Thiol-ene/hyperbranched polymer hybrid thin films: Cure behavior and gas barrier properties

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ABSTRACT

In this work, novel thiol-ene (TE)/hyperbranched polymer(HBP) hybrid thin films have been prepared by a simple photopolymerization method and the TE/HBP system was also investigated in terms of thermocuring behavior and gas barrier properties. The effect of added HBP on thermal curing (cross-linking) of TE polymer was examined with dynamic and isothermal differential scanning calorimeter (DSC) and compared with photocuring reaction of identical system. The structure of prepared TE/HBP hybrid thin film was analyzed by X-ray diffraction (XRD). Themomechanical analysis (TMA) provided extensive data on the coefficient of linear thermal expansion (CTE), dimensional change upon heating, and isothermal profile of TE/HBP hybrid thin films. Light transmittance as well as water/oxygen permeability of the resulting TE/HBP hybrid thin film was also measured depending on the HBP content.

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1. Introduction

Thiol-ene photopolymerization provides numerous advantages over acrylate photo-polymerization such as fast polymerization rates in the presence of oxygen, photoinitiatorless reactions, low shrinkage at high monomer conversion and, most importantly, versatility in ene monomer selection [1–4]. Any type of ene monomer commercially available can participate in a thiol-ene polymerization with fast rates of cure [2]. The basic thiol-ene photopolymerization is two-step radical chain process involving a propagating/chain transfer resulting in thiol addition across the ene double bond. The step-growth nature of the polymerization requires that a constant stoichiometric relationship between the functional groups must be maintained to ensure that the reaction reaches a high conversion. A chemically crosslinked polymer is formed when at least one of the components has a functionality greater than two. Because of essentially quantitative conversions and a free-radical step-growth process, photopolymerized thiol-ene films are highly uniform with dense network structures [5]. Thus photopolymerization is an efficient method for producing cross-linked materials with thicknesses ranging from a few microns to several millimeters [6].

On the other hand, nonlinear polymers such as hyperbranched polymers (HBPs) and dendrimers have attracted a significant and increasing interest during recent years. Dendrimers consist of AB_x type ($x>2$) monomers attached in layers around a central core, where each layer is called a generation. They have perfectly branched structures.

HBPs resemble dendrimers with the difference that they have randomly branched structures and contain varying amounts of linear segments. Compared with dendrimers obtained from multistep syntheses [7,8], HBPs are more advantageous as they can be easily synthesized through one-step polymerization processes [9,10]. Because of their highly functionalized globular structures, HBPs exhibit different properties from those of linear polymers of the same molar mass, such as less entanglement in the solid state [11], high solubility in various solvents, and low melt viscosity [12–14]. Terminal groups of HBPs have a great influence on their physical properties such as glass transition temperature (T_g) [15], relaxation process [16], viscosity [17], and solubility [18]. Although there has been much progress in the structural understanding and the methods of synthesis of HBPs, applications of HBPs to practical situations have rarely been carried out. Boogh and coworkers reported that HBPs showed outstanding performance as tougheners in epoxy resins [19]. Gopala's group employed hyperbranched polyester as a rheological modifier and toughening agent in bismaleimide [20]. In spite of high potential for good performance, the blends of HBPs with other linear polymers have rarely been studied. Novel blends of HBPs with linear polymers were studied by Massa and colleagues [21]. It has been reported that the addition of small perfect dendritic polyesters to poly (ethylene terephthalate) (PET) can yield miscible blends [22].

Based on these facts, a synergistic effect can be expected by combination of advantageous attributes of TE, highly stable network, transparency, and optical clarity with those of HBPs such as less entanglement, low viscosity, and gas inhibition performance. However, so far, the use of HBPs as organic filler in TE based hybrid thin film has not been reported yet, although TE/HBP hybrid films are expected to provide improved performances. Therefore, novel thiol-ene/HBP hybrid thin films with a thickness of hundreds of micrometer were

prepared by a simple photopolymerization in this work. The effect of HBP on the cure behavior of TE polymer was investigated compared with that of pristine TE system using dynamic and isothermal DSC analyses. Thermal expansion properties of resulting TE/HBP hybrid thin films were also studied with TMA method. The influence of HBP on the gas barrier properties of TE/HBP hybrid thin films was examined. Inherently excellent gas barrier property of TE polymer combined with the attributes of HBP such as toughening and rheological modifier might lead to the formations of novel transparent barrier films.

2. Experimental

2.1. Materials

Tetrafunctional thiol-[pentaerythritol tetrakis(3-mercaptopropio-nate)], trifunctional ene-[1,3,5-triallyl-1,3,5-triazinane-2,4,6,-trione], photoinitiator-[Irgacure 754], and hyperbranched polymer-[Hyper-branched bis-MPA polyester-64-hydroxyl, 4 G] were purchased from Aldrich (Milwaukee, WI) and used as received. Fig. 1 displays the chemical structures of thiol and ene employed in this work.

2.2. Mixing TE/HBP solution

An amount of thiol (0.8 g) and ene (0.528 g) was mixed by a mechanical method and diluted in acetone. Then, HBP (1–10 wt.%) was introduced into the solution and sonicated about 5 min. Subsequently, acetone was evaporated and the resulting TE/HBP solution was degassed under vacuum. Finally, a trace amount of photoinitiator (Irgacure 754) was added to the obtained solution and mixed mechanically.

2.3. Formation of TE/HBP thin films

An amount of TE/HBP solution was poured between two glass plates covered with an alumina coated film. The distance between alumina coated films was determined by the thickness of spacer (200–400 μm). Then the film making apparatus containing TE/HBP solution was inserted into UV (10 mW/cm^2) curing chamber. The TE//HBP solution was cured for 10–30 min and the resulting TE/HBP film was detached from the alumina coated film manually. The thickness was consistent with that of spacer.
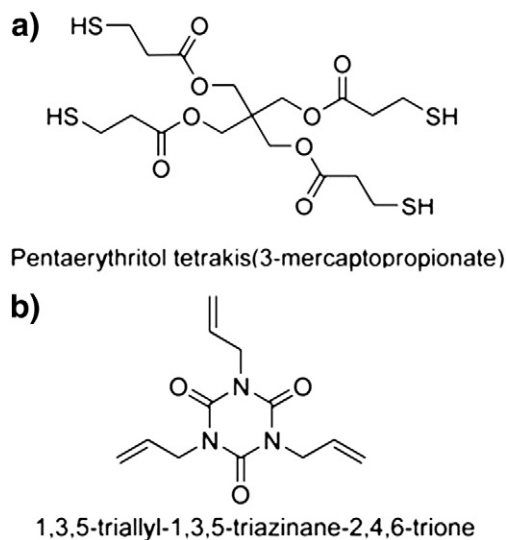

Fig. 1. Chemical structures of (a) tetrafunctional thiol and (b) trifunctional ene monomers.

2.4. Instrumental analysis

The dynamic thermograms of the prepared film were recorded on a TA2010 differential scanning calorimeter (DSC) with a heating rate of 2.5, 5, and 10 °C/min under nitrogen. Isothermal DSC was also conducted with TA 2010 DSC at a fixed temperature for at least 2 h under N$_2$. XRD patterns were obtained on a Rigaku D-max/3 C X-ray diffractometer. Thermomechanical analysis (TMA) was conducted with a TA Q400 with an applied force of 0.05 N. Light transmittance was measured with a Minolta CM3600d spectrophotometer. Water vapor/oxygen permeability of the films were monitored with a MOCON Aquatran model 1 and MOCON Oxytran 2/21 instrument, respectively. A continuous-flow testing cell method approved by the ASTM (D3985) was employed. All measurements were conducted at 23 °C and 0% relative humidity. In this method, water vapor/oxygen is the test gas and inert nitrogen is the carrier gas. The samples of 5 cm^2 testing area were loaded into the testing cell and flushed with nitrogen gas to purge out excess gases and to develop a zero point [23].

3. Results

The cross-linking reaction of TE network can be achieved by thermal annealing or UV exposure. To elucidate the effect of the presence of HBP as organic filler, the thermal curing and photocrosslinking of TE and TE/HBP system were conducted separately. Thermal curing reaction of TE and TE/HBP system was extensively monitored by DSC method. The thermal expansion behavior and gas permeabilities of thermally cured TE/HBP thin film was compared with photocrosslinked TE/HBP film.

3.1. Cure behavior

The dynamic DSC thermograms of TE and TE/HBP system were illustrated in Fig. 2. Table 1 summarizes the basic and important parameters derived from dynamic DSC measurements such as exother-mic peak temperature (T$_{peak}$), conversion at the peak temperature, and heat of cure (ΔH). First, the initial curing temperature and the peak temperature increased with increasing the heating rate in both systems. Remarkably, the exothermic peak temperature increased with the addition of HBP at the same heating rate [24]. It is thought that the addition of HBP into TE system might induce a slight retardation effect in mobility of TE molecules, because the molecular dimension of HBP is relatively large. On the other hand, the heat of cure was nearly independent of the heating rate at a constant concentration of HBP. As shown in Table 1, the heat of cure slightly decreased–approximately 5% with increasing the heating rate at a fixed amount of HBP. This reduction is nearly negligible in terms of curing reaction enthalpy. In most experiments using DSC analysis, the temperature lagging always happens between thermocouple and real sample. The degree of temperature lagging is proportional to the heating rate. Therefore, the heat of cure usually exhibits a smaller value at relatively higher heating rate. Addition of HBP into TE network did not change the overall stoichiometry of thiol-ene functionality thus the overall cure behavior of TE polymer was not considerably influenced by the addition of HBP. As we take a look at the degree of cure values in Table 1, we can see that all the degree of cure values are higher than 0.66. These values indicate that the TE and TE/HBP thermoset polymer systems are macroscopically cured, because the residual curing reaction cannot be detected by normal DSC experiment as will be shown in Fig. 4. That is, both TE and TE/HBP are macroscopically cured but the degree of cure value is slightly different. This phenomenon means that the initial concentration and composition of thiol-ene functional group would determine the extent of cure reaction. It is important to note in Table 1 that the peak temperatures in TE/HBP system were higher than those of TE system. The heat of cure in TE was also slightly higher than TE/HBP system, which indicates directly that the extent of cure was decreased with the incorporation of HBP molecules into TE matrix. It is thought that dominant thiol-ene reaction