Relationship between polymerization kinetics and microstructure in reactive polymer blends: An Avrami-Erofeev study

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ABSTRACT

It's well known that the microstructure in the thermoset/thermoplastic blends is difficult to predict as it depends on many factors like compatibility, viscosity, crosslinking density. In this study, we investigated the relationship between polymerization kinetics and microstructure in bisphenol-A polycarbonate/diallyl phthalate (BAPC/DAP) blends *via* Avrami-Erofeev equation, which has been widely used to describe the phase transition in solid state. When the values of the exponent n in Avrami-Erofeev equation were greater than 1.73, between 1 and 1.73, and less than 1, the poly(DAP)-rich phases possessed fiber-like three-dimensional network with a relatively small diameter of ~ 20 nm, partially connected nodule-like crosslinking structure, and perfect nodule-like three-dimensional network, separately. The results showed that Avrami-Erofeev method could be used to well correlate the polymerization kinetics with the final microstructure in reactive polymer blends.

1. Introduction

In recent 40 years, the polymerization induced phase separation (PIPS) has been widely used in designing materials [1–4], like thermoset/thermoplastic (TS/TP) blends [5–7], polymer-dispersed liquid crystals (PDLC) [8,9], shape memory blends [10,11]. Among them, the TS/TP blends have been widely studied for their applications in TP toughing TS [12,13] and TS monomers assisting TP processing [14,15]. As the crosslinking degree of TS largely affects the mechanical strength and thermal resistance of the blends, it is necessary to investigate the curing kinetics.

Nowadays, the curing kinetics of TS is mainly expressed by phenomenological model [16,17], mechanistic model [18] and Avrami equation [19]. The phenomenological model is about the main features of reaction kinetics and ignores the individual reactions. Though the mechanistic model is obtained from the balance of species involved in the reaction, it is hard to achieve the complicated curing process. Avrami equation, which is based on the phase change, has been widely used to study the crystallization kinetics of polymers [20,21]. As the crystallization can be considered as physical crosslinking and somewhat like the crosslinking process of TS, Kim et al. have successfully studied the curing kinetics of diglycidylether of bisphenol A/methylene

dianiline (DGEBA/MDA) and DGEBA/MDA/carboxyl-terminated butadiene-acrylonitrile blends through Avrami equation [19]. Compared with pure TS, the polymerization process of TS monomers in the TS/TP blends is more complicated because the physical state would change simultaneously [22]. In other words, the polymerization behaviors and the microstructure in the TS/TP blends interplay with each other [23–25]. In addition to the reaction degree of TS, the microstructure of the TS/TP also greatly impacts the properties of TS/TP blends [6]. Much attention has been paid to identifying the factors that affect the microstructure of TS/TP blends, such as compatibility, viscosity, catalyst content, crystallization [26–31], while little work directly links the polymerization process to the formed microstructure. As the polymerization of TS monomers happens during the new phase formation in TS/TP blends, it may be described by Avrami-Erofeev equation, which has been widely used to describe the phase transformations [32–34]. Lipatov et al. have studied the relationship between reaction kinetics and microphase structure in the interpenetrating networks (IPNs) of polyurethane/poly(butyl methacrylate) (PU/PBMA) by Avrami-Erofeev equation. Although their results showed that the exponent in the equation had some relations with the microstructure [35,36], neither a quantitative nor a semi-quantitative conclusion between them was made in their works.

In our previous work, diallyl phthalate (DAP) was used as reactive plasticizer to assist the processing of bisphenol-A polycarbonate (BAPC). Under suitable processing conditions, BAPC/poly(DAP) blends with high optical transparency, good flowability and high mechanical properties were achieved [37]. However, the interrelation between DAP polymerization and the microstructure of BAPC/poly(DAP) blends is still unclear. Based on Avrami-Erofeev equation, the polymerization process of DAP in BAPC/DAP blends has been investigated in this study. Besides, a semi-quantitative relationship between the exponent of Avrami-Erofeev equation and microstructure in BAPC/DAP blends has also been established, which would shed light on the microstructure prediction in reactive polymer blends.

2. Experimental

2.1. Materials

Commercial bisphenol-A polycarbonate (BAPC, PC-110, M_n 32.6 kg/mol) was purchased from Chimei Corporation of Taiwan. Diallyl phthalate (DAP) was purchased from Shanghai Hushi Co. Ltd and purified through neutral alumina column. Dicumyl peroxide (DCP, Shanghai Reagent Station) was re-crystallized in ethanol twice before using. Dichloromethane was purchased from Sinopharm Chemical Reagent Co. Ltd and used as received.

2.2. Sample preparation

As shown in Scheme S1 in Supporting Information, BAPC pellets were dissolved in dichloromethane by stirring at room temperature. DCP, 10 wt% relative to DAP, was ultrasonically solved in DAP at room temperature. Then, the DAP/DCP mixture was added into BAPC solution with different ratio of 10 wt%, 15 wt%, 20 wt% and 25 wt% corresponding to BAPC. After stirred for several minutes, the solutions were cast on a glass plate to form thin films with a thickness of about 45 μm to eliminate the influence of film thickness. Afterwards, the films were dried at room temperature for 48 h, and then put into the vacuum oven for another 12 h to ensure complete removal of dichloromethane.

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To investigate the morphology of BAPC/poly(DAP), the films with 25 wt% DAP were heat-treated at 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 190 °C and 210 °C, respectively.

2.3. Characterization

The isothermal polymerization kinetics of as-prepared BAPC/DAP-DCP films and DAP-DCP mixture were characterized under nitrogen atmosphere on Q2000 differential scanning calorimeter (DSC, TA Instruments, USA) at different temperature.

To observe the morphology of BAPC/poly(DAP) blends, the thermally treated films were fractured in liquid nitrogen. Also, the BAPC/poly(DAP) films with 25 wt% poly(DAP) were immersed into dichloromethane to remove BAPC and the residuals were extracted, washed and dried. The morphologies of the fractured surfaces of BAPC/poly(DAP) blends and the residuals were observed through scanning electron microscopy (SEM, Sirion 200, FEI Company, Netherland) with an acceleration voltage of 10 kV. A thin layer of platinum was sputtered onto the samples prior to SEM imaging.

3. Results and discussion

3.1. Polymerization kinetics of DAP in BAPC/DAP-DCP blends

The polymerization kinetics can be obtained by the DSC thermograms of BAPC/DAP-DCP blends during the isothermal polymerization. The polymerization rate (R_p) and double bonds conversion (α) can be
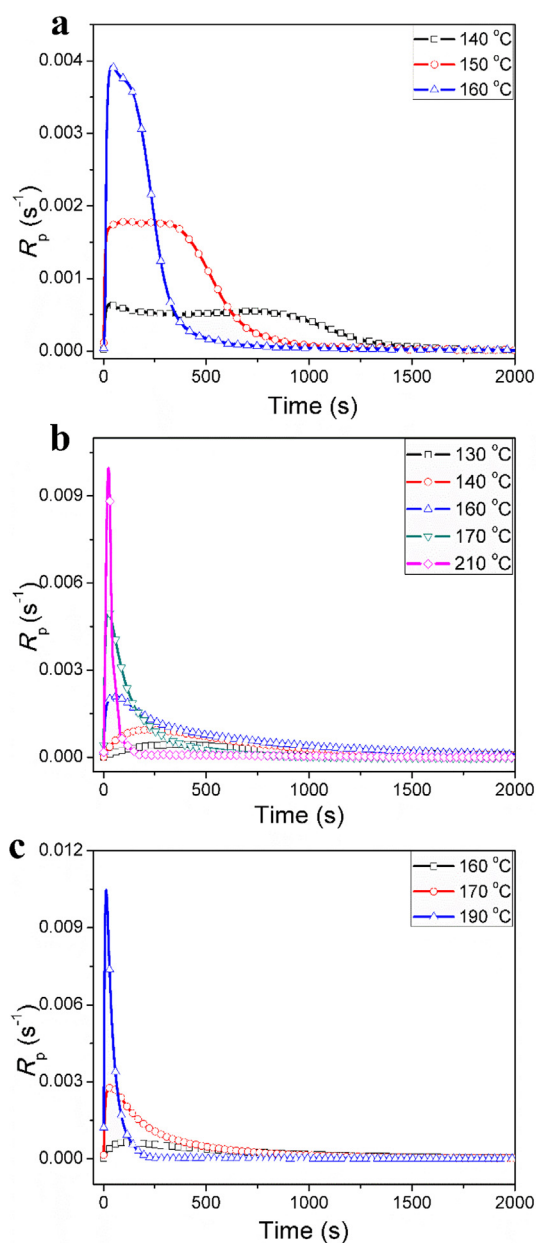

Fig. 1. Relationship between polymerization rate (R_p) and polymerization time in the BAPC/DAP-DCP blends with different DAP content, (a) bulk DAP; (b) 25 wt% DAP and (c) 10 wt% DAP.

calculated as follows.

$$R_p = \frac{d\alpha}{dt} = \frac{dH/dt}{m \cdot w \cdot \Delta H_0} \tag{1}$$

$$\alpha(t) = \frac{\Delta H(t)}{m \cdot w \cdot \Delta H_0} \tag{2}$$

where w is the weight fraction of DAP in BAPC/DAP-DCP blends, m is the weight of polymer blends used for DSC measurement, ΔH_0 with a value of 638 J/g is the enthalpy of DAP allylic groups fully reacted [38].

According to Eq. (1), the relationship between polymerization rate (R_p) and time (t) for the BAPC/DAP-DCP blends with different DAP content is shown in Fig. 1. It can be seen that the R_p increases with increasing t at first and then decreases. Furthermore, the higher the DAP content and polymerization temperature, the higher the R_p at the initial stage of polymerization. For instance, when the mixture was polymerized at 160 °C, the maximum values of R_p are $3.9 \times 10^{-3} \text{s}^{-1}$