



Remarkable modulus enhancement of polylactide ion gels via network formation induced by a nucleating agent



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ARTICLE INFO

Article history:

Received 19 November 2015

Received in revised form

24 December 2015

Accepted 14 January 2016

Available online 18 January 2016

Keywords:

Polylactide

Ion gel

Nucleating agent

ABSTRACT

Ion gels have been obtained by crystallization of polylactide (PLA) in an ionic liquid. The modulus of the resulted ion gels is increased with PLA content in the ionic liquid, whereas ionic conductivity follows an opposite tendency. Isolated spheres, caused by PLA crystallization, are responsible for low modulus in the ion gels with low PLA content. By adding a nucleating agent isolated spheres are transformed into interconnected network due to the increased nucleation density during PLA crystallization in the ionic liquid. It in turn significantly enhances the modulus by more than three orders of magnitude, while ionic conductivity remains nearly intact.

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1. Introduction

Ion gels are a kind of gels where ionic liquids are trapped in the network constructed by inorganic nanoparticles, organic gelators or polymers [1–11]. The nonvolatility and high ionic conductivity of ionic liquids enable ion gels to be a promising class of solid-like electrolytes. Correspondingly, ion gels have great potentials in the applications such as actuators, organic thin film transistors, lithium ion batteries and supercapacitors [12–20]. Network formation in the ion gels, for instance, relies on the solution phase separation induced by self-assembly of block polymers [21–25]. That is, insoluble segments of block polymers in the ionic liquids generate physical cross-links to sustain the network where ionic liquids are dissolved by soluble segments. In such a sense, this type of ion gels is thermoreversible. It offers a facile route for processing of ion gels at high temperatures and use of ion gels at low temperatures.

Ionic conductivity of ion gels is very critical for its application as solid-like electrolytes. High conductivity means rapid diffusion of cations and anions in the ion gels under an electrical field. In general, ionic conductivity is reduced with increasing polymer content in the ion gels, as a result of the decrease in the amount of ionic liquids. In contrast, modulus of ion gels is improved with polymer content due to formation of dense network. High modulus

is beneficial for withstanding external forces during the use of ion gels. Thus, it is a challenge for fabrication of ion gels to achieve a balance between ionic conductivity and modulus. A perfect example is reported in a recent study [26]. By decreasing the size of midblock of ABA triblock polymers, modulus and ionic conductivity of the ion gels are synergistically enhanced.

Polylactide (PLA), produced from renewable resources, is biocompatible and biodegradable [27,28]. It is most likely to replace conventional petroleum-based polymers in many applications. PLA can be dissolved in the ionic liquids with similar solubility parameters at high temperatures to generate transparent solutions. Upon cooling PLA crystallization from the solutions results in the formation of opaque gels. In our previous study [29], the presence of an ionic liquid significantly enhances molecular mobility of PLA, thus contributing to easy generation of stereocomplex crystals. However, detailed insights into the properties of PLA ion gels is still absent.

In this case, modulus and ionic conductivity of PLA ion gels were systematically investigated. High ionic conductivity and low modulus are achieved at low PLA content in an ionic liquid, and vice versa. Formation of isolated spheres is responsible for low modulus of the ion gels with low PLA content. By increasing nucleation density with aid of a nucleating agent, PLA crystallization in the ionic liquid results in the network formation. It in turn significantly enhances the modulus of the ion gels by more than three orders of magnitude. At the same time, high ionic conductivity of the ion gels is retained because of constant amount of the ionic liquid.

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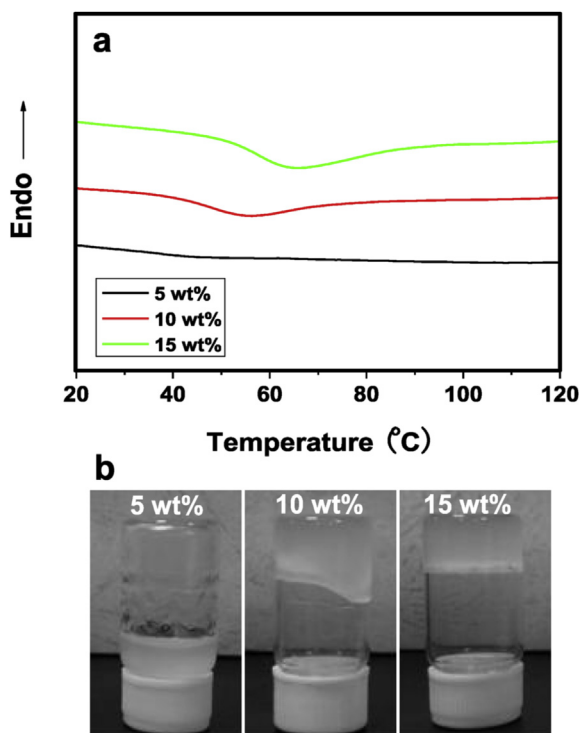


Fig. 1. (a) DSC cooling traces and (b) room temperature optical photographs of PLA with the indicated content in the ionic liquid.

2. Experimental section

2.1. Materials and sample preparation

The poly (ϵ -lactide), abbreviated as PLA, was purchased from Changchun Sinobiomaterials Co., Ltd, China. It had a viscosity-average molecular weight of 193 kg/mol and a melting point of about 174 °C. The ionic liquid, 1-ethyl-3-methylimidazolium bis((trifluoromethyl) sulfonyl) imide ([EMIM]NTf₂), were supplied by Lanzhou institute of Chemical Physics, China. It had a melting point of about -15 °C and ionic conductivity of 9.2 mS/cm. The nucleating agent N, N', N''-tricyclohexyl-1, 3, 5-benzenetricarboxylamide (TMC-328) was kindly provided by Shanxi Provincial Institute of Chemical Industry, China. N, N- dimethylformamide (DMF) and ethanol were analytical agent, and used as-received. Weighted PLA and [EMIM]NTf₂ were dissolved in DMF at 90 °C under stirring to generate a transparent solution. Thereafter, the solution was poured into a petri dish to allow evaporation of DMF, and thus the mixture of PLA and [EMIM]NTf₂ was obtained. To further remove the residual DMF the mixture was vacuum dried at 50 °C for 48 h. The final samples for following measurements were prepared by heating of the mixture up to 170 °C, followed by cooling down to room temperature. The PLA content in the samples was 5, 10 and 15 wt%, respectively. Similarly, above procedures were applied to fabricate samples containing the nucleating agent. The nucleating agent was incorporated in the step of solution blending, and its loading was 1 and 2 wt%, respectively (based on the weight of PLA).

2.2. Characterizations

The modulus was measured by a TA discovery hybrid rheometer (DHR-2) with parallel-plate geometry having a gap of 1 mm at 30 °C under a flow nitrogen atmosphere. The diameter of parallel plates was chosen as 25 or 40 mm, depending on the modulus of samples.

Dynamic oscillatory shear measurements were carried out in the linear viscoelastic regime that was determined by a prior strain sweep. The microstructure was probed by a Nova NanoSEM 450 scanning electron microscope (SEM). Samples for SEM measurements were obtained by washing with ethanol at room temperature to remove the ionic liquid. Ionic conductivity was determined by a Princeton PARSTAT 2273 electrochemical workstation at 30 °C using two-probe technique. Samples were sandwiched between two stainless steel electrodes with a space of 0.2 mm. Impedance spectra was collected over the frequency range from 1 Hz to 1 MHz. The resistance was deduced from high frequency intercept on the real axis of the impedance spectra. The ionic conductivity was calculated from the resistance with aid of sample thickness and the area of the electrodes. Crystallization behavior of PLA in the ionic liquid was analyzed by a TA Q2000 differential scanning calorimetry (DSC) instrument under a flow nitrogen atmosphere. After being held at 170 °C for 3 min samples were cooled down at a rate of 10 °C/min to record cooling traces.

3. Results and discussion

Due to similar solubility parameters PLA can be completely dissolved in the ionic liquid [EMIM]NTf₂ at high temperatures [29,30]. During cooling process PLA crystallization occurs, as demonstrated by the exothermic peak in the DSC traces (Fig. 1a). The crystallization temperature is about 56 and 65 °C for samples with PLA content of 10 and 15 wt%, respectively. Of note, PLA crystallization in the ionic liquid is insignificant at the content of

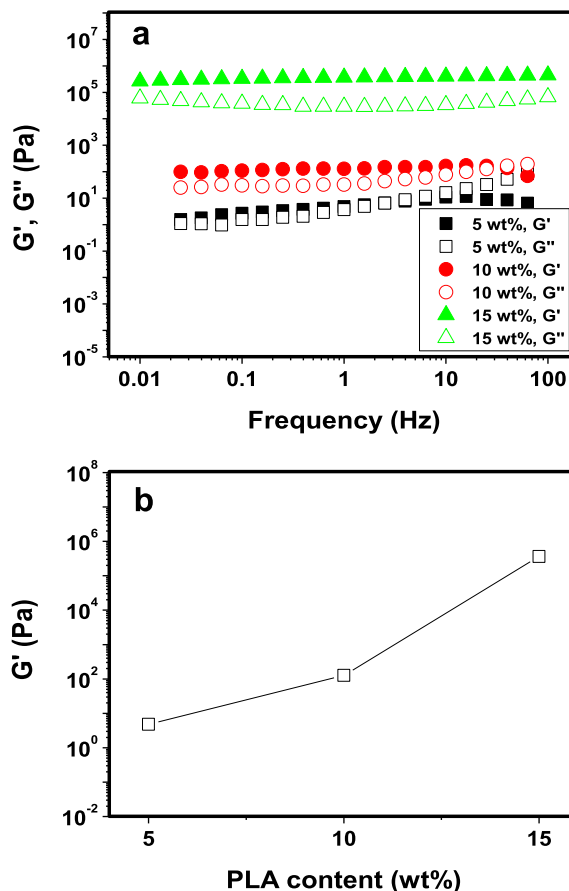


Fig. 2. (a) frequency dependent storage G' and loss modulus G'' of PLA with the indicated content in the ionic liquid, and (b) variation of storage modulus G' at a frequency of 1 Hz with respect to PLA content.

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