

Processing and Chemorheology of Epoxy Resins and Their Blends with Dendritic Hyperbranched Polymers

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ABSTRACT: Toughened epoxy systems have found increasing applications in automotive, aerospace, and electronic packaging industries. The present article reported work done for elucidation of gelation and vitrification for various epoxy systems and their blends with dendritic hyperbranched polymers (HBPs) having epoxy and hydroxyl functionality. Gel time was found to increase with increasing functionality from diglycidyl ether of bisphenol A (DGEBA) to tetraglycidyl diaminodiphenyl methane (TGDDM). The vitrification point was clearly identified from rheological

experiments for triglycidyl *p*-amino phenol (TGAP) and TGDDM. In the case of DGEBA a clear display of vitrification was not observed. TGDDM underwent vitrification sooner than did TGAP. Hydroxyl-functionalized HBP reduced the gel time of the blends because of the accelerating effect of -OH groups to the epoxy curing reaction. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1604–1610, 2004

Key words: gelation; thermosets; rheology; hyperbranched polymers (HBPs); curing of polymers

INTRODUCTION

Dendritic hyperbranched polymers (HBPs) are characterized by three-dimensional spherical structures like dendrimer with a large number of surface functional groups.^{1,2} However, unlike dendrimer, which is monodisperse, the HBPs are polydispersed systems with lesser precision of molecular structure.^{3,4} HBPs are made by a cost-effective single-step process and are available in sufficient quantities to allow for investigation of their utility in conventional engineering applications.

Because of their compact 3D structure these molecules mimic the hydrodynamic volume of spheres in solution or in melt and flow easily past each other under applied stress. This results in a low melt viscosity, even at high molecular weights, attributed to a lack of restrictive interchain entanglements.⁵ In fact dendritic polymers have been shown to exhibit melt and solution viscosities that are an order of magnitude lower than their linear analogues of similar molecular weights.^{6,7} The high density of surface functional groups on dendritic polymer also offers the potential for tailoring their compatibility either through conversion of dendritic polymer end groups to chemically suitable moieties or through *in situ* reaction to form covalently bound networks. These two properties—

low viscosity and tailorable compatibility—make them excellent candidates for additives that could act simultaneously as toughening agents.^{8,9}

Recently we reported an excellent processable thermosetting system based on difunctional epoxy/HBP blends and proposed for potential application as matrix for fiber-reinforced plastic composites.^{10,11} From the perspective of application, the effective use of any thermosetting system requires one to be able to predict the cure kinetics of the system¹² to consistently obtain the maximum glass-transition temperature and also to predict the flow behavior of the curing resin, in particular to precisely locate when the sol–gel transitions occurs. This is because the polymer can be easily shaped or processed only before the gel point, where it can still flow and can be easily formed with stresses applied relaxed to zero thereafter. Accurate knowledge of the gel point (GP) would therefore allow estimation of the optimum temperature and time for which the sample should be heated before being allowed to set the mold. The GP is also useful in that it can be used to determine the activation energy for the cure reaction of the system.¹³

The GP of a crosslinking system is defined¹⁴ unambiguously as the instant at which the weight-average molecular weight reaches infinity and as such is an irreversible reaction. Crosslinked polymer at its GP is a transition state between a liquid and a solid. The polymer reaches its GP at a critical extent of crosslinking (α_{gel}). Before the GP, that is $\alpha < \alpha_{\text{gel}}$, the polymer is called a sol, because it is typically soluble in appropriate solvent. Beyond GP, that is $\alpha > \alpha_{\text{gel}}$, at least part

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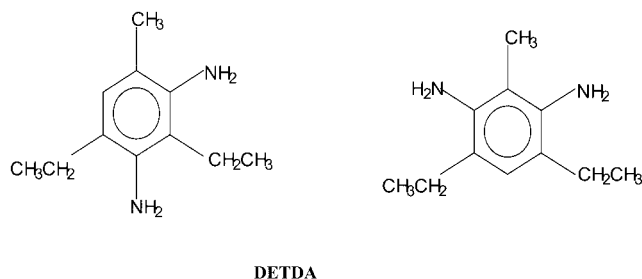


Figure 1 Chemical structures of epoxy resins and hardener.

of the polymer is typically not soluble in any solvent and is called a gel. Kinetically, gelation does not usually inhibit the curing process so the conversion rate remains unchanged; thus it is not detectable by techniques that are sensitive only to chemical reaction like differential scanning calorimetry (DSC) and thermogravimetric analysis.

There are various methods to determine gel point.¹⁵ In the present study GP was determined by a rheological method. Another important process, which a thermoset resin undergoes, during cure, is vitrification, which can also be determined by the rheological method. Vitrification is defined as the point at which the glass-transition temperature of the network becomes the same as the cure temperature. At this point the material is transformed from a rubbery gel to a gelled glass. The chemorheology of epoxy resins with varying number of epoxy functionality and their blends with HBP are reported in the present article.

EXPERIMENTAL

Materials

The conventional difunctional epoxy resin was a liquid diglycidyl ether of bisphenol A (DGEBA, Araldite LY 556; Ciba-Geigy, Summit, NJ). The multifunctional resins used in this study were triglycidyl *p*-amino phenol (TGAP, Araldite MY 0510; Ciba Speciality Chemicals) and tetraglycidyl diaminodiphenyl methane (TGDDM, Araldite MY-720; Ciba Speciality Chemicals).

The curing agent, Ethacure 100 (Albemarle Corp.), is a mixture of the two diethyltoluene diamine (DETDA) isomers (74–80% 2,4 isomer and 18–24% 2,6 isomer). The chemical structures of the epoxy resins and hardener are shown in Figure 1.

The epoxy functional dendritic hyperbranched polymer (Boltorn E1), with an epoxy equivalent weight of about 875 g/eq and a molecular weight of about 10,500 g/mol, was supplied by Perstorp Speciality Chemicals (Sweden). E1 consists of a highly branched aliphatic polyester backbone with an average of 11 reactive epoxy groups per molecule.

The hydroxyl-functionalized HBP used was a fifth-generation (G-5) Perstorp hyperbranched polyol. These are developmental materials based on polyester chemistry and have on average 128 –OH end groups per molecule and theoretical molecular weight and polydispersity index of 14,000 g/mol and 2.0, respectively. The HBP molecules were synthesized from a pentaerythritol (C₅H₁₂O₄) core and multiple 2,2-diethylol propionic acid (C₅H₁₀O₄) chain extenders or repeat units. The developmental resins are available in moderate quantities under the trade name of Boltorn.

The chemical structures of HBP(OH) and Boltorn E1 are shown in Figure 2.

Preparation of blends and curing

Both HBPs were mixed with epoxy to obtain various blend compositions. The epoxy functional HBP(E1), a viscous liquid, was mixed with epoxy with thorough stirring. The hydroxyl-functionalized HBP [HBP(OH)], a solid, was mixed with epoxy using acetone as solvent. HBP was first dissolved in acetone and the solution was added to the epoxy. The mixture was stirred and heated until a homogeneous solution was obtained. The acetone was then removed under reduced pressure.

The epoxy/HBP blends were homogeneous at 100°C in the case of both epoxy- and hydroxyl-functionalized HBP. DETDA was added with the homogeneous mixture under stirring. The concentration of HBP was restricted to 20% because in blends containing higher concentrations, the bubbles could not be completely removed. In this work, epoxy/HBP blend means the blend including a stoichiometric amount of DETDA. The epoxy and the blends were cured at different temperatures (120, 140, and 160°C) in a parallel-plate rheometer to study the rheological property.

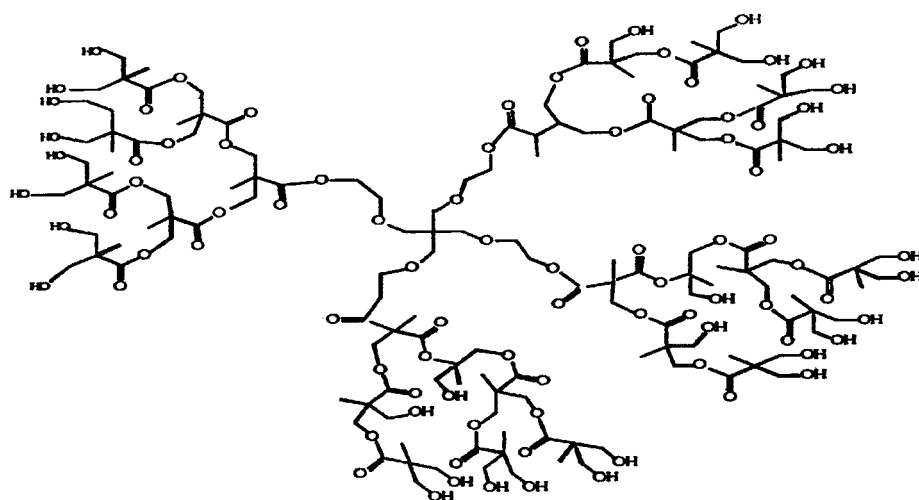
Rheological study

A Bohlin CS 10 controlled-stress rheometer was used to study the variation in rheological properties during cure. A parallel-plate assembly (40 mm diameter) was used in the oscillatory mode. All the data reported here were taken using a constant frequency of 43 Hz.

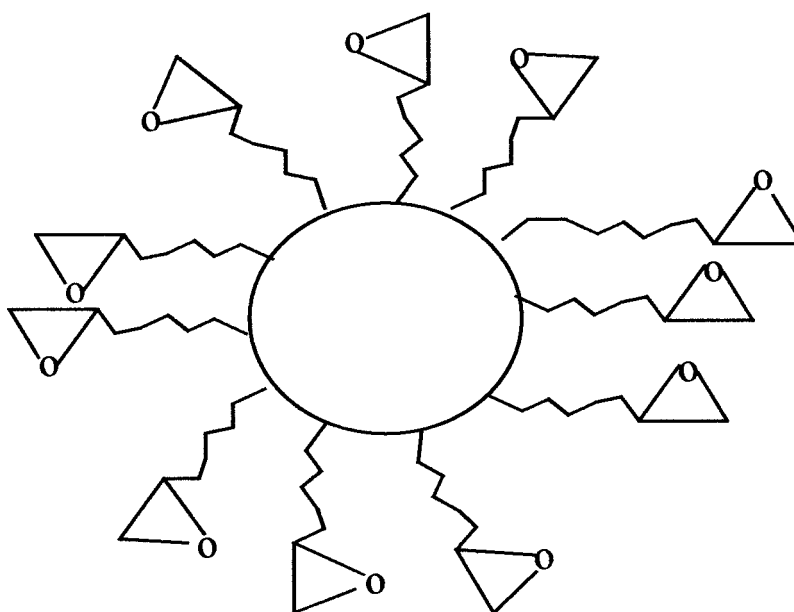
The rheometer was first preheated to the desired temperature, after which the sample was incorporated and the evolution of loss modulus was recorded.

RESULTS AND DISCUSSION

Rheological measurement, carried out as just discussed, permitted the characterization of the gelation and vitrification processes during curing. The evolution of loss modulus (G'') for DGEBA, TGAP, and TGDDM against the curing time at 140°C using



HBP (OH)



E1

Figure 2 Chemical structures of HBP(OH) and E1.

DETDA as curing agent is shown in Figure 3. The point at which a clear increase in G'' occurs is defined as gel point and G'' maximum is defined as the vitrification point. It is evident from the figure that TGAP and TGDDM show both gelation and vitrification (loss modulus maximum), whereas in the case of DGEBA the vitrification is not obvious. This supports the work

by Gillham and coworkers^{16,17} who showed, using torsional braid analysis, that vitrification is not necessarily observed because it can depend on the cure temperature and reaction kinetics. They found that at higher cure temperatures the time to vitrify increases relative to gelation, whereas the loss modulus peak becomes less intense, until it reaches a point where it

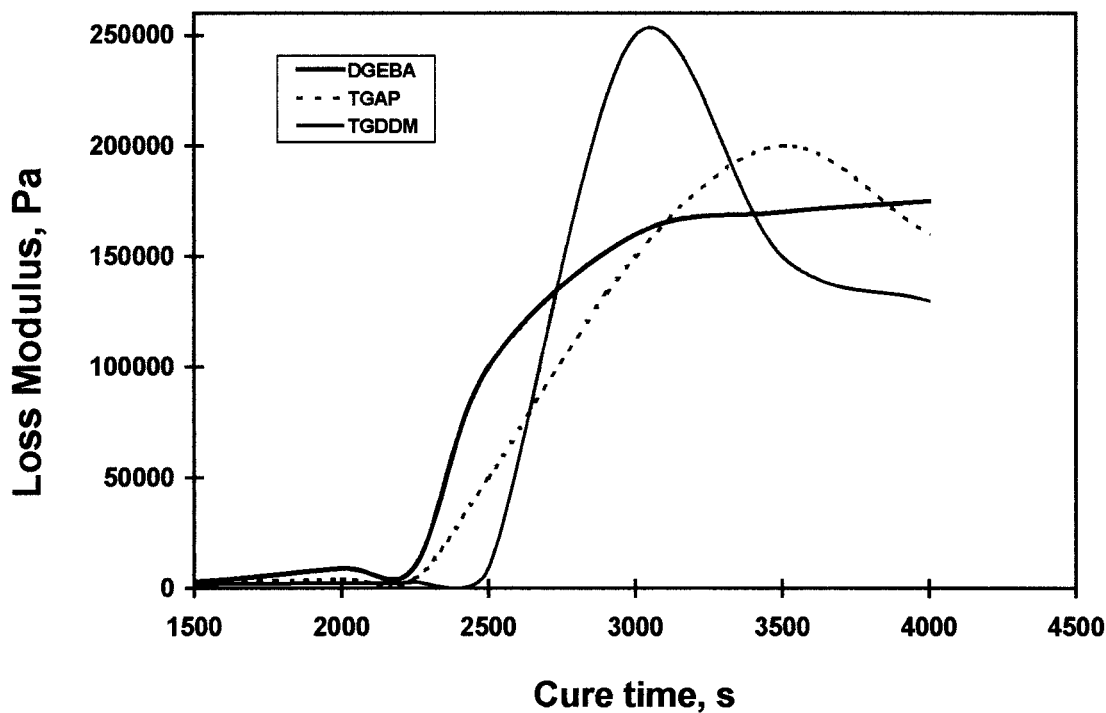
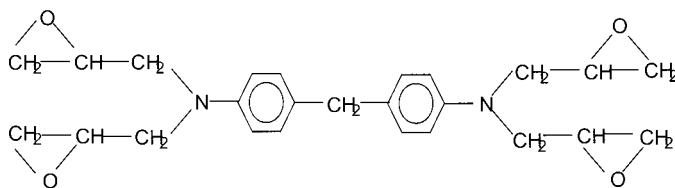
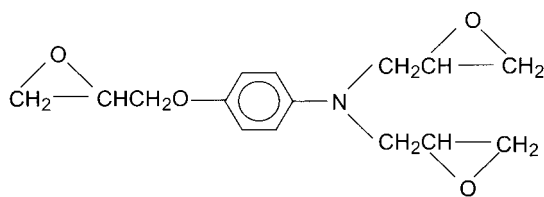
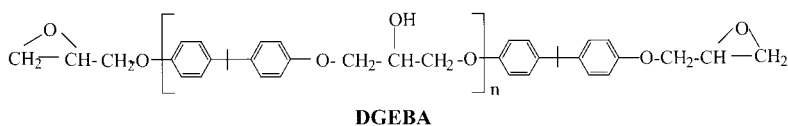


Figure 3 Evolution of loss modulus versus cure time at 140°C.

is so diffuse that it is readily observed. Conversely, Varlay et al.¹⁸ showed, using more highly crosslinked systems such as TGAP/diamino diphenyl sulfone, during flexural braid analysis, that vitrification always

occurs soon after gelation with no evidence of any decrease in intensity. It appears that a similar process occurs here, in that TGAP and TGDDM systems display clear vitrification soon after gelation.



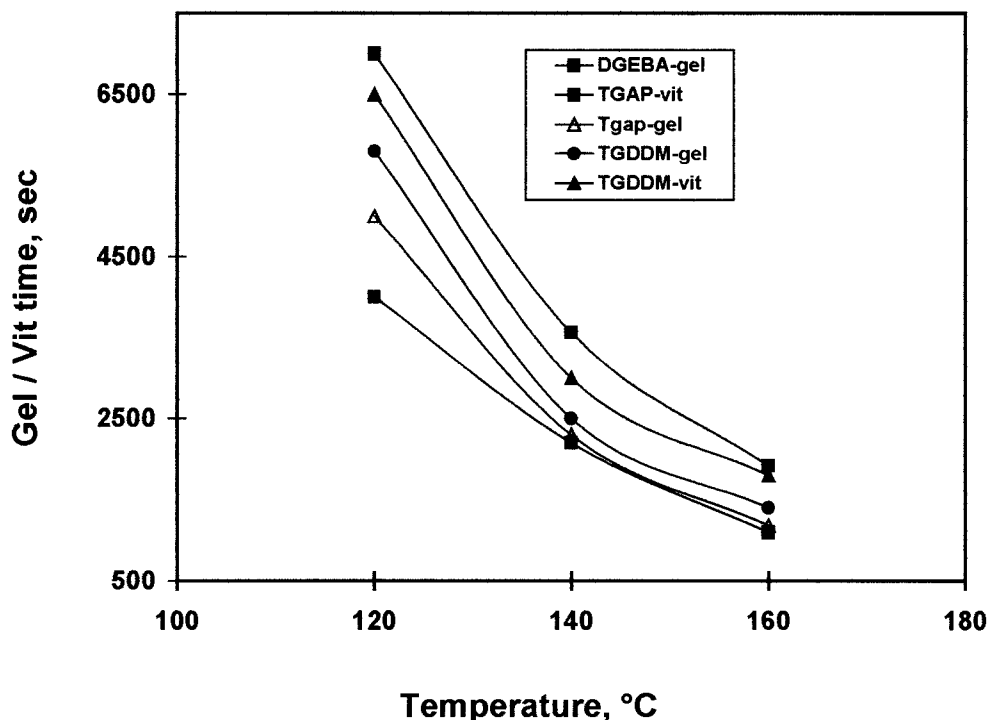


Figure 4 Effect of cure temperature on gel time and vitrification time.

Gel point conversion (α_{gel}) is inversely proportional to the functionality of a monomer.¹⁴ Hence the gel time is expected to decrease from DGEBA to TGDDM with increasing functionality of the resin. However, a reverse trend was observed in this work. This can be explained by considering the fact that the epoxy resins are basically prepolymer and their initial viscosity and increase in viscosity during curing play an important role in controlling the rate of curing reaction. An increase in viscosity of the medium retards the chemical reaction attributed to restricted molecular mobility. The increase in viscosity during cure is higher in the case of resin with higher functionality. This explains why TGDDM gels later than TGAP and DGEBA. Beyond gelation the system becomes highly viscous and then functionality rather than viscosity controls the curing, and thus TGDDM vitrifies sooner than does TGAP. The maximum loss modulus value of TGDDM was found to be higher than that of TGAP (Fig. 3). This can be explained in terms of chemical structures of TGAP and TGDDM (Fig. 1). The molecular weight between crosslinks (M_c) for the TGAP network is lower than that for the TGDDM network.

The gel time and vitrification time for various epoxy systems were determined at various temperatures and results are presented in Figure 4. At decreasing cure temperature the gelation and vitrification times increase exponentially as would be

expected from the Arrhenius equation. The effect of addition of epoxy-functionalized HBP on gelation and vitrification at 160°C for epoxy/HBP blends is shown in Figure 5. The figure indicates that addition of epoxy-functionalized HBP has hardly any effect on gelation and vitrification, although HBP is known to cure at a slower rate compared to that of epoxy resin.¹⁹ This behavior is different from that observed in the case of other liquid rubbers like carboxyl-terminated poly(2-ethyl hexyl acrylate) (CTPEHA), reported earlier,²⁰ where a significant increase in gel time was observed. In those cases the delay was attributed to the viscosity effect, which retards the movement of reactive molecules. Blending of HBP with epoxy, however, does not lead to any significant change in viscosity and hence the reaction rate remains unaffected. The viscosity of HBP at 25°C (15 Pa s^{-1}) is about 3 times lower than that of the acrylate-based liquid rubber CTPEHA (42 Pa s^{-1}) reported earlier.^{21,22}

Addition of hydroxy-functionalized HBP was found to decrease the gel time of epoxy/HBP blends (Fig. 6). This indicates that epoxy- and hydroxyl-functionalized HBP blends undergo curing faster than the epoxy alone. This substantiates our earlier observation that the temperature corresponding to the peak exotherm T_{peak} (determined from DSC thermogram) decreases with the incorporation of the same HBP into the difunctional and tetrafunctional epoxy systems.^{23,24} In the case of epoxy-functionalized HBP no significant change in T_{peak} was

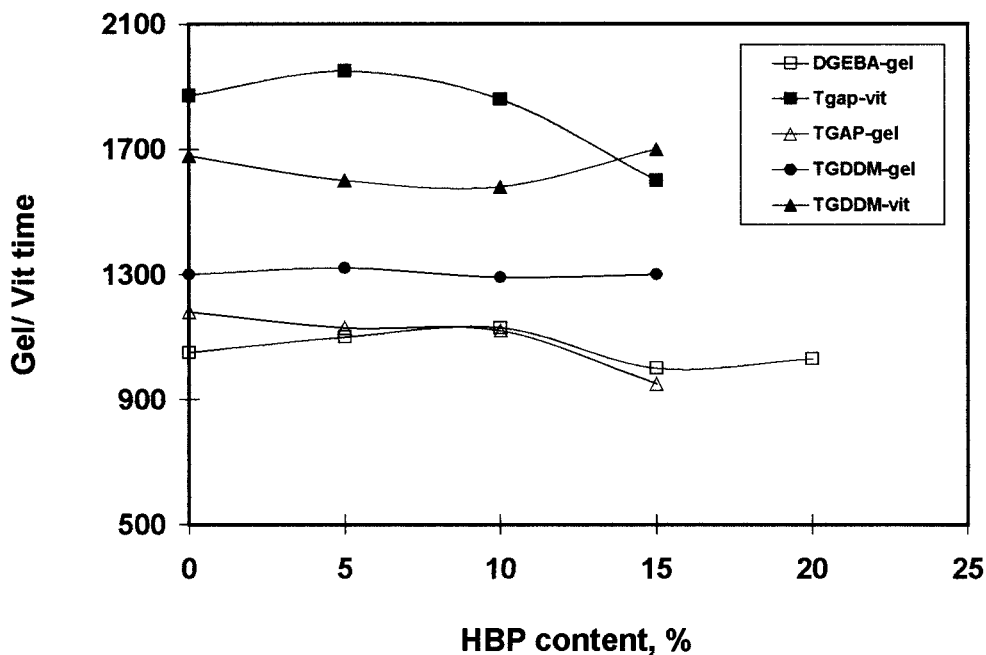


Figure 5 Effect of addition of epoxy-functionalized HBP on gel time and vitrification time at 160°C for various epoxy systems.

observed.²⁵ The catalytic effect of hydroxyl-functionalized HBP on epoxy curing can be interpreted in terms of intermolecular transition state; according to this mechanism²⁶ strong hydrogen-bonding species, such as acid and alcohols, stabilize the transition state and encourage the nucleophilic attack of amine.

CONCLUSIONS

Gelation and vitrification of various epoxy systems and epoxy/HBP blends were investigated by the rheological method. The functionality of the resin and the corresponding branching of the network were found

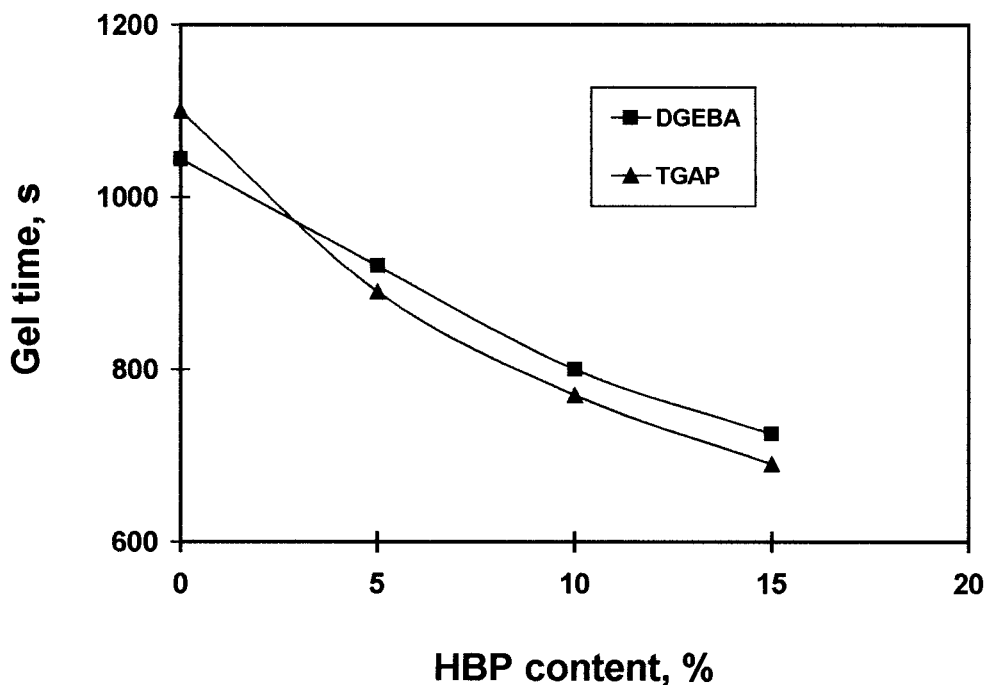


Figure 6 Effect of addition of hydroxyl-functionalized HBP on gel time at 160°C for DGEBA and TGAP.

to determine how the systems will gel and vitrify. The blend containing hydroxyl-functionalized HBP undergoes gelation faster compared to the blend containing epoxy-functionalized HBP.

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