

Cationic Photopolymerization of Oxetane-Functionalized Hyperbranched Polymers

M. Sangermano,¹ A. Di Gianni,¹ G. Malucelli,¹ C. Roncuzzi,¹ A. Priola,¹ B. Voit²

¹*Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Corso so Duca degli Abruzzi 24, 10129 Torino, Italy*

²*Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany*

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ABSTRACT: An aliphatic–aromatic phenolic hyperbranched starting material (HBP-OH) with phenolic end groups was 85% functionalized by a Mitsunobu reaction with oxetane groups (OXT-HBP). This new hyperbranched polyester was used, at a concentration of 5–20 wt %, as an additive for the cationic photopolymerization of a commercial oxetane-based resin, 4,4'-bis[(3-ethyl-3-ethyl-3-oxetanyl) methoxymethyl]biphenyl (OXB). HBP-OXT acted as a multifunctional crosslinker, copolymerizing with the oxetane ring of the OXB resin, reacting through chain transfer with the remaining phenolic OH groups, or doing both. The

result was an increase in the glass-transition temperature due to the increase in the crosslinking density. An increase in the weight residue at a high temperature was found in the presence of HBP-OXT and was attributed to the presence of phenolic groups, which are commonly used as antioxidant additives. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 293–299, 2005

Key words: hyperbranched; cationic photopolymerization; thermal properties

INTRODUCTION

Hyperbranched polymers, like dendritic macromolecules, have peculiar and often unique properties.^{1,2} They are particularly interesting because they resemble dendrimers, but they can be produced more easily on a larger scale at reasonable costs.³ Hyperbranched polymers are characterized by a highly branched backbone, which provides access to a large number of reactive groups that can be further modified.^{4,5} Their branching pattern, characterized by a low amount of intermolecular or intramolecular entanglements, gives them excellent flow and processing properties, which have attracted great attention, especially for coating and resin applications. Hyperbranched polyesters (HBPs) with acrylate, vinyl ether, allyl ether, or epoxy functions have been studied as multifunctional crosslinkers in coatings and in thermosets, with thermal and UV-curing methods.^{6–11}

Considering their characteristics, we were interested in investigating HBPs in UV-curable formulations. Hyperbranched polymers had already been in-

troduced to the field of UV curing in the past, but mainly in radical photopolymerization.^{8,9}

Just recently, our attention was focused on the use of HBPs in cationic photopolymerization.^{5,12–14} The cationic photoinduced process presents some advantages over the radical process,¹⁵ particularly a lack of inhibition by oxygen, low shrinkage, good mechanical properties for UV-cured materials, and good adhesion properties for various substrates. Moreover, the monomers employed are generally less toxic and irritating.

Different types of monomers and oligomers, mainly epoxides,^{16–18} vinyl ethers,^{19–21} and propenyl ethers,^{22–24} have been proposed and reported in the literature for cationic systems.

More recently, attention has been devoted to the synthesis and cationic photopolymerization of oxetane monomers.^{25–27} The high ring strain, very similar to that of epoxides, and the higher basicity make oxetanes interesting alternative monomers for cationic UV-curing applications.

In this framework, an aliphatic–aromatic HBP, HBP-OH, carrying phenolic end groups was modified completely with oxetane functionalities. The product was previously used in the cationic photopolymerization of vinyl ether components exhibiting rather low curing activity.⁶ In this study, we used a similar oxetane-modified HBP in combination with a commercially available difunctional oxetane as the comonomer, 4,4'-bis[(3-ethyl-3-ethyl-3-oxetanyl) methoxymethyl-

Correspondence to: M. Sangermano (marco.sangermano@polito.it).

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lbiphenyl (OXBP). The rate of cationic photopolymerization was investigated, and the properties of the cured films were evaluated.

EXPERIMENTAL

Materials

Triphenyl phosphine and tetrahydrofuran (THF) were purchased from Fluka. Diethoxyazodicarboxylate (DEAD) was purchased as a 40% solution in toluene from Fluka. 3-Hydroxyethyl-3-ethyloxetane was purchased from Aldrich. The dioxetane OXBP, supplied by UBE Industries, Ltd. (Japan), was used as a photocurable resin. Aliphatic-aromatic HBP-OH, based on bis(4'-hydroxyphenyl)pentanoic acid, was prepared via melt polycondensation as described in refs. 5 and 28, and a sample with a broad molar mass distribution (number-average molecular weight = 1100 g/mol, weight-average molecular weight = 7600 g/mol, polydispersity index = 9.9) was used as the starting material for the modification reaction. The modified HBP-OXT was employed in the curing reactions as a comonomer in the concentration range of 5–20 wt %. Triphenyl sulfonium hexafluoroantimonate (Cyracure UVI 6974, Dow), as a 50 wt % solution in propylene carbonate, was used as a photoinitiator (always 3 wt %). The monomer structure, along with a schematic representation of functionalized HBP-OXT, is reported in Table I.

Synthesis of oxt-hbp

The hyperbranched polymer (HBP-OXT) was synthesized as reported in ref. 5. The previously synthesized HBP-OH⁵ (AZ153; 4.3 g, 0.0039 mol) was dissolved in 40 mL of dry THF, and 2.25 g of 3-hydroxymethyl-3-

ethyloxetane (0.0194 mol) and 5.59 g of triphenyl phosphine (0.021 mol) were added. The solution was cooled to 0°C with an ice bath, and 9.13 g of DEAD (0.021 mol) was added dropwise under vigorous stirring. During the addition of DEAD, the formation of a solid precipitate was observed. The precipitate dissolved during the reaction, and a clear and transparent reaction mixture was obtained. After the addition of DEAD, the ice bath was removed, and the reaction continued for 2 days at room temperature. The product was precipitated twice in diethyl ether and dried *in vacuo*. After it was dried, 2.5 g of the product was obtained.

¹H-NMR (DMSO-*d*₆, δ): 9.25 (Ar—OH), 7.55 (Ar—H), 7.65 (Ar—H), 7.30–6.65 (Ar—H), 4.45 (O—CH₂), 4.35 (O—CH₂), 2.20–2.55 (CH₂—CH₂—CO), 1.75 (CH₂—CH₃), 1.5–1.7 (CH₃), 0.9 (CH₂—CH₃). Degree of modification: 85% (evaluation of the ¹H-NMR signals at 7.55–6.65 and 0.9 ppm).

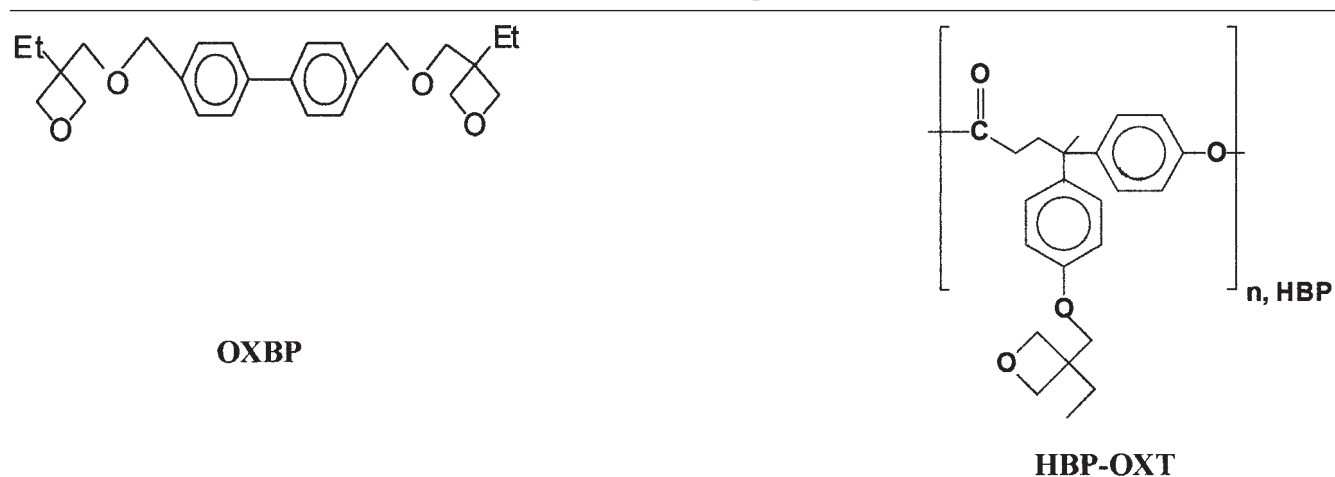
Film preparation

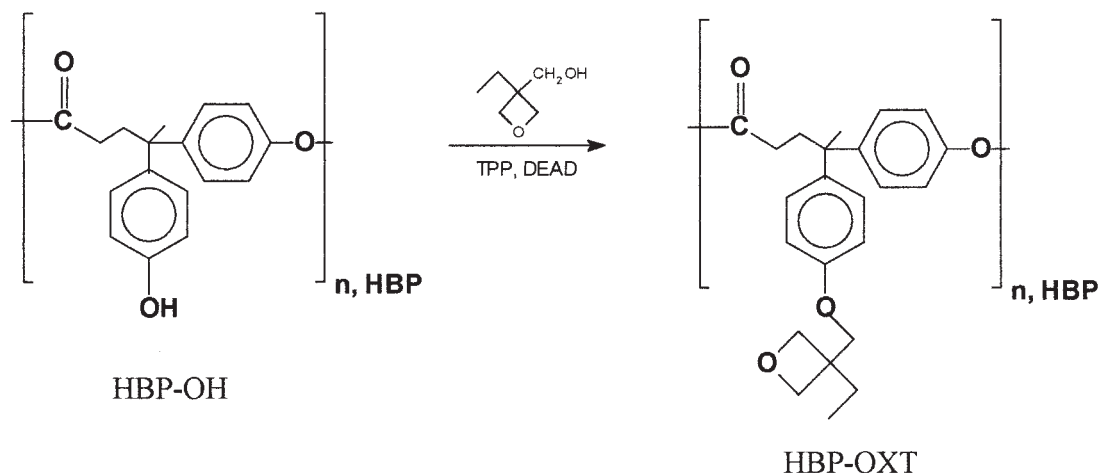
The photopolymerizable formulations were prepared by the bulk mixing of OXBP with HBP-OXT in different ratios. To the formulations, the photoinitiator (3 wt %) was added, and the mixtures were applied to a glass substrate with a wire-wound applicator. The wet film was exposed to UV irradiation with a Fusion lamp (H bulb); the radiation intensity on the surface of each sample was 280 mW/cm², and the belt speed was 6 m/min. The number of passes needed to achieve a full cure was 1 or 2.

Analysis and characterization

The kinetics of photopolymerization were determined by Fourier transform infrared (FTIR) spectrometry

TABLE I
Monomer Structure and a Schematic Representation of HBP-OXT





Scheme 1

from the decrease in the band at 980 cm^{-1} attributable to the oxetane ring.²⁹ A SiC plate was coated with the photocurable mixture, and the reaction was followed after different times of irradiation with a medium-pressure Hg lamp (Italquartz, Milan, Italy) with a light intensity of 25 mW/cm^2 . The FTIR instrument was a ATI Mattson (United States) Genesis series spectrometer. Differential scanning calorimetry (DSC) measurements were performed with a Mettler (Switzerland) DSC30 instrument equipped with a low-temperature probe. Dynamic mechanical thermal analysis (DMTA) was performed with a Rheometric Scientific (United Kingdom) MKIII instrument at a frequency of 1 Hz in a tensile configuration. Thermogravimetric analysis (TGA) was performed with a Leco TGA-601 instrument between 20 and 950°C at a heating rate of 3°C/min in air. The atomic force microscopy (AFM) measurements were performed on the films coated on glass substrates in the tapping mode with a Dimension 3100 Nanoscope IV (Veeco, United States). A Point-probe silicon SPM sensor (Nanosensor, Germany) with a spring constant of approximately 3 N/m and a resonance frequency of approximately 75 KHz was used. The scanning conditions were chosen according to Maganov et al.³⁰ (free amplitude $> 100\text{ nm}$, set-point amplitude ratio = 0.5) to obtain stiffness contrast in the phase image; this meant that bright features in the phase images were stiffer than dark features. For the removal of any dust and surface-attached impurities, the films were rinsed with ethanol and air-dried before analysis.

The gel content of the films was determined by the measurement of the weight loss after 20 h of extraction at room temperature with chloroform.

All the testing of the photocured films was performed after 24 h of storage of the samples.

RESULTS AND DISCUSSION

Aromatic-aliphatic HBP-OH with phenolic end groups was synthesized as previously reported⁵ and subsequently modified with an oxetane functionality by a Mitsunobu reaction with 3-hydroxymethyl-3-ethyloxetane at a low temperature, as reported in Scheme 1. A degree of modification of approximately 85% was achieved, and so in addition to the oxetane functions, some unmodified phenolic groups were present, too, in HBP-OXT. On the basis of the molar mass of the starting HBP-OH, we estimated that the modified HBP-OXT had on average 4–28 oxetane functions per macromolecule.

The modified HBP-OXT was employed as a multifunctional comonomer in the cationic photopolymerization of an oxetane-based system; 5–20 wt % with respect to OXBP was used (Table I), along with Cyra-

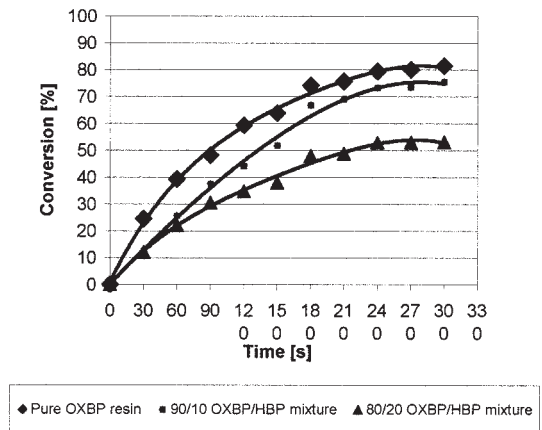


Figure 1 FTIR conversion curves as a function of the irradiation time for OXBP and mixtures containing different amounts of HBP-OXT: (◆) pure OXBP resin, (■) 90/10 OXBP/HBP mixture, and (▲) 80/20 OXBP/HBP mixture.

TABLE II
Properties of the UV-cured Films

UV-cured sample	T_g (°C)		Gel content (%)	Weight residue (% at 450°C)
	DSC	DMTA		
Pure OXBP	125	140	98	25
90/10 OXBP/HBP-OXT	130	142	97	35
80/20 OXBP/HBP-OXT	145	160	97	45

cure UVI 6974 as a photoacid generator (i.e., a photoinitiator).

When photoinitiated crosslinking polymerization is studied, some information is needed on the rate of chain propagation because it not only governs the reaction kinetics but also affects the extent of cure and, therefore, the final properties of the polymer material produced. For this reason, we monitored the photopolymerization process of the pure oxetane resin and its mixtures with oxetane-functionalized HBP-OXT by FTIR.

In Figure 1, the conversion curve for the oxetane ring-opening polymerization of the pure OXBP resin is plotted as a function of the irradiation time and compared with those of mixtures containing 10 or 20 wt % HBP-OXT. A decrease in the rate of polymerization and oxetane conversion with an increasing concentration of HBP-OXT in the photocurable formulation was observed.

To understand this polymerization behavior, we investigated the thermal characterization of the photocured films with DSC and DMTA. The results, to-

gether with the gel content after 20 h of extraction in chloroform, are reported in Table II.

The gel content was very high (always >97%), and this indicated that the hyperbranched additive was tightly linked to the polymeric network. The DSC and DMTA data showed an increase in the glass-transition temperature (T_g) with an increasing concentration of HBP in the mixtures. Figures 2 and 3 present DMTA thermograms for pure OXBP and 80/20 (w/w) OXBP/HBP-OXT photocured films, respectively. In the T_g region, a strong decrease in E' is evident, and the $\tan \delta$ curve shows a maximum that corresponds to T_g of the cured film. A comparison of the two DMTA curves shows a shift in the maximum of the $\tan \delta$ curve toward higher temperatures in the presence of HBP-OXT.

This behavior can be explained by an increase in the crosslinking density due to the multifunctional crosslinker behavior of the HBP-OXT molecule. The synthesized oxetane HBP contained a large number of reactive groups that could copolymerize with the oxetane resin, and at the same time it contained a significant number of phenolic groups that could interact with the carbocationic propagating species through a chain-transfer reaction, as demonstrated in previous works for epoxy¹³ and oxetane¹⁴ systems.

These two reaction mechanisms were responsible for the increase in the crosslinking density through the incorporation of the highly branched and compact hyperbranched macromolecules and, therefore, for the increase in the T_g values. By this, an earlier vitrification effect was induced, which slowed down the rate of polymerization; thus, a larger number of oxetane

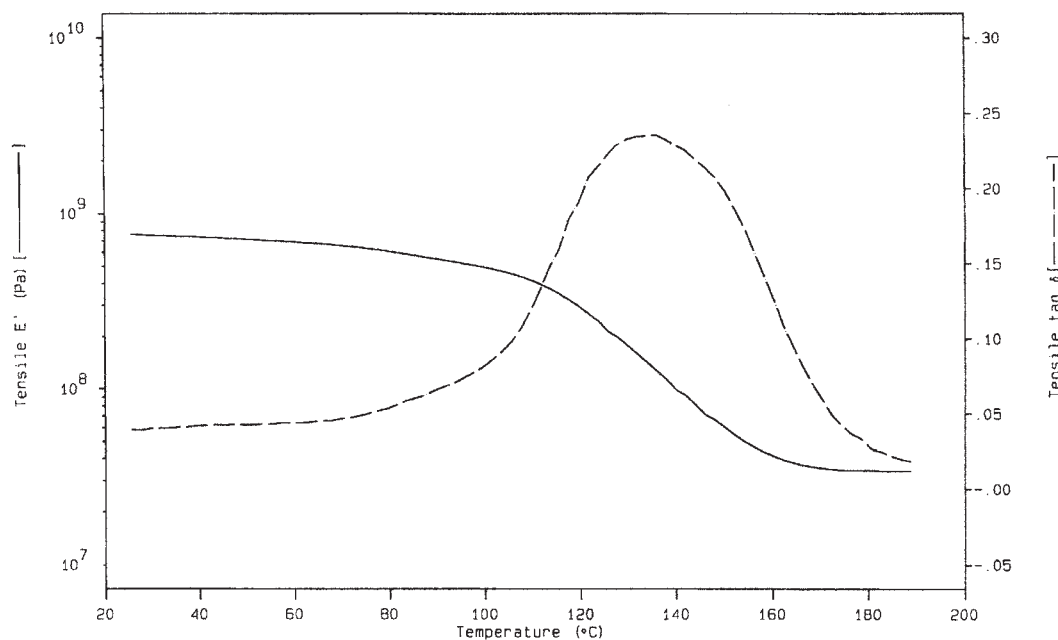


Figure 2 DMTA thermogram of pure OXBP photocured film.

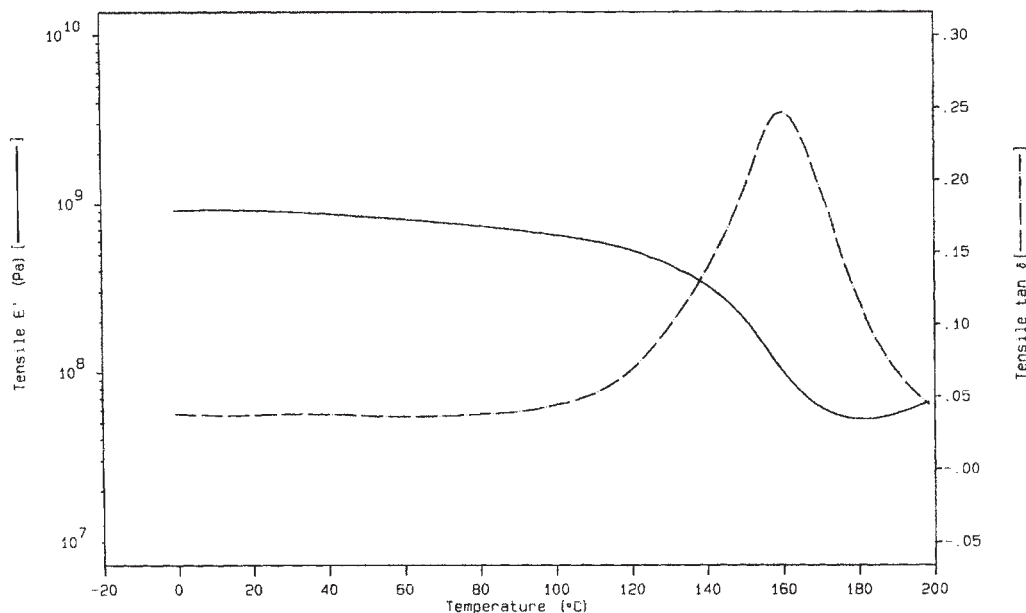


Figure 3 DMTA thermogram of OXBP/HBP-OXT (90/20) photocured film.

reactive groups remained trapped in the glassy polymeric network, and this explains the FTIR kinetic data described earlier.

The successful random copolymerization of the di-oxetane and HBP-OXT without major phase-separation effects was evidenced by the presence of single T_g values and confirmed by AFM analyses. In Figures 4 and 5, AFM images (topographic and phase-contrast) of pure OXBP and 80/20 (w/w) OXBP/HBP-OXT photocured films, respectively, are shown. For both

crosslinked materials; a smooth surface with a nearly regular pattern (spherical areas with a diameter less than 50 nm) can be observed, and it might have been induced by the precleaning procedure of the films: for the removal of any dust and surface-attached impurities, the films were rinsed with ethanol and subsequently air-dried just before analysis. The ethanol might have caused a slight swelling of the film, which showed stiffer areas (brighter spots in the phase image) in the highly crosslinked parts. However, the two

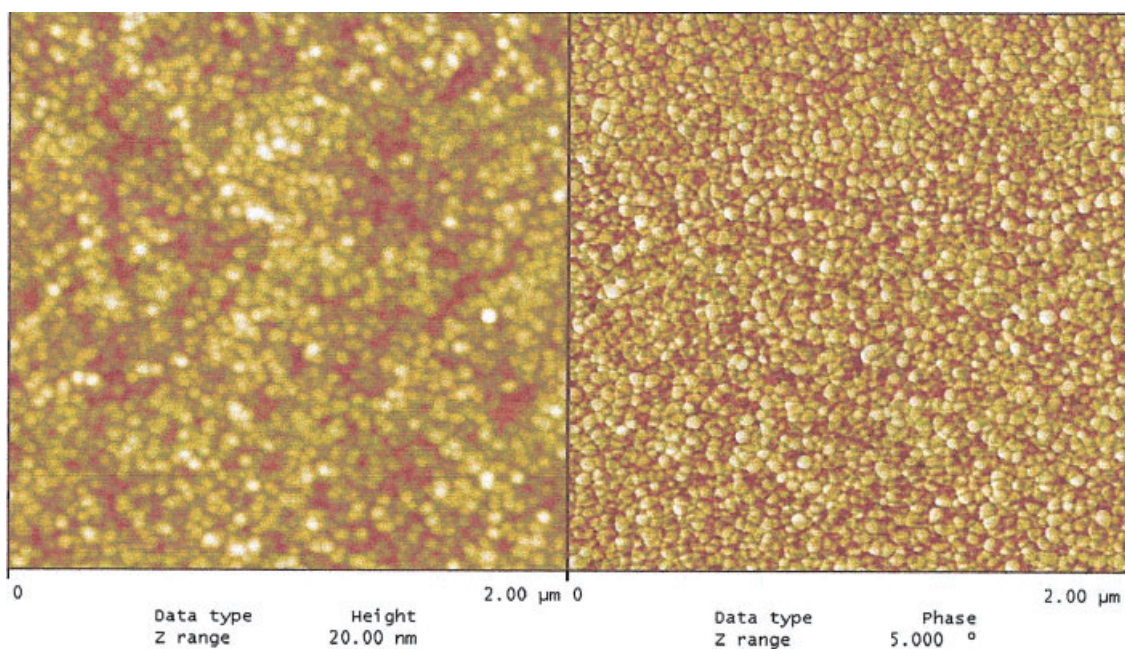


Figure 4 AFM topographic (left) and phase (right) images of pure photocured OXBP.

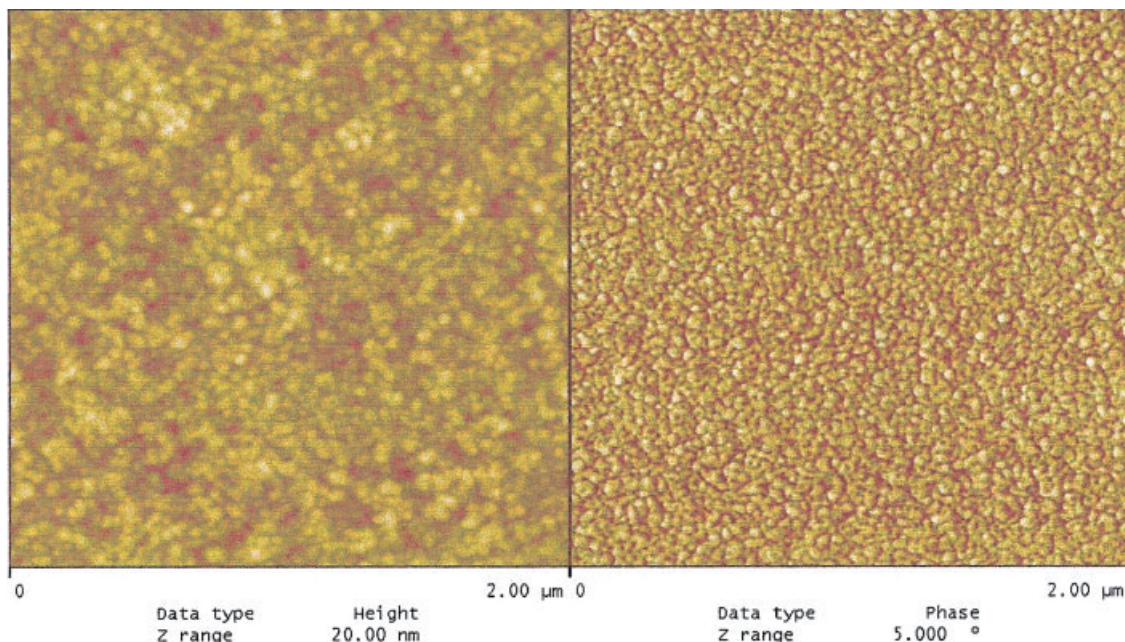


Figure 5 AFM topographic (left) and phase (right) images of photocured OXBP/HBP-OXT (80/20).

films did not show any differences, and this indicated that no major phase separation occurred during polymerization in the presence of HBP-OXT and that no specific domains were formed by the hyperbranched macromolecules. Therefore, we could conclude that a rather homogeneous system was formed through the copolymerization.

Additionally, thermal investigations were performed with TGA of the photocured films. The TGA curves are presented in Figure 6. An interesting increase in the weight residue at a high temperature ($>450^{\circ}\text{C}$) was observed with an increase in the concentration of HBP in the photocurable mixture; this behavior could be important for applications of these polymers in electronic devices for which high-temperature resistance is required. This effect was probably due to the introduction of phenolic moieties into the

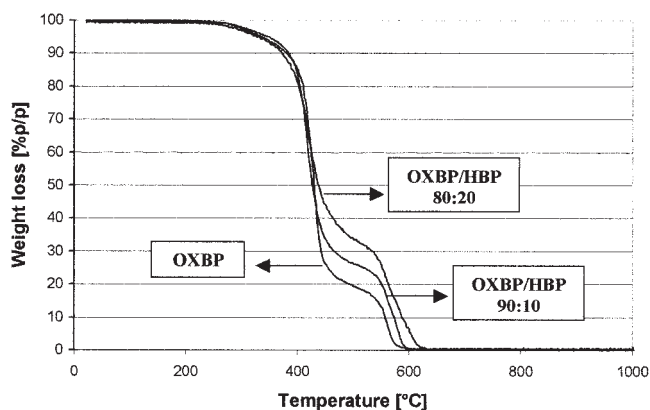


Figure 6 TGA of UV-cured films.

polymeric network. In the literature, it is reported that phenol-cured epoxides show better thermal properties at higher decomposition temperatures,³¹ and hindered phenols are commonly used as antioxidants because of their ability to limit the propagation of alkyl radicals and the resulting chain scission.³²

CONCLUSIONS

An aliphatic–aromatic HBP-OH with phenolic end groups was 85% functionalized by a Mitsunobu reaction with oxetane groups. The obtained product was added to a commercial available dioxetane resin in the concentration range of 5–20 wt %. When the concentration of HBP-OXT was increased in the photocurable mixture, a decrease in the conversion rate and final oxetane conversion was found. These results were explained by an earlier vitrification due to the increase in T_g induced by the multifunctional HBP-OXT crosslinker behavior. The HBP macromolecules were linked to the polymeric network through a copolymerization with the oxetane ring of the OXBP resin, through a chain-transfer reaction with the remaining phenolic OH groups, through both. An increase in the weight residue at a high temperature was found in the presence of HBP-OXT and was attributed to the presence of phenolic groups, which are commonly used as antioxidant additives.

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