



Simultaneous stiffening, strengthening and toughening of poly(vinylidene fluoride)/propylene carbonate gels by thermal annealing near peak melting temperature

Noboru Osaka*, Keiji Hamamoto

Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama, 700-0005, Japan

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ABSTRACT

Polymer physical gels composed of poly(vinylidene fluoride) (PVDF) and propylene carbonate with networks of interconnected spherulites were thermally annealed near peak melting temperature (T_m). Although the gels prepared at high gelation temperature showed the brittle mechanical properties, the gels annealed near T_m were simultaneously stiffened, strengthened and toughened in addition to increase in T_m . By *in-situ* Hv light scattering, it was found that recrystallization was highly enhanced during the cooling process after annealing while partial melting of small crystallites of PVDF occurred at around annealing temperature near T_m during heating process and recrystallization proceeded over the thermal treatment. Since growth of the spherulites was also found to proceed during heating and annealing processes, the strengthened interspherulitic boundaries obtained by SEM were ascribed to the growth of the spherulites during the heating and annealing processes and the enhanced recrystallization during the subsequent cooling process. Crystalline phase of PVDF was revealed to transform from the dominant β phase to the dominant γ phase during the annealing process by WAXS and FT-IR/ATR measurements, which in part contributed to the increase in T_m . Fracture surface images obtained by SEM and *in-situ* digital microscope images during stretching of the annealed gels revealed that the spherulites with both the increased crystallinity and the strengthened boundaries could be deformed uniaxially in the stretching direction without morphological transformation into fibrils. Based on the results of the hierarchical structure characterizations, not only increase in crystallinity but also formation of the strengthened interspherulitic boundaries is the possible origin of the significant improvement of the mechanical properties of the gels annealed near T_m .

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1. Introduction

From a microscopic-structural viewpoint, physical gels are characterized by formation of cross-linking points via physical bonds such as van der Waals interactions, hydrogen-bonds and crystal formation [1]. Since they are non-covalently bonded, they show the reversible sol-gel transition induced by external stimulus.

When solutions comprising of semi-crystalline polymers and solvents are cooled, the semi-crystalline polymers mutually form crystallites. They acted as the cross-linking points and the so-called crystalline gels are formed. This kind of crystalline gels possess weak mechanical properties. Therefore, they are often blended

with other polymers [2] or mixed with nanoparticles [3] or fibers [4] to improve the mechanical properties. In addition to the compounding strategy, the inherent crystalline structures of polymers are controlled in preparation or in post-process. When preparing the gels, gelation temperature [5], solvent composition [6], and processing [7] were changed. As a post-processing, the freeze/thawing [8–10] is one of the major method to increase the crystallinity. High temperature annealing after drying the gels [11] and ageing the gels [12] are also used in the post-thermal processing.

Post-thermal treatments have been widely applied to the various polymeric materials to control the structures and properties in science and industry. Self-nucleation or self-seeding were originally applied by Blundell et al. to prepare polymer single crystals with similar sizes via epitaxial nucleation in solution [13,14]. Since Fillon et al. have established the general scheme for the experimental thermal protocol on neat isotactic polypropylene

* Corresponding author.

E-mail address: osaka@chem.ous.ac.jp (N. Osaka).

[15], the self-nucleation method has been widely used to improve the physical properties of polymeric materials [16–20]. The unmelted crystal fragments or the ordered segmental structures remained by annealing near peak melting temperature acted as nuclei. Since the self-seeded nuclei are considered to be the best possible heterogeneous nucleation sites, the subsequent crystallization rate was enhanced. The resultant thickening of lamellar crystal caused increase in melting temperature and the enhanced crystallinity lead to the mechanical strengthening [21]. From the previous studies, both the Young's modulus and break stress have been well known to be often increased by increase in crystallinity. However, break strain is usually considered to be a trade-off against the improvements. Therefore, the simultaneous increase in all of the Young's modulus, break strain and break stress by the structure change without adding or blending have been less reported.

In this study, post-thermal treatments of annealing near peak melting temperature were applied to polymer physical gels in order to improve the thermal and the mechanical properties, which would be in the scheme of self-nucleation technique. The gels consist of poly(vinylidene fluoride) (PVDF) and propylene carbonate. They form spherulites via thermally induced phase separation followed by crystallization and the spherulites were interconnected each other to form the three-dimensional networks of the gels [22,23]. This kind of crystalline gels with spherulitic structures are observed everywhere [24–27]. Although our system is simple one consisting of semi-crystalline polymer and solvent, we expect that the underlying mechanism to improve the properties of the gels would be useful to other complex systems such as polymer gel electrolytes and polymer membranes. Hierarchical structure changes of the gels were investigated by various microscopes and scattering measurements to understand the mechanism of the improved thermal and mechanical properties. Furthermore, we also performed the *in-situ* observation of the annealed gels during deformation to understand the deformation behavior by digital microscope in order to confirm the results. To our knowledge, this is the first time to observe the *in-situ* morphological changes of the spherulites in the crystalline gels during deformation. Thus, the aim of this study is focused to investigate the effect of thermal annealing near peak melting temperature on the mechanical properties of the polymer physical gels and to understand the possible origin from the structural viewpoints.

2. Experimental

PVDF ($M_w = 3.7 \times 10^5$, $M_w/M_n = 2.2$, KF1300) was purchased from Kureha Chemical Industry Co., Ltd. Propylene carbonate (PC, 99.7%) was purchased from Sigma-Aldrich Corp. They were used without further purification. PVDF was dissolved in PC at 135 °C and the concentration was fixed at 30 wt%. The concentration was rather high compared with previous studies on polymer gels (~ca. 20 wt%) [5,10,22,23]. Similar, but less mechanical improvements were confirmed at a lower concentration of 21 wt%. However, 30 wt% was selected because of easy handling for the following experiments. After cooling to prepare gels, they were cut and placed between two cover glasses with a rectangular spacer of 1 mm thickness. Then, they were heated at 135 °C for 5 min and transferred into hot-stage (HS82, Mettler-Toledo Inc.) at an aimed gelation temperature (T_{gel}) for sufficient gelation time. For thermal annealing, the gels prepared at $T_{gel} = 20$ °C were heated to an aimed annealing temperature (T_a) at a heating rate of 60 °C/min by the hot-stage and kept for 30 min. Then, they were cooled to 20 °C at a cooling rate of 10 °C/min. The change of the polymer concentration was less than 0.5 wt% after annealing at $T_a = 100$ °C for 30 min.

Differential scanning calorimetry (DSC) measurements were

conducted with a Q10 (TA Instruments, Inc.) at ambient pressure condition. 1–5 mg of the gels were cut and cramped in an aluminum sample pan. DSC scans were carried out at a heating rate of 60 °C/min to depress recrystallization during heating.

Tensile-deformation measurements were carried out at room temperature of about 20 °C at a crosshead speed of 10 mm/min by using the tensile-testing machine 90FD (IMOTO MACHINERY CO., LTD.). Dumbbell-shaped samples with a gauge length of 12 mm, a width of 3.8 mm and a thickness of 1 mm were cut from the gels and used for the measurements. Both ends of the samples were uniaxially stretched keeping the central region stationary.

A polarized optical microscope (BX-53P, Olympus Corp.) equipped with sCMOS camera (SR-130, Wraymer Inc.) was used to monitor the structure changes of the spherulites during the thermal treatment. For *in-situ* observation, the hot-stage was set on the stage.

For *in-situ* Hv light scattering measurements, a polarized He–Ne laser with a wavelength of 632.8 nm was applied vertically to the gels placed between the two cover glasses with a rectangular spacer of 1 mm thickness in the hot-stage. We employed a Hv geometry in which the optical axis of the analyzer was set perpendicularly to that of the polarizer [28]. The scattered light passed through the analyzer and then onto a highly sensitive charge-coupled device (CCD) camera with 800 × 600 pixels (pco.1600, TOKYO INSTRUMENTS, INC.). The exposure time and the interval were 0.2 s and 10 s, respectively. The input data from the CCD camera was stored in a personal computer for further analysis.

Wide-angle X-ray scattering (WAXS) measurements were performed at the BL40B2 of Spring-8 at 20 °C. Wavelength of the incident X-ray was 0.10 nm. The sample to detector distance was 110 mm. A flat panel detector (C9728DK-10, Hamamatsu Photonics K. K.) with 1032 × 1032 pixels (pixel resolution: 50 μm) was used and the exposure time was 2.4 s. The scattering intensities were corrected with respect to the background and the transmittance.

For Fourier-Transform Infrared/attenuated total reflection (FT-IR/ATR) spectroscopy, Nicolet is50 (Thermo Fisher Scientific Inc.) equipped with Continuum FT-IR Microscope was used at ambient temperature. A spectrum at 4 cm⁻¹ resolution and 64 scans was obtained after pressing the sample onto the Ge crystal of ATR accessory.

Scanning electron microscope (SEM) observation was carried out by JSM-6490 (JEOL Ltd.) with 20 or 30 kV accelerating voltage. Gels before stretching were vacuum dried at 20 °C for overnight and freeze fractured with liquid nitrogen. Gels stretched and fractured were immediately vacuum dried at 20 °C for overnight. The fractured surfaces were coated by sputtered Ag for observation.

In-situ digital microscope observation on morphological changes of the spherulites during stretching was carried out on the gels annealed at $T_a = 95$ °C. The tensile-testing machine 90FD which stretches the sample on both ends was set to digital microscope (VHX-1000, KEYENCE Corp.). The frame rate was 15 fps. The sample was stretched at a crosshead speed of 10 mm/min. Observed area was confirmed to be almost the central region of the sample by the obtained movie. The Supplementary Movie S1 in Supplementary Data was saved at double speed for shortening.

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.polymer.2018.03.003>.

3. Results and discussion

3.1. Mechanical properties of PVDF/PC gels

To better understand the effect of annealing the polymer physical gels near peak melting temperature, the mechanical

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