitude of high-tech and electronic applications, such as coating on optical fibers, microelectronics and the fabrication of printed circuit boards, have been developed.[23]

This polymerization technique allows obtaining a fast transformation of a liquid monomer into a solid film with tailored physico-chemical and mechanical properties. In the case of the cationic polymerization, onium salts are used as photoinitiators

---

[1] Politecnico di Torino, Dipartimento di Scienza dei Materiali e Ingegneria Chimica, C.so Duca degli Abruzzi 24, 10129 Torino, Italy
E-mail: marco.sangermano@polito.it
[2] Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

to generate very strong Brönsted acids upon photodecomposition.[24] The cationic photoinduced process presents some advantages compared to the radical one,[25] in particular lack of inhibition by oxygen, low shrinkage, good mechanical properties of the UV cured materials and good adhesion properties to various substrates. Besides, the monomers employed are generally characterized by being less toxic and irritant.

This paper intends to be a review of our recent works on the synthesis of different functionalized HBP and their use in cationic UV-curable formulations. The synthesized HBP were inserted into the polymeric network either by a copolymerization or through a chain transfer reaction involving the phenolic hydroxyl groups. By varying the type and concentration of HBP a modification of the bulk properties of photocured films was induced; in the presence of fluorine-containing HBP, a surface modification was also achieved.

2. Experimental Part

2.1 Materials

The following resins were employed: a bis-cycloaliphatic diepoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate, (*UVR 6110* from Dow, **CE**), a difunctional epoxy resin 1,6-hexanediol-diglycidyl ether by EMS (Switzerland, RV1812, **HDGE**) and a dioxetane 4, 4′-bis[(3-ethyl-3-ethyl-3-oxetanyl) methoxymethyl]biphenyl (**OXBP**), gently supplied by UBE Industries Ltd Japan).

A phenolic polyester HBP based on based on bis-(4′-hydroxyphenyl)pentanoic acid (**HBP-OH,** Mn = 4000 g/mol, Mw = 5500 g/mol, PD = 1.38),[24] a oxetane functionalized HBP (**HBP-OXT,** Mn = 1100 g/mol, Mw = 7600 g/mol PD = 9.9),[25] and a fluorinated functionalized HBP (**HBPF**, Mn = 5100, Mw = 22800, PD = 4.52)[26] were synthesized as elsewhere reported.

A commercially available mixture of antimonate sulfonium salts (UVI 6976) was supplied from Dow: it is given as solution with propylene carbonate (50 wt%) and it was added to the curable mixtures at a concentration equal to 2% wt/wt.

2.2 Samples Preparation and Characterization

The photocurable formulations were prepared by bulk mixing the HBPs with the corresponding resins in different ratio. The cationic photoinitiator was than added at 2 wt% to all the formulations. The hybrid formulations were prepared by adding to the HBP resin GPTS (20 wt%) as coupling agent and TEOS (from 10 to 50 wt%) as inorganic precursor. The photochemical curing was performed by using a Fusion lamp (H bulb), with radiation intensity on the surface of the sample of 280 mW/cm^2 and a belt speed of 6 m/min. For the hybrid samples a dual curing step was performed for allowing hydrolysis and condensation reaction: the UV-cured samples were stored in an oven at 75 °C for 4 hours in a chamber with constant humidity (95–98% relative humidity) controlled by a saturated solution of aqueous $NH_4H_2PO_4$.

The kinetics of photopolymerization was determined by FT-IR spectrometry in Real-Time. The FT-IR instrument used was a Genesis Series ATI Mattson (USA) spectrometer.

DSC measurements were performed using a Mettler DSC30 (Switzerland) instrument equipped with a low temperature probe. Dynamic-mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in tensile configuration. TGA analyses were performed using a LECO TGA-601 instrument in the range between 20 and 950 °C, with a heating temperature of 3 °C/min in air.

The gel content of the films was determined by measuring the weight loss after 20 hours extraction at room temperature with chloroform (ASTM D2765–84). The pencil hardness was evaluated on photocured films according to the standard test method ASTM D 3363.

The AFM measurements were done on the films coated on glass substrates in the

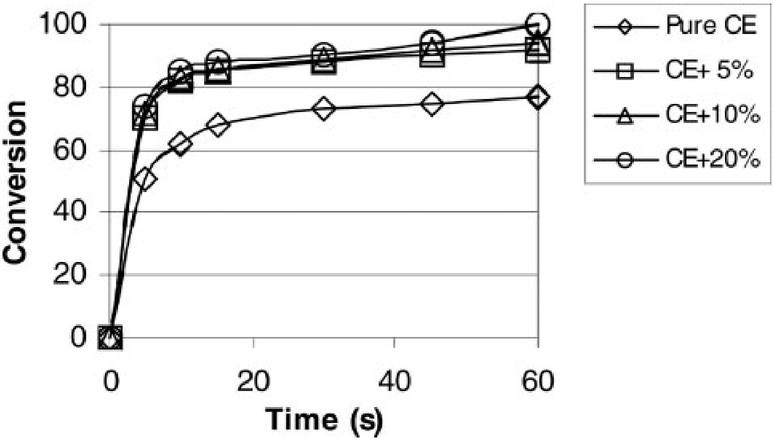


Figure 1.
FT-IR conversion curves as a function of irradiation time for CE/HBP-OH systems.

tapping mode using a Dimension 3100 Nanoscope IV (Veeco, USA). A Pointprobe silicon-SPM-sensor (Nanosensor, Germany) with spring constant of ca. 3 N/m and resonance frequency of ca. 75 KHz was used. The scan conditions were chosen according to Maganov (30) (free amplitude >100 nm, set-point amplitude ratio 0.5) in order to get stiffness contrast in the phase image that means bright features in the phase image are stiffer than dark. In order to remove any dust and surface attached impurities the films were rinsed with ethanol and air dried before analysis.

Samples were prepared for TEM observation by Argon ion polishing system GATAN PIPS, working at 3.5 keV at an angle of 7°. They were examined in a 300 keV transmission electron microscope (TEM) Philips CM30. TEM micrographs were processed with a slow scan CCD camera and analyzed with the Digital Micrograph program. The TEM observations were always performed using a very low electron flux in order to avoid any structural modification of the sample induced by the electron beam.

3. Results and Discussion

We started our investigations by studying the effect of HBP-OH as additive in cationic UV curing of CE resin. When studying photoinitiated crosslinking polymerization it is important to have some information on the rate of chain propagation because it does not only govern the reaction kinetics but will also affect the extent of cure and therefore the final properties of the polymer material produced. For this reason we performed some Real-Time FT-IR investigations: in Figure 1 the conversion curves as a function of time are reported for the CE monomer and its mixture in the presence of HBP-OH ranging from 5 to 20 wt%. The curves are obtained by FT-IR analysis following the decrease of the epoxy group peak at 750 cm^{-1}; the slope of the curves gives an indication of the rate of polymerization, while the plateau indicates the final epoxy group conversion.

The results of Figure 1 indicate that the epoxy group conversion increases by increasing the amount of the HBP in the photocurable mixture, reaching complete conversion values for the mixture containing 20 wt% of HBP. These results can be explained on the basis of a chain transfer mechanism involving the hydroxyl groups present on the surface of the HBP.

In order to modify the curing process of epoxide systems, the use of alcohols was first indicated by Penczek and Kubisa,[27] then confirmed by Crivello.[28,29] Recently hydroxyl functionalized particles were

Table 1.
Properties of UV cured films based on CE/HBP-OH.

UV cured sample	Gel Content (%)	Tg °C (DSC)	Tg °C (DMTA)	Impact Resistance J/cm^2	E′ MPa @ 50 °C
Pure CE	90	170	224	0.27	633
CE/HBPOH 95:5	99	160	180	0.27	1010
CE/HBPOH 90:10	100	155	183	0.30	1393
CE/HBPOH 80:20	98	158	180	0.33	1290
CE/HBPOH 70:30	100	150	178	0.40	1300

employed as chain transfer agents in the cationic polymerization of cycloaliphatic epoxy monomers.[30] The occurrence of a chain transfer reaction involving the OH groups causes the change of the kinetics of the process and of the properties of the cured networks. The same mechanism can be proposed for the increased epoxy group conversion observed in our case in the presence of the phenolic-OH group of the HBP additive.

The gel content in the product is very high (97–98%) in the presence of HBP, and it is even increased with respect to the pure CE photocured film (Table 1). This result indicates that the hyperbranched additive is tightly linked into the polymer network.

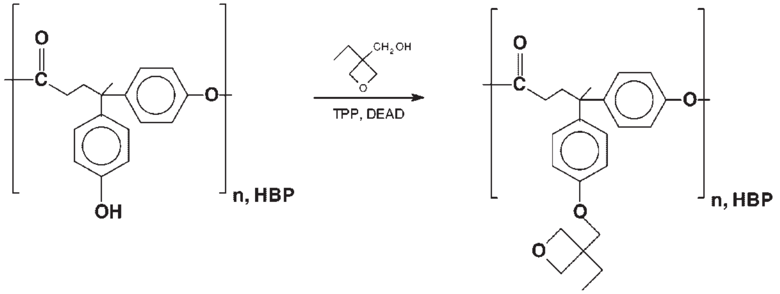
Thermal and dynamic-mechanical characterizations of the photocured films have been performed by means of DSC and DMTA analysis; the results are reported in Table 1.

It is possible to observe a decrease of glass transition temperature in the presence of the HBP additive. This flexibilization of the cured network is induced because of the low Tg of HBP (Tg = 55 °C) compared to pure CE networks. By decreasing the Tg of the system the mobility of the reactive species increases, thus the polymerization can reach completion, as already demonstrated in Figure 1 and previously discussed.

In agreement with the observed network flexibilization, an increase of the impact resistance by increasing the amount of HBP in the photocurable resin is obtained.

The modulus E′ was also assessed by DMTA analysis and the data are reported in Table 1. It is particularly interesting to observe that the increase in toughness is accompanied by a modulus increase, which is unusual. We can explain this results taking into account that the HBP additive behaves as a multifunctional crosslinker. The neat result is therefore a flexibilization induced by the introduction of the flexible HBP structure, but at the same time, as the HBP molecule acts as multifunctional crosslinker due to the large number of chain transfers, an increase of the crosslinking density of the network; this behavior is particularly interesting for high-scratch resistance coating preparation.

The aromatic-aliphatic hyperbranched polyester HBP-OH, with phenolic end groups, was subsequently modified with an oxetane functionality by a Mitsunobu reaction at low temperature with 3-hydroxymethyl-3-ethyloxetane, as reported in Scheme 1.



Scheme 1.

The modified HBP-OXT was employed as multifunctional comonomer in the cationic photopolymerization of an oxetane based system mixing it in the range between 5 to 20 wt% with OXBP.

The gel content of the cured networks was very high (always higher than 97%) indicating that the hyperbranched additive is tightly linked into the polymeric network.

The thermal (DSC and DMTA) investigations on UV-cured films showed an increase on glass transition temperature by increasing the amount of HBP in the mixture (Table 2). This behavior is explained on the base of an increase of crosslinking density due to the multifunctional cross-linker behavior of the HBP-OXT molecule.

The synthesized oxetane functionalized HBP contains a large number of reactive groups that can copolymerize with the oxetane resin, and at the same time it contains still a significant amount of phenolic groups that can interact with the carbocationic propagating species through a chain-transfer reaction, as previously demonstrated; therefore in this case the HBP molecule take part to the network formation both via a chain-transfer reaction involving the hydroxyl groups and via a copolymerization reaction involving the oxetane functionalities.

The successful random copolymerization of the dioxetane and HBP-OXT without major phase separation effects was evidenced by the presence of single Tg values, and confirmed by AFM analyses: topography and phase contrast of pure OXBP and OXBP/HBP-OXT 80:20 wt% photocured films were investigated and for both crosslinked materials a smooth surface with a nearly regular pattern was observed indicating that no major phase separation has occurred during polymerization in the presence of HBP-OXT and no specific domains are formed by the hyperbranched macromolecules. Therefore one can conclude that a rather homogeneous system has been formed through the copolymerization.

Finally the modification of HBP-OH via a Mitsunobu reaction with perfluoroeicosanol ($CF_3(CF_2)_9(CH_2)_{10}OH$) was performed; the reaction was conducted at low temperature with a degree of modification of the original OH end groups of about 60%, as determined by ^1H NMR spectroscopy.

The fluorinated HBPF was employed as additive, in the range of 1–5 wt%, to HDGE and photocured via a cationic process. Because of the large amount of unmodified hydroxyl groups, this additive behaves as multifunctional cross-linkers through a chain-transfer mechanism, as previously discussed for HBP; the properties of cured films were evaluated.

The gel content of photocured films, in the presence of HBFP, is very high (97–98%) indicating that the hyperbranched additive is tightly linked to the polymer network.

DSC analysis showed an increase in Tg values from –30 °C, for the pure HDGE resin, up to –20 °C for the cured mixture containing 5 wt% of HBPF.

Hardness, chemical resistance and adhesion of photocured films were also investigated (see Table 3). It is interesting to note that the cured films exhibited an increase on hardness in the presence of HBFP, according to the results of the pencil test. The increase on surface hardness can be due either to the increase on crosslinking density, as discussed previously, as well as to the presence of phenolic structure on the top layer of the film due to the surface migration of the HBFP.

Table 2.
Properties of oxetane cured films.

UV cured sample	Gel Content (%)	Tg °C (DSC)	Tg °C (DMTA)
Pure *OXBP*	98	125	140
OXBP/HBP-OXT 90:10	97	130	142
OXBP/HBP-OXT 80:20	97	145	160

Table 3.
properties of cured films containing HBPF.

Sample	Gel content %	Tg °C DSC	Hardness	MEK Resistance	Cross-cut adhesion %
HDGE	95	−30	6H	90	100
HDGE + 1 wt% HBFP	97	−30	6H	150	100
HDGE + 3 wt% HBFP	97	−24	6H–7H	260	100
HDGE + 5 wt% HBFP	98	−20	8H	260	100

In addition, the chemical resistance of the photocured films was improved as indicated by the increase of the MEK resistance. This behavior is attributable to the presence of fluorine on the film surface which induces high chemical resistance.

The presence of the fluorinated groups on the surface of the cured films is confirmed by a strong decrease on surface wettability with water for the UV cured films obtained in the presence of HBFP in the range between 1–5 wt% (see Figure 2).

Particularly interesting was to observe that the modified coatings containing HBFP showed a 100% adhesion on polar substrate (glass) as well as the pure epoxy resin.

It is well known that fluorinated coatings show poor adhesion because of their very low surface tension. The high adhesion values measured for the fluorine modified systems suggest a selective surface enrichment of the lower surface energy additive, HBFP, toward the less polar interface (air) during the curing process.

This behavior was further confirmed checking the wettability of the coatings on the glass side (see Figure 2). Small pieces of the coatings were detached from the glass substrates with some difficulties, because of their high adhesion, and water wettability measured.

The side of the coating in contact with glass did not report any modification in the presence of HBFP, showing an advancing contact angle of 70°, as the pure HDGE resin.

In this way it is possible to obtain highly hydrophobic surfaces without affecting the good adhesion properties, typical for epoxy resins.

Thus, notwithstanding its very low concentrations, the HBFP additive can protect the coatings from aggressive solvents, induced an increased hardness and it allows the preparation of a low energy surface: for

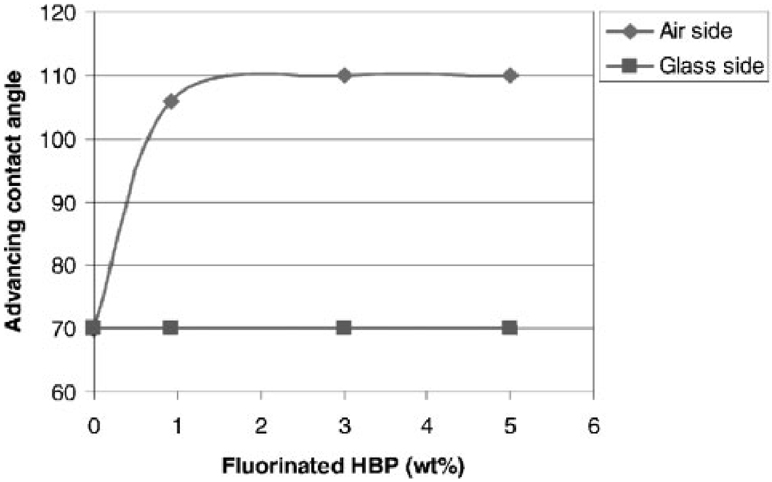


Figure 2.
Advancing contact angle values with water as a function of HBPF content.

all these reasons it may find suitable applications for engineering and developing advanced protective coatings.

4. Conclusions

A wide range of hyperbranched polymers was investigated as additives in cationic photopolymerization of epoxy and oxetane systems. The HBP were inserted into the polymeric network either by a copolymerization or through a chain transfer reaction involving the hydroxyl groups. By varying the type and concentration of HBP a modification of the bulk properties of photocured films was induced, with an increase of toughness properties together with an increase on modulus In the presence of fluorine-containing HBP a surface modification was also induced, with an increase in hydrophobicity without affecting the good adhesion properties of epoxy films.

In conclusion it has been demonstrated the powerful potential of the use of HBPs to modulate and tailor the final properties of the UV cured coatings, simply by varying the type of HBP component and its concentration in the UV curable system.

[1] Y. H. Kim, *J. Polym Sci Part A: Polym Chem* **1998**, *36*, 1685.

[2] B. Voit, *J Polym Sci Part A: Polym Chem* **2000**, *38*, 2505.

[3] J. M. J. Fréchet, D. A. Tomalia, *Dendrimers and Other Dendritic Polymers*, John Wiley & Sons, Chichester UK **2001**.

[4] C. Gao, D. Yan, *Prog. Polym. Sci.* **2004**, *29*, 183.

[5] D. Schmaljohann, B. Voit, J. Janssen, P. Hedriks, J. A. Loontjens, *Macromol Mater Eng* **2000**, *275*, 31.

[6] M. Johansson, E. Malmstrom, A. Hult, *J Polym Sci Part A: Polym Chem* **1993**, *31*, 619.

[7] M. Rogunova, T. Y. S. Lynch, W. Pretzer, M. Kulzick, A. Hiltner, E. Baer, *J Appl Polym Sci* **2000**, *77*, 1207.

[8] M. Johansson, E. Malmstrom, A. Hult, *J. Polym. Sc. Polym. Chem.* **1993**, *31*, 619.

[9] D. Schmaljohann, B. Voit, J. Jansen, P. Hedriks, J. A. Loontjiens, *Macromol. Mat. Eng.* **2000**, *275*, 31.

[10] M. Johansson, A. Hult, *J. Coat. Tech.* **1995**, *67*, 35.

[11] A. Hult, M. Johansson, E. Malmstrom, *Macr. Symp.* **1995**, *98*, 1159.

[12] A. Gopala, H. Wu, J. Xu, P. Heiden, *J. Appl. Polym. Sc.* **1999**, *71*, 1809.

[13] W. M. Lackowski, J. G. Franchina, D. E. Bergbreiter, R. M. Crooks, *Adv. Mat.* **1999**, *11*, 1368.

[14] G. Belge, D. Beyerlein, C. Betsch, K.-J. Eichhorn, G. Gauglitz, K. Grundke, B. Voit, *Anal. Bioanl. Chem.* **2002**, *374*, 403.

[15] Y. Zhang, L. Wang, T. Wada, H. Sasabe, *Macromol. Chem. Phys.* **1996**, *197*, 667.

[16] G. Maier, T. Griebel, *Polym. Preprints, ACS* **2000**, *41*(1), 89.

[17] A. Sunder, R. Mulhupt, R. Haag, H. Frey, *Adv. Mater.* **2000**, *12*, 235.

[18] H. F. Chow, T. K. K. Mong, N. F. Nongrum, C. W. Wan, *Tethraedron* **1998**, *54*, 8543.

[19] Boogh, B. Petterson, J. A. E. Manson, *Polymer* **1999**, *40*, 2249.

[20] D. J. Massa, K. A. Shriner, S. R. Turner, B. I. Voit, Macromolecules. **1995**, *28*, 3214.

[21] Z. Jianhua, Z. Yongbin, S. Wenfang, S. Xiaofeng, N. Kangming, *Polym. Adv. Technol.* **2005**, *16*, 55.

[22] S. P. Pappas, Ed., "*Radiation Curing, Science and Technology*", Plenum Press, New York **1992**.

[23] S. Davidson, "*Exploring the science, technology and applications of UV and EB curing*", Sita Technology, London **1999**.

[24] M. Sangermano, A. Priola, G. Malucelli, R. Bongiovanni, A. Quaglia, B. Voit, A. Ziemer, *Macromol. Mat. Eng.* **2004**, *289*, 442.

[25] M. Sangermano, A. Di Gianni, G. Malucelli, R. Bongiovanni, C. Roncuzzi, A. Priola, B. Voit, *J. Appl. Polym. Sci.* **2005**, *97*, 293.

[26] M. Sangermano, A. Di Gianni, R. Bongiovanni, A. Priola, B. Voit, D. Pospiech, D. Appelhans, *Macrom. Mat. Engin.* **2005**, *290*, 721.

[27] S. Penczek, P. Kubisa, R. Szamanski, *Macromol.Chem Macromol Symp.* **1986**, *3*, 203.

[28] J. V. Crivello, D. A. Conlon, D. R. Olson, K. K. Webb, *J.Radiat. Curing* **1986**, *13*, 3.

[29] J. V. Crivello, R. Acosta Ortiz, *J. Polym. Sci.: Part A: Polym.Chem.* **2002**, *40*, 2298.

[30] L. Valette, J.-P. Pauscault, B. Magny, *Macromol. Mater. Eng.* **2003**, *288*, 751 and 762.