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Gelation of attractive particles in polymer melt

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ABSTRACT

The physical gelation of the attractive carbon black particles in the isotactic polypropylene melt is studied. Following the method proposed by Winter and Chambon, oscillatory rheology is used to study the kinetic gelation process. The gel time, the relaxation exponent of the critical gel, the gel stiffness and the activation energy for the gelation are determined. The influences of the filler concentration and the experimental temperature on the gelation process are also investigated. The results suggest that the gelation of the filler particles in the polymer melt mainly follows second-order kinetics, and the critical gel should be formed by the rigid particles and the inter-particle polymer layers.

1. Introduction

Filler particles are widely added to polymer matrix to improve their mechanical, electrical and thermal properties et al. [1–10]. These properties are related to the internal filler network. Once the composite is in the molten state, the structure of the filler network can change due to the diffusion and aggregation of the initially dispersed particles [11–16]. This process is triggered by the thermodynamic instability [17–19], and it is a typical physical gelation process [13,18,20–22]. Study on the gelation of the filler particles in the polymer melt should be extended because of its scientific interest and technological significance. First, the polymer melt is a more complex liquid compared to the low-molecular-weight liquid, and it is still a challenge to describe in detail how the attractive particles aggregate in the polymer melt. As widely reported in the literatures, the attractive particle would adsorb the polymer chains on its surface resulting in an immobilized interfacial polymer shell, and once two particles approach the overlap of the polymer shells (~2 nm) would impede the direct contact between the particles [21,23–27]. It would be interesting to show how this interfacial effect influences the gelation kinetics and the property of the gel. Second, from a technological point of view, the significance comes from the fact that most of the inorganic filler/polymer composites are fabricated through melt processing [10,28]. The gelation kinetics would influence the network structure in the final product and consequently the physical properties.

Oscillatory rheology has been widely used to study the chemical and physical gelation processes based on the theory proposed by Winter and Chambon [29–31]. They show that the critical gel relaxes with a continuous power-law relaxation time spectrum (CW spectrum)

$$H(\lambda) = \frac{S}{\Gamma(n)}\lambda^{-n} \quad \lambda_0 < \lambda < \infty \tag{1}$$

which results in a relaxation modulus

$$G(t) = St^{-n} \quad \lambda_0 < \lambda < \infty \tag{2}$$

where S is the gel stiffness, n is the relaxation exponent, λ is the relaxation time, and $\Gamma(n)$ is the gamma function. λ_0 marks the crossover to the faster dynamic, e.g., the glass transition or the relaxation of the entangled polymer chains depending on the structural details. The relaxation exponent n has a value between 0 and 1. The case of $n = 0$ corresponds to the limiting behavior of a Hookean solid (the relaxation modulus is a constant) and the restriction of n to values less than unity is necessary to assure a diverging zero-shear viscosity at the gel point. The critical gel is generally very soft when the relaxation exponent is large ($n \rightarrow 1$) and S is small, and a small relaxation exponent ($n \rightarrow 0$) and a large S reflect a stiff critical gel [31].

For the dynamic characterization, at the gel point, the storage modulus (G') and the loss modulus (G'') are correlated as

$$G' = G''/\tan\delta_c = S\Gamma(1-n)\cos\frac{n\pi}{2}\omega^n \quad 0 < \omega < 1\lambda_0 \tag{3}$$

where $\tan\delta_c$ is the critical loss tangent and ω is the frequency. The loss tangent is independent of frequency at the gel point:

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$$\tan\delta_c = \frac{G''}{G'} = \tan\frac{n\pi}{2} = \text{constant} \tag{4}$$

Following this criterion, the gelation process can be monitored by performing cyclic frequency sweeps [21,29–33]. Each data point in the cyclic frequency sweeps represents a different state of the internal structure, and the gel time (when the critical gel is formed) can be determined when a frequency-independent tanδ is observed.

The Winter–Chambon method has been successfully used to detect the existence of the gel (filler network) in the polymer melt. It is found that when the concentration of the filler particles increases to a percolation value, the composite melt would exhibit a melt-gel transition [34,35]. It is also reported that there exists a percolation temperature above which a gel structure can be detected in the composite melt [21,36]. In addition, the effect of melt annealing time on the gel structure has also been studied [13,15,16]. It has been shown that the initially dispersed filler particles can form a gel spontaneously during melt annealing. However, despite its ubiquity and significance, the gelation kinetics is far from understood. The systematic study on the gelation kinetics in the filler/polymer system, with full consideration of the filler concentration and temperature, has not emerged to the best of our knowledge.

Here we focus on the gelation kinetics in the filler/polymer system and the essential property of the critical gel. At first, the polar filler (carbon black, CB) [37] is dispersed into a non-polar polymer (isotactic polypropylene, iPP) homogenously. Then the as-formed composites are heated to a temperature higher than the melting temperature of iPP. The gelation process proceeds spontaneously and the cyclic frequency sweeps are used to determine the gel time and the critical gel property. The influences of the filler concentration and the temperature on the gelation kinetics are studied. Our results imply that the critical gel should be formed by the rigid filler particles and the interparticle polymer layers which give a typical frequency- and temperature dependence to the property of the gel.

2. Experimental

2.1. Materials and processing

A carbon black (VXC 68, Cabot) with a dibutyl phthalate (DBP) volume of 1.23 ml/g and a primary particle size of 25 nm was used as received. A commercial isotactic PP (iPP, trade name T30S, melt flow rate = 2.3 g/10 min, at 230 °C and 2.16 kg load, supplied by Lanzhou petroleum Chemical Co, Ltd., China) was used as the matrix. The composites were fabricated by melt processing using a twin-screw extruder. The test samples were prepared by compression molding at a temperature of 200 °C and a pressure of 10 MPa for 5 min. The CB particles (the smallest dispersed unit should be the primary aggregates) and some aggregated structures were homogenously dispersed in the polymer matrix in the test samples as shown in Fig. 1. In this paper, the filler concentration is expressed as volume fraction (using a density of 0.90 g/cm^3 for iPP and 1.8 g/cm^3 for CB).

2.2. Characterization

Scanning electron Microscopic (SEM) observation was carried out using an INSPECT F scanning electron microscope (FEI). The samples were fractured in liquid nitrogen and the fracture surfaces for observation were coated with gold.

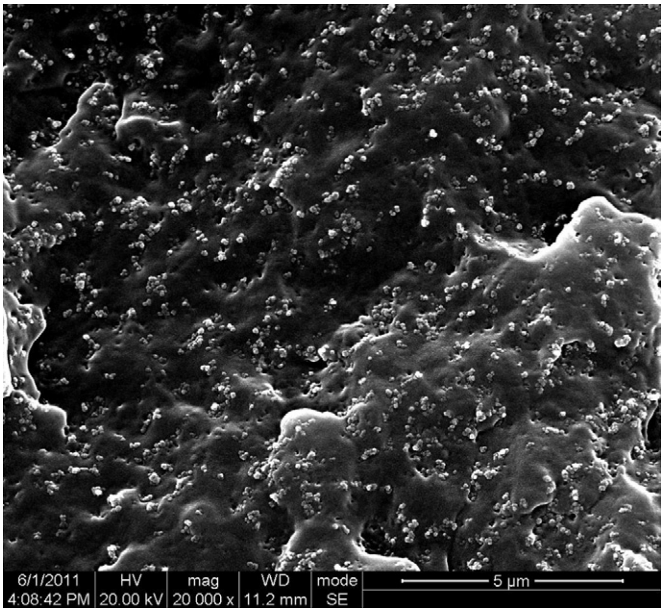

Fig. 1. SEM image showing the dispersion of the CB particles (8.7%) in the iPP matrix.

The dynamic rheological properties for the samples were studied with a stress-controlled rheometer (AR 2000ex, TA Instruments) equipped with parallel-plate geometry (diameter of 25 mm). The gap was fixed at 1.8 mm and the applied strain was 0.1% (It is in the linear viscoelastic region of the composite melts. We used the relatively low strain in order to weaken the influence of the oscillation shear on the gelation kinetics). The frequency sweep was conducted in a frequency (ω) range from 0.1 to 100 rad/s and six data points were collected in every decade (as the time to obtain a data point was $2\pi/\omega$, the time for a single frequency sweep was about 8 min). The zero viscosity of the neat iPP was determined by carrying out the creep experiments with a fixed stress of 10 Pa. To prevent the thermal degradation of the matrix, all the rheological experiments were conducted in a nitrogen atmosphere.

3. Results and discussion

3.1. Dynamic rheological property of the initial composite melts

Fig. 2 shows that the storage modulus (G') of the composite melts increases with increasing CB concentration, especially at the low frequencies. This should be ascribed to the following effects: (1) The particle–polymer interactions (dispersive interactions [37]) slow down the polymer segments near the filler surface, leading to a change in the relaxation spectrum and an enhancement in the modulus [38]. (2) The addition of the filler particles causes a hydrodynamic effect which would also lead to an enhancement of G' [4]. (3) The particle–particle interactions can also lead to the increase of G' [39]. For a neat polymer, a typical Newton liquid behavior ($G' \sim \omega^2$, $G'' \sim \omega$, $\tan\delta \sim \omega^{-1}$) would be observed at sufficiently low frequencies. However, a smaller exponent ($\sim$1.55) is found in our system (see Fig. 2). This may be caused by the polydispersity of the commercial polymer and the limited frequency window in our experiment. The low-frequency plateau of G', which reflects the fact that some internal structure is difficult to relax even within a long time, is not observed for all composite melts in our system, revealing that no filler network exists in the initial composite melts [40,41]. When the filler concentration is high, the low-frequency G' is more frequency-dependent (see the dash circle in Fig. 2). This should be attributed to the structural changes during the sweep cycle: as the time to obtain a data point in the frequency