Dynamic Mechanical Analysis on Highly Thermally Stable Polybenzoxazines with an Acetylene Functional Group

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ABSTRACT: Dynamic mechanical analysis is performed on polybenzoxazines from acetylene-terminated benzoxazine monomers, and glass transition temperatures of these polybenzoxazines are found in the range of 329–368°C. It has been identified that the high glass transition temperature and high thermal stability are due to polymerization of the acetylene terminal group, in addition to oxazine ring polymerization through a comparison study with analogous polybenzoxazines that are obtained from monomers without an acetylene functional group. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 857–862, 1999

Key words: polybenzoxazine; acetylene-functional polymer; dynamic mechanical analysis; glass transition temperature

INTRODUCTION

Polymers with high thermal stability are in increasing demand in an advanced composite system as a matrix resin and in the electronic industry for packaging application. At the same time, it is required to have low melt viscosity that enables easy impregnation or processing, no evolution of volatile components during polymerization, and long shelf-life at room temperature. Incorporating aromatic or heterocyclic ring components into polymer structures enables us to synthesize polymers with high thermal resistance, but with poor processability (e.g., high melt viscosity or inherent insolubility).[1] One of the approaches to making thermally stable polyimides with easy processability is to use low molecular weight amic-acid prepolymers end-capped with reactive alicyclic rings that polymerize by addition reaction.[1,2] Other approaches to a processable polyimide with improved solvent resistance and thermal properties used an internal acetylenic unit as a

crosslinking site.[3] Studies on many other acetylene-terminated resins have been reported,[4–13] because oligomers and polymers containing acetylenic groups can be polymerized into three-dimensional void-free networks under moderate conditions, and the polymers show solvent resistance, moisture resistance, and excellent thermo-oxidative stability.[14]

A recently developed family of benzoxazine-based phenolic resins has thermal properties of phenolic resin with mechanical performance and molecular design flexibility of epoxy resin.[15–17] Benzoxazine resins show excellent processability through their low melt viscosity. As they cure through ring-opening polymerization with or without a catalyst, no byproducts are released during polymerization, which eliminates the formation of voids in the products and gives near zero shrinkage.[16,17] To improve further the thermal properties of polybenzoxazines, a polymerizable side functional acetylene group was introduced into the structure of benzoxazine monomers, and high char-yielding polybenzoxazines were obtained.[18] To understand better the final properties, as well as processing conditions, polymerization of benzoxazine resins with side func-

Scheme 1

tional groups was studied by differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy after polymerization of each functional group and oxazine ring polymerization.[19] The focus of this work is to characterize acetylene functional benzoxazine resins as a high performance resin through the investigation of dynamic moduli and glass transition temperature of the polymerized resins.

EXPERIMENTAL

Novel solventless technique[20] was used for preparation of benzoxazine monomers, 3-phenylacetylene-3,4-dihydro-2*H*-1,3-benzoxazine (Ph-apa), bis(3-phenylacetylene-3,4,dihydro-2*H*-1,3-benzoxazinyl)isopropane (BA-apa), bis(3-phenylacetylene-3,4-dihydro-2*H*-1,3-benzoxazinyl)methane (BF-apa), and bis(3-phenylacetylene-3,4-dihydro-2*H*-1,3-benzoxazinyl)hexafluoroisopropane (BAF-apa). The details of synthesis and characterizations of acetylene-terminated benzoxazine monomers have been described previously.[18] Other benzoxazine monomers, bis(3-phenyl-3,4,dihydro-2*H*-1,3-benzoxazinyl)isopropane (BA-a) and bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)methane (BF-a) were synthesized by the method using a solvent.[16,19] Chemical structures and abbreviations for their corresponding benzoxazine monomers that will be used through the text are illustrated in Scheme 1. Ring-opening polymerization

and acetylene polymerization of the aforementioned monomers are described elsewhere.[19]

Samples for dynamic mechanical analysis were prepared by thermally polymerizing degassed benzoxazine monomers (Ph-apa, BA-apa, BAF-apa, and BA-a), in a vertical mold that consists of a U-shaped silicone rubber spacer between two glass plates that is treated with a silicone-based mold-release agent. The degassed benzoxazine monomers were polymerized by placing the resin-filled mold either in an air-circulating oven or in nitrogen, and by heating for 3 h at 160°C or 190°C. The black-colored polybenzoxazines were slowly cooled to room temperature. The specimen was prepared by cutting into appropriate dimensions using a diamond saw, sanding, and further polishing to obtain a smooth surface.

Dynamic mechanical spectra were obtained with a Rheometrics Dynamic Mechanical Spectrometer (RMS-800) equipped with a 2000–200 g-cm dual range force rebalance transducer. Specimens with dimensions of $\sim 48 \times 12 \times 3$ mm were tested in a rectangular torsion fixture. A maximum strain of 0.1% was applied sinusoidally during each temperature sweep at a frequency of 1 Hz. Strain sweep was used to determine the strain within linear viscoelastic limit. Measurements were collected at 2°C intervals, and the samples were heated at a rate of 2°C min^{-1} from −140°C to 400°C. Samples were provided with a thermal soak time of 30 s for each temperature change.

Polymerization of BA-apa benzoxazine monomer was followed by FTIR spectroscopy on a Michelson 110 MB FTIR spectrometer. One hundred coadded scans were taken at a resolution of 2 cm^{-1} using liquid nitrogen-cooled, mercury-cadmium-telluride (MCT) detector after 20 min purge with nitrogen. The monomers used for FTIR analysis were dissolved in tetrahydrofuran at a concentration of 10 wt %. The solution was cast on a KBr plate using a spin coater. The KBr plate with a drop of sample solution on it was spun at a speed of 2000 rpm for 2 min to obtain sufficiently thin and uniform film. The solvent was removed by placing the coated KBr plate in a vacuum oven overnight at 40–50°C. For polymerization study, the coated benzoxazine monomers on KBr plates were isothermally polymerized in an oven under either circulating air or nitrogen atmosphere. Normalized ratio A/A_0 represents an integrated area of the specific FTIR band (A) related to the integrated area of an internal standard band (A_0).

Figure 1 Dynamic mechanical spectra of Ph-apa, polymerized at 190°C for 3 h in air: (■) G', (▲) G'', and (○) tan δ.

DSC was performed on TA Instruments Modulated DSC 2920 with the same heating rate as dynamic mechanical analysis, 10°C min^{-1}, using nitrogen purge and an empty aluminum pan as a reference. A hermetic pan was used for all tests. DSC experiments were conducted with a BA-apa monomer and BA-apa polybenzoxazine that were polymerized at 160°C and 190°C for 3 h in air or nitrogen.

RESULTS AND DISCUSSION

Dynamic mechanical analysis is performed on high char-yielding Ph-apa, BA-apa, BF-apa, and BAF-apa polybenzoxazines that are obtained from acetylene-terminated monofunctional and bifunctional benzoxazine monomers.[18]

Usually, monofunctional benzoxazines without any reactive side functional groups do not crosslink but form only low molecular weight oligomers. However, Ph-apa resin was thermally polymerized into a strong solid sample without any catalyst, and dynamic mechanical spectra of the Ph-apa polybenzoxazine show the characteristic features of crosslinked thermosetting resin (as seen in Fig. 1). The Ph-apa polymer shows a high storage modulus, G', as can be seen by the value of 2.2 GPa at room temperature. The glass transition temperature (T_g) is centered at 329°C, as determined by the maximum of the loss spectrum, G''. Loss modulus G'' also shows three sub-T_g transitions at −100°C, transition in the range of 90–120°C, and an additional transition at 225°C. Even though the type of phenol used for Ph-apa is

monofunctional, the obtained T_g was surprisingly high. This high T_g of Ph-apa polymer suggests that polymerization of the acetylene group during polymerization was very effective.

Figure 2 shows the dynamic mechanical spectra of the BA-apa and BA-a polymers that are polymerized at 160°C for 3 h in nitrogen. At this condition, loss modulus, G'', of BA-a showed γ-transition at −80°C, broad β-transition from room temperature to ~ 120°C, and α-transition at 173°C. Loss modulus, G'', of the BA-apa polymer showed three transitions around the same temperature range as the BA-a polymer, and showed two more transitions in the region of 250–350°C. Above T_g of BA-a, the G' and G'' spectra of the BA-apa polybenzoxazine are attributed by the presence of the polymerizable acetylene terminal group in the structure of BA-apa. Polymerization of the acetylene functional group contributed to the crosslinked structure and increased T_g to 350°C from 170°C for BA-a, which does not have a reactive acetylene group. The G' and G'' spectra of BA-apa in the glassy region can be divided into two regions below and above 190°C, at which storage modulus, G', showed drop, from 1.7 GPa to 1.1 GPa. Below 190°C, G' and G'' spectra of this region are very similar to those of the analogous BA-a polybenzoxazine. Increasing temperature slowly during the experiment brought further crosslinking, and G' was recovered from the drop and increased to 1.7 GPa at 245°C. It resulted in high T_g (347°C). Changes in the crosslinked structure above 190°C are consequences mainly from further polymerization reactions of the unreacted acetylene group or its secondary reac-

Figure 2 Dynamic mechanical spectra of BA-apa and BA-a polymer, polymerized at 160°C for 3 h in nitrogen: (■) G' of BA-apa, (▲) G'' of BA-apa, (□) G' of BA-a, and (△) G'' of Ba-a.

Figure 3 Normalized A/A_0 versus reaction time of oxazine ring polymerization of BA-apa at: (●) 160°C, (■) 190°C, (▲) 200°C, and ×220°C.

Figure 5 DSC thermograms of BA-apa polymer, polymerized for 3 h at: (a) 160°C/N_2, (b) 160°C/air, (c) 190°C/N_2, and (d) 190°C/air.

tions. Polymerization temperature at 160°C was not high enough to bring the complete reaction of the acetylene group. This result can be related to the FTIR study of polymerization of the BA-apa resin, where 25% of the unreacted acetylene group was found at the same polymerization condition as this dynamic mechanical analysis specimen. It was further reduced to 7% when temperature was increased to 190°C (Fig. 3). It was also found that increasing temperature to higher than 200°C was effective to polymerize the residual oxazine ring (Fig. 4). These have also been supported by the DSC experiment (Fig. 5). From the DSC thermogram, the first exotherm centered at 188°C, which is assigned to the residual acetylene

group, disappeared when polymerization was increased from 160°C to 190°C by further polymerization. From Figure 2, the residual acetylene group and oxazine ring polymerization can be found from the recovery of G' above 190°C.

Figure 6 shows dynamic mechanical spectra of the BA-apa polymer prepared at 190°C for 3 h in nitrogen. In this condition, ~ 78% of the oxazine ring and 94% of the acetylene triple bond were consumed (as can be seen in Fig. 7). In this case, minor drop of G' in the glassy region was observed ~ 200°C. The transition in G'' around this region was smaller than the same transition in Figure 2, and the center of the transition shifted to 215°C. It also showed recovery of G' with increasing temperature during the experiment. It

Figure 4 Normalized A/A_0 versus reaction time of acetylene group polymerization of BA-apa at: (●) 160°C, (■) 190°C, (▲) 200°C, and ×220°C.

Figure 6 Dynamic mechanical spectra of BA-apa, polymerized at 190°C for 3 h in nitrogen: (■) G', (▲) G'', and (○) tan δ.

Figure 7 Normalized A/A_0 versus reaction time of BA-apa polymerization at 190°C in air and nitrogen for oxazine ring and acetylene group: (■) 953 cm^{-1}/N$_2$, (○) 953 cm^{-1}/air, (▲) 3283 cm^{-1}/N$_2$, and (△) 3283 cm^{-1}/air.

Figure 9 Dynamic mechanical spectra of BA-apa, polymerized at 190°C for 2 h and at 220°C for 1 h: (■) G', (▲) G'', and (○) tan δ.

suggests that increasing the polymerization temperature to 190°C in nitrogen was enough to bring significant changes to the crosslinked structure of the BA-apa polymer, but it was not enough for the development of a fully crosslinked structure. Figure 8 shows the dynamic mechanical spectra of the BA-apa polymer prepared at 190°C for 3 h in air. From the FTIR study in Figure 7, it was found that ~ 85% of the oxazine ring and 97% of the acetylene triple bond were consumed in this condition. It showed no significant drop in G' around 200°C and resulted in T_g at 356°C. This suggests that the presence of air is a favorable condition for the polymerization of acetylene functional benzoxazine resin. The dynamic mechanical spectra of postcured BA-apa polymer is

shown in Figure 9, and no major difference was found from the spectra in Figure 8.

The same tendency can be seen from G' and G'' of the BF-apa and BF-a polymers in Figure 10. The BF-a polymer without the acetylene group shows T_g at 173°C, whereas the BF-apa polymer shows T_g at 368°C. For the same reason, the BAF-apa polymer shows a high T_g of 362°C in Figure 11. For acetylene-terminated polybenzoxazines, which are based on bifunctional phenols, the general features of the dynamic mechanical behavior remain the same despite the differences in the type of bifunctional phenol used. They show three distinctive transitions approximately centered at −80°C, 260–270°C, and 356–368°C.

Figure 8 Dynamic mechanical spectra of BA-apa, polymerized at 190°C for 3 h in air: (■) G', (▲) G'', and (○) tan δ.

Figure 10 Dynamic mechanical spectra of BF-apa and BF-a, polymerized at 190°C for 3 h in air: (■) G' of BF-apa, (▲) G'' of BF-apa, (□) G' of BF-a and (△) G'' of BF-a.

Figure 11 Dynamic mechanical spectra of BAF-apa and BAF-a, polymerized at 190°C for 3 h in air: (■) G' of BAF-apa, (▲) G'' of BAF-apa, (□) G' of BAF-a, and (△) G'' of BAF-a.

It is also noteworthy that T_g's of this class of resins are much higher than polymerization temperature. This characteristic will be a great advantage for a high-performance polymer system that can be processed at a moderate temperature at 190°C, but exhibits a high T_g of 330–368°C. Few thermosetting polymers show such characteristics of higher T_g than the polymerization temperature.[21] Other important factors to be considered for a high-performance resin system is easy processability that is directly related to the melt viscosity of resins. This series of acetylene functional benzoxazine resins offer exceptionally beneficial processing characteristics and moderate polymerization temperature with high final T_g.

CONCLUSIONS

Dynamic mechanical properties have been measured for acetylene functional polybenzoxazines that are obtained from the BA-apa, BF-apa, BAF-apa, and Ph-apa monomers. A comparison was made with the dynamic mechanical properties of analogous polybenzoxazines that do not have an acetylene functional group. The storage modulus, G', of those acetylene-terminated polybenzoxazines, was in the range of 1.9–2.2 GPa at room temperature. The resulting T_g's were in the range of 330–368°C, which were significantly higher than the analogous polybenzoxazines and, also,

much higher than their polymerization temperature (190°C). Their higher T_g's were attributed to the presence of a polymerizable acetylene functional group that provided an additional crosslinking site. These monomers polymerize at moderate temperatures without any added catalyst.

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