Gelation of a Composite of Ceramic Fibers and Polypropylene Modified with Maleic Anhydrate in Naphthenic Oil

Shigeru Machida, Yasuhiro Matsuda,* and Shigeru Tasaka
Department of Materials Science and Chemical Engineering, Shizuoka University,
3-5-1 Johoku, Naka-ku, Hamamatsu 432-8561

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The physical gelation of isotactic polypropylene in naphthenic oil was drastically enhanced by adding a small amount of ceramic fibers after modification of polypropylene with maleic anhydrate. The micrograph of the gel showed the network of ceramic fibers crosslinked with polypropylene crystals formed by nucleation at the surface of the fibers.

Gels of crystalline polypropylene have been attracted both academic and industrial interests because of its excellent thermal stability.[1–3] Okabe et al.[1,2] prepared isotactic polypropylene (it-PP) gel in decaline, tetralin, *o*-xylene, or toluene and investigated its structure by microscopy. They concluded that the spherulites of it-PP overlapped with each other to form gel when the concentration of it-PP was above ca. 0.05 g cm^{-3} ($\approx$6 mass %).

The transcrystallization of PP is enhanced at the surface of some fibrous materials such as asbestos,[4] glass,[4] carbon,[5] polysaccharide,[6] and synthetic polymer[7,8] fibers. In this communication, we report the preparation of gel of it-PP in naphthenic oil, of which gelation concentration was no more than 0.01 mass %, by adding a small amount of ceramic fibers (CFs). While the crystals of PP themselves prevents the flow of solvent in the traditional PP gels, the gel reported in this communication hold solvent by its framework of CFs crosslinked by the transcrystals of PP. The reduction of the amount of PP in our gel improves the brittleness of PP gel at low temperature.

The it-PP sample used in this study was J106 (homo) from Mitsui Chemicals. The weight-average molecular weight (M_w) was 3.17×10^5. Maleic anhydrate-modified it-PP (M-it-PP) was prepared according to the procedure of Fujiyama et al.[9] The graft ratio of maleic anhydrate and M_w determined by gel permeation chromatography were 0.27 mol % and 1.55×10^5, respectively. The determination of the graft density of M-it-PP is described in Supporting Information.[10]

Refractory ceramic fibers (TOMBO No. 5100) were supplied by Nichiasu Co., Ltd. The average diameter and length were 2–3 µm and 1–2 mm, respectively. Some of these were cut into shorter fibers with a pitched-blade propeller mixer (L4RT, Silverson) at 3000 rpm for 30 min. Naphthenic oil (SNH220, Sankyo Kogyo) and *o*-xylene (guaranteed grade, Kanto Chemical) were used as solvents without further purification.

Test solutions for viscoelastic measurements were prepared as follows: M-it-PP or it-PP and CF were added into naphthenic oil heated at 170 °C and mixed with a general purpose agitator (Three-One Motor BLh600, Shinto Scientific) equipped with home-made glass blade (1.5 cm) at 600 rpm for 30 min. No precipitation was observed for the gel samples at least two months after the preparation.

Viscoelastic measurements were carried out in order to determine the gelation concentration of PP or CF. The modulus of a sample with the thickness of 1.0 mm was measured with a Rheoplus MCR101 (Anton Paar) at 1 Hz by heating at 5 °C/min.

While the storage modulus G′ for gel samples decreased at −20 to 0 °C for the glass transition of it-PP (ca. −1 °C for bulk it-PP[11]), but plateaued (>100 Pa) above 0 °C, G′ for sol samples continued to decrease above 0 °C and had low value. The samples of which G′ had plateau above 100 Pa at sufficiently high temperature (125 °C) was defined as gel in this manuscript.

The samples for microscopy were prepared as follows: Because viscous and colored naphthenic oil was unsuitable for the sample preparation for microscopy, *o*-xylene was used as solvent. The CF (0.1 g) and M-it-PP or it-PP (0.05 g) was added to 100 mL of *o*-xylene and stirred at 140 °C for 10 min to dissolve PP completely. After allowing to stand and cool to room temperature, the CFs were picked up and put on a glass plate and dried at 25 °C for 24 h. The samples were observed with an Olympus BX 51 polarizing microscope. The light source for this observation was unpolarized.

Figure 1 summarizes the G′ for sol and gel samples in order to determine the gelation concentration of PP for (a) it-PP in naphthenic oil, (b) M-it-PP in naphthenic oil, (c) it-PP and CF in naphthenic oil, and (d) M-it-PP and CF in naphthenic oil. The circles show the data for gel samples of which mass fraction

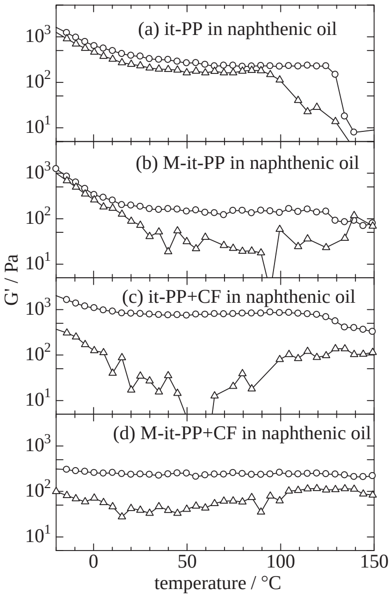

Figure 1. The G′ for gel (circles) and sol (triangles) samples of (a) it-PP, (b) M-it-PP, (c) it-PP and CF, and (d) M-it-PP and CF. See the text for the concentration of the samples.

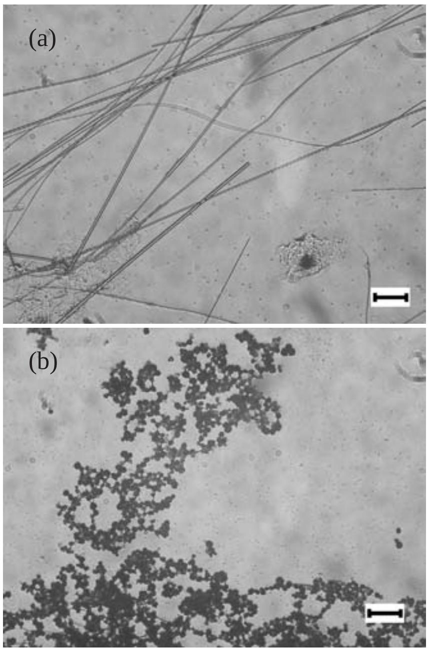

Figure 2. The micrograph of it-PP (a) and M-it-PP (b) with ceramic fibers ($c_{PP} = 0.05$ mass %, $c_{CF} = 0.1$ mass %). The scaling bars in the figures indicate 50 µm.

of PP c_{PP} was (a) 2.0%, (b) 2.3%, (c) 1.0%, and (d) 0.01%, whereas the triangles show the data for the sol samples of which mass fraction of PP was (a) 1.9%, (b) 2.2%, (c) 0.9%, and (d) 0.002%. The mass fraction of CF c_{CF} in (c) and (d) was fixed at 1.0%. The higher gelation concentration of (b) than that of (a) may be caused by the lower molecular weight of M-it-PP. While the gelation concentration of (c) slightly decreased for the enhancement of viscosity by adding CF, the gelation concentration of (d) was much lower than those of other samples.

Figure 2 illustrates the micrographs of (a) it-PP and (b) M-it-PP with CF. Whereas there were only bare ceramic fibers in Figure 2a, many spherulites of M-it-PP attached to the ceramic fibers were observed in Figure 2b. These micrographs suggest that some specific interaction between the CF and the maleic anhydrate in M-it-PP enhances the nucleation of M-it-PP at the interface of the CF. The spherulites of M-it-PP in Figure 2b crosslink CF to form network structure.

Considering the results in Figures 1 and 2, we propose a gelation mechanism of M-it-PP and CF that the CF in naphthenic oil is crosslinked with the spherulites of M-it-PP, forming network structure as shown in Figure 2b, and prevents the oil from flowing. In order to confirm this assumption, viscoelastic measurements were carried out with M-it-PP and CF shortened with the propeller mixer.

Figure 3 shows the G′ for (a) M-it-PP and long (original) CF in naphthenic oil and (b) M-it-PP and short CF in naphthenic oil in order to determine the gelation concentration of CF. The circles show the data for gel samples of which mass fraction of CF was (a) 0.2% and (b) 0.8%, whereas the triangles show the data for the sol samples of which mass fraction of CF was (a) 0.1% and (b) 0.7% The c_{PP} was fixed at 1.0%.

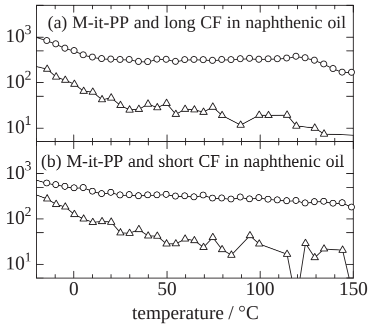

Figure 3. The G′ for gel (circles) and sol (triangles) samples of (a) M-it-PP and long CF, and (b) M-it-PP and short CF. See the text for the concentration of the samples.

The viscosity of the solutions of rigid polymers or dispersoid has been studied by both theoretical[12–15] and experimental[14–16] approaches. The critical concentration when rigid rods with the length of L begin to contact is proportional to L^{-3}. The experimental results that the shorter CF needed higher concentration to form gel with M-it-PP can be explained by the decrease of contacts between CF to form network preventing the oil from flowing.

In conclusion, we propose the gelation mechanism of the naphthenic oil with M-it-PP and CF as follows: CFs in sufficient concentration are entangled with each other to form a network in naphthenic oil. This framework can be easily loosened and allow the oil to flow without M-it-PP. The maleic anhydrate in M-it-PP interacts with the interface of CF and induces the nucleation of M-it-PP. The spherulites of M-it-PP attached on the CF crosslink the entanglement points of the network. The crosslinked framework no longer allows the flow of oil and changes the oil into gel.

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