

# Polymeric Gels Prepared From the Mixtures of Polar Polymers and Ionic Liquids for Thermally Re-mendable Coating Systems

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## Abstract

A new kind of physical gel was prepared using mixtures of poly(vinyl alcohol) (PVOH) and high melting ionic liquid (IL), 1-ethylpyridinium bromide. As the IL content was increased, the stiffness of the mixtures decreased sharply while extensibility increased significantly, exhibiting rubber-like elasticity. X-ray scattering studies indicated that IL is highly miscible with PVOH and forms a modified amorphous phase that coexists with the crystalline phase of PVOH. Thermal analysis showed that both melting temperature ( $T_m$ ) and glass transition temperature ( $T_g$ ) of the IL/PVOH mixtures decreased noticeably as IL content increased. The peak intensity associated with the melting transition decreased as well, indicating decreased overall crystallinity. Due to the highly suppressed  $T_g$  of the mixtures, thermal flow can be induced easily by mild heating. A noticeable healing effect via thermal flow was observed for scratched films prepared from IL-rich mixtures, suggesting that these mixtures could be used for thermally re-mendable coating systems.

## Introduction

Considerable efforts have been expended to develop self-healing polymeric materials, and a wide variety of strategies have been explored. Early strategies used simple chain entanglement at the interface to mend cracks in thermoplastics<sup>1</sup> while later attempts employed more complex systems such as an epoxy resin consisting of a catalyst and encapsulated reactive monomers dispersed in the epoxy matrix<sup>2</sup> or thermally reversible crosslinking systems containing specially synthesized molecules that undergo Diels-Alder reaction.<sup>3</sup> More recently, supramolecular assembly was utilized to develop self-healing and thermoreversible rubbers.<sup>4</sup> In this strategy, reversible hydrogen bonds were used to form both macromolecular chains and cross-links. The resulting material showed self-repairing properties through reversible bonds and rubber-like elasticity since the strong physical association prevents viscous flow. In typical commercial self-healing automotive coating systems, scratch resistance is controlled by the density of the constituent molecules (cross-link density) while low to moderate glass transition temperature ( $T_g$ ) facilitates thermal flow under mild heating to heal small scratches.

Another possibility to implement reversible interactions and low  $T_g$  for self-healing materials could be found in thermoreversible physical gels. Since the physical gels are composed of supramolecular networks based on noncovalent van der Waals interactions with the energy involved on the order of  $kT$ , these gels are 'heat-reversible'. For example, poly(vinyl alcohol) (PVOH) gel is a well-known crystallization-induced physical gel. Initially transparent hydrogels containing a few percent (ca. 0.5 %) of crystallized chain segments that form primary crystallite junctions transform into a fibrillar network with increased crystallinity (ca. 5 %) by aging. The aging effect in PVOH hydrogels is likely due to the relatively weak hydrogen bonding interaction between water and hydroxyl group of PVOH, as well as the PVOH's tendency to crystallize.<sup>5</sup> Water molecules that are weakly bound to PVOH via hydrogen bonding can be squeezed out of the hydrogel when PVOH undergoes crystallization through

aging, leading to phase-separated, milky white physical gels composed of an expelled water phase and PVOH-rich phase with few water molecules between polymer chains.

We investigate a new kind of PVOH physical gel in which the volatile water is replaced with a non-volatile ionic liquid (IL). High melting IL containing Br<sup>-</sup> anion was chosen so that the hydrogen-bond accepting Br<sup>-</sup> can enhance miscibility with PVOH while high melting point can lead to solid mixtures at room temperature. Our objective is to explore the possibility of using this material for thermally re-mendable coating systems. The thermal and mechanical properties of the mixtures of IL and PVOH were investigated and the results are discussed in terms of the interaction between the two components. Thermal healing properties were evaluated visually by optical microscopy for macroscopic scratches after mild heating treatment.

## Experimental

**General.** Equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology (NIST), nor does it imply the materials are necessarily the best available for the purpose.

**Sample Preparation.** PVOH (98 % to 99 % by saponification and 85k to 114k in mass average molecular mass, as quoted by the supplier) was dissolved in de-ionized water at 90 °C to yield an aqueous solution (5 % by mass). Mixtures of IL (1-ethylpyridinium bromide, melting point of 117 °C to 120 °C, as quoted by the supplier) and PVOH were made by adding IL into the aqueous PVOH solution, followed by mixing at 90 °C to yield aqueous solutions in various compositions. Each mixture was transferred to a petri dish, followed by slow evaporation of water and subsequent vacuum drying at 60 °C to yield polymeric films. Samples were kept inside a desiccator under vacuum until used for analysis. IL/PVOH mixtures thus treated contain up to 5 % by mass of water.

**Characterization.** Differential scanning calorimetry (DSC) data was acquired using a TA Instrument (DSC Q2000) with a scan rate of 10 °C/min to determine the melting temperature and glass transition temperature of the IL/PVOH mixtures. Tensile stress-strain curves were collected with a Texture Analyzer (TA-XT2i) at a cross-head speed of 10 mm/min using 2 to 5 replicates of rectangular film specimens (4 mm in width, 40 mm in length, 30 μm to 50 μm in thickness) which were cut from the dried bulk films. X-ray scattering patterns were acquired using a copper source for 11 h at room temperature. Intensities are presented against the scattering vector defined as  $q = (4\pi/\lambda) \sin(\theta/2)$ , where  $\theta$  is the scattering angle and  $\lambda$  is the wavelength of the radiation (Cu K<sub>α</sub>:  $\lambda = 1.54 \text{ \AA}$ ). Thermal healing properties were evaluated visually using scratched films. A sharp edge of a razor blade with an added load of 22 g was in contact with a film supported on a glass substrate, and a macroscopic scratch was made by pulling the film sample at a rate of 1 mm/s. An optical microscope was used to observe dimensional changes in the scratch after thermal treatment (70 °C, 6 h).

## Results and Discussion

Mixtures of a high melting ionic liquid (1-ethylpyridinium bromide) and a polar polymer (PVOH) were prepared using de-ionized water as a co-solvent to facilitate homogeneous mixing. Optically transparent films composed of IL and PVOH could be obtained after removing

water by slow evaporation. Prepared compositions ranged from 0 % up to 70 % by mass of IL in 10 % intervals, above which a homogeneous binary mixture could not be formed after drying.

PVOH, which is prepared by hydrolysis of radically polymerized poly(vinyl acetate), is atactic yet crystalline.<sup>6</sup> Upon adding IL, the melting temperature ( $T_m$ ) of the mixture decreases from 223 °C to 102 °C as the IL content increases from 0 % to 50 % by mass, indicating good miscibility (Figure 1). The endothermic peak becomes broader and weaker in intensity as the IL content increases, possibly due to the interaction between IL and PVOH that might result in the formation of crystals with broad size distribution as well as a reduced overall apparent crystallinity of the mixture. Further increase in IL content (higher than 50 % by mass) causes the endothermic melting peak to almost disappear, indicating highly reduced crystallinity. The glass transition temperature ( $T_g$ ) shows a similar trend:  $T_g$  decreases from 79 °C to -27 °C as the IL content increases from 0 % to 50 % by mass, while further increase in IL content no longer affects the observed  $T_g$ . These observations indicate that thermal properties can be controlled by adjusting the composition of the mixtures, which is useful to control the thermal flow properties for re-mendable coating systems.

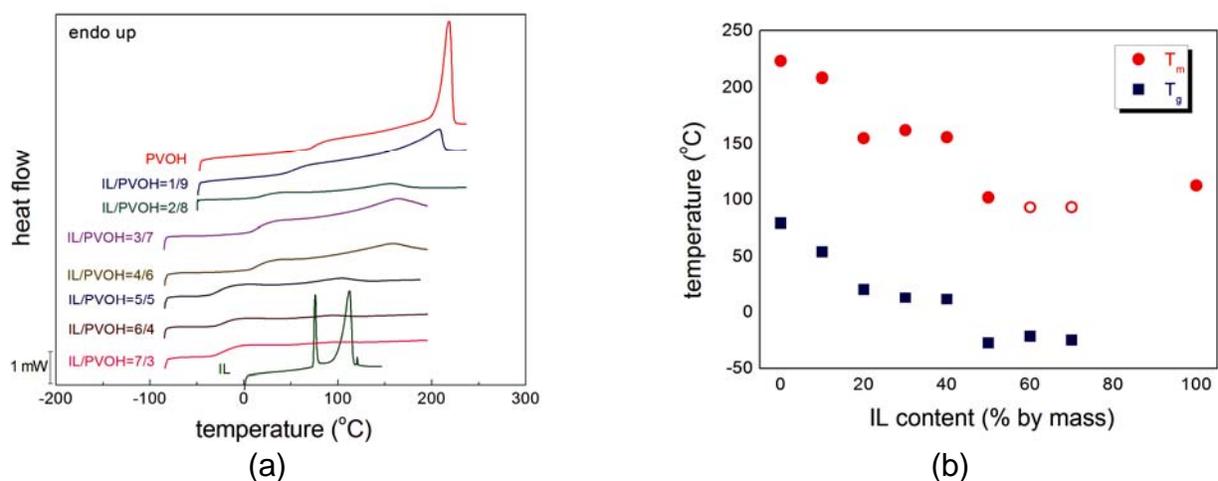


Figure 1. (a) DSC thermograms of the IL/PVOH mixtures obtained from re-heating scans. (b) Melting temperature ( $T_m$ ) and glass transition temperature ( $T_g$ ) as a function of IL content.  $T_m$  was determined from the endothermic peak maximum while  $T_g$  was estimated from the midpoint of the inflection points. Open symbol in  $T_m$  reflects that the corresponding peak intensity in the thermogram is very weak.

Wide angle X-ray diffraction (WAXD) profiles are shown in Figure 2. WAXD of neat PVOH is composed of an amorphous halo centered at  $q = 14.2 \text{ nm}^{-1}$  and a crystalline peak centered at  $q = 13.9 \text{ nm}^{-1}$  while that of neat IL shows many diffraction peaks due to the polymorphism inherent in most ILs.<sup>7,8</sup> WAXD of mixtures exhibits systematic changes as a function of the mixture composition. As the IL content in PVOH increases (up to 40 % by mass of IL), the peak associated with the amorphous halo increases in intensity and shifts to higher  $q$  values while the crystalline diffraction peak position of PVOH is not affected. Since the characteristic Bragg spacing ( $d$ ) is inversely proportional to the scattering vector at the peak's maximum ( $q_{\text{max}}$ ), it is likely that the amorphous phase of PVOH is affected by IL and IL/PVOH mixtures may contain a different amorphous phase than neat PVOH with a shorter interchain distance. It should be noted that the diffraction peaks from IL crystals are absent for IL-lean

mixtures, although IL crystals tend to show very strong diffraction peaks due to their electron-rich structure. The absence of such peaks in the mixture suggests that IL is almost completely miscible with PVOH and can form a new amorphous phase that coexists with the crystalline phase of PVOH. If the IL content is further increased, characteristic diffraction peaks from IL crystals begin to appear in the scattering profiles of the mixtures. However, the angular positions of some peaks in the mixture do not match exactly to those in the neat IL, possibly due to destruction of the solid-state structures of the IL and the formation of new ordered structures. The appearance of new diffraction peaks that are absent in neat IL is more evident in high  $q$  range, suggesting that the new ordered structures are very small in size ( $d$  in the range between 0.35 nm and 0.45 nm).

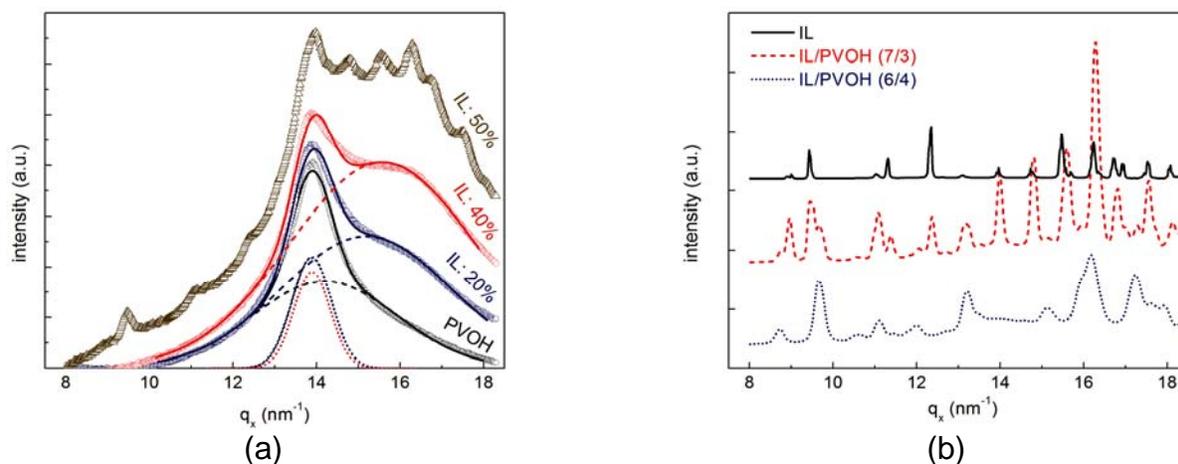


Figure 2. Circularly averaged 1-D scattering profiles from the 2-D WAXD patterns. (a) IL-lean mixtures. Dashed curves represent decomposed Gaussian curves and symbols represent experimental data. Solid curves are best-fit of the experimental results constructed from the addition of each Gaussian curves. (b) IL-rich mixtures. Each curve is from experimental data. Decomposed Gaussian curves are not shown for clarity.

Mechanical properties of the mixtures were investigated by uniaxial tension tests. As the IL content in the mixture was increased, the stiffness of the material decreased sharply while the extensibility increased significantly, exhibiting rubber-like elasticity (Figure 3). Due to the good miscibility between PVOH and IL as inferred from the X-ray scattering results at low to moderate concentrations, IL acts as an efficient plasticizer. Young's modulus changes by 3 orders of magnitude over the range of IL concentrations (0 % to 70 % by mass). The interaction between IL and the hydroxyl groups of the PVOH is likely to form physical junctions that prevent viscous flow upon deformation, leading to an elastic response.

Thermal healing properties as observed by optical microscopy are shown in Figure 4. While neat PVOH did not show any significant change after thermal treatment (70 °C, 6 h inside an oven), PVOH mixed with 10 % of IL by mass, designated as IL/PVOH (1/9) in Figure 4, showed slight healing effect. The healing effect of the mixtures increased as IL content increased, presumably due to the enhanced thermal-flow properties caused by lower  $T_g$ . If 70 % of IL by mass was mixed with PVOH, noticeable healing effect was observed. However, this

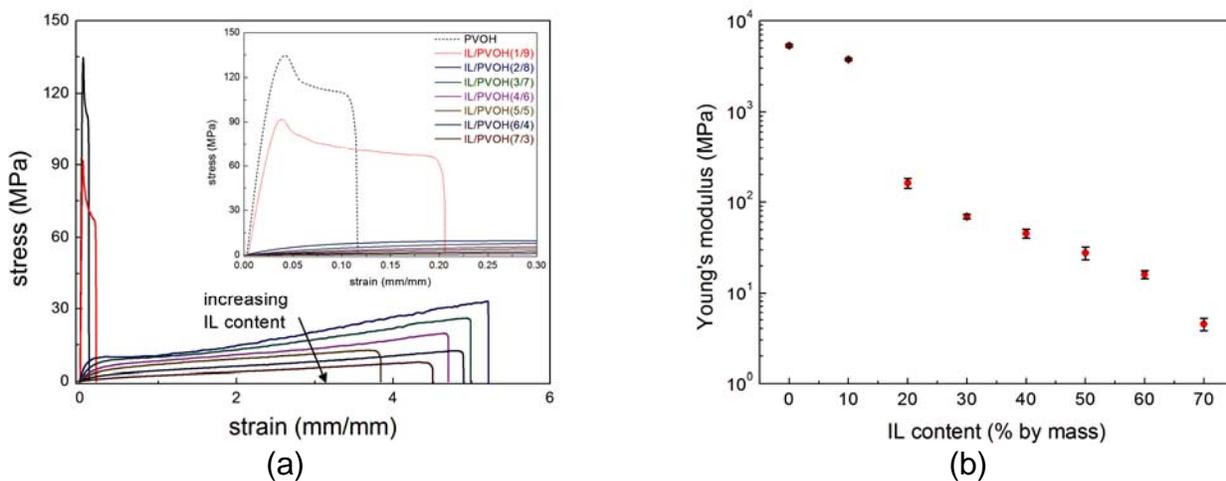


Figure 3. Tensile properties for the mixtures of PVOH and IL. (a) Stress-strain curves from uniaxial tension tests. Inset is for small strain region. (b) Young's modulus as a function of IL content in the mixture. The error bars represent one standard deviation of the data, which is taken as the uncertainty of the measurement.

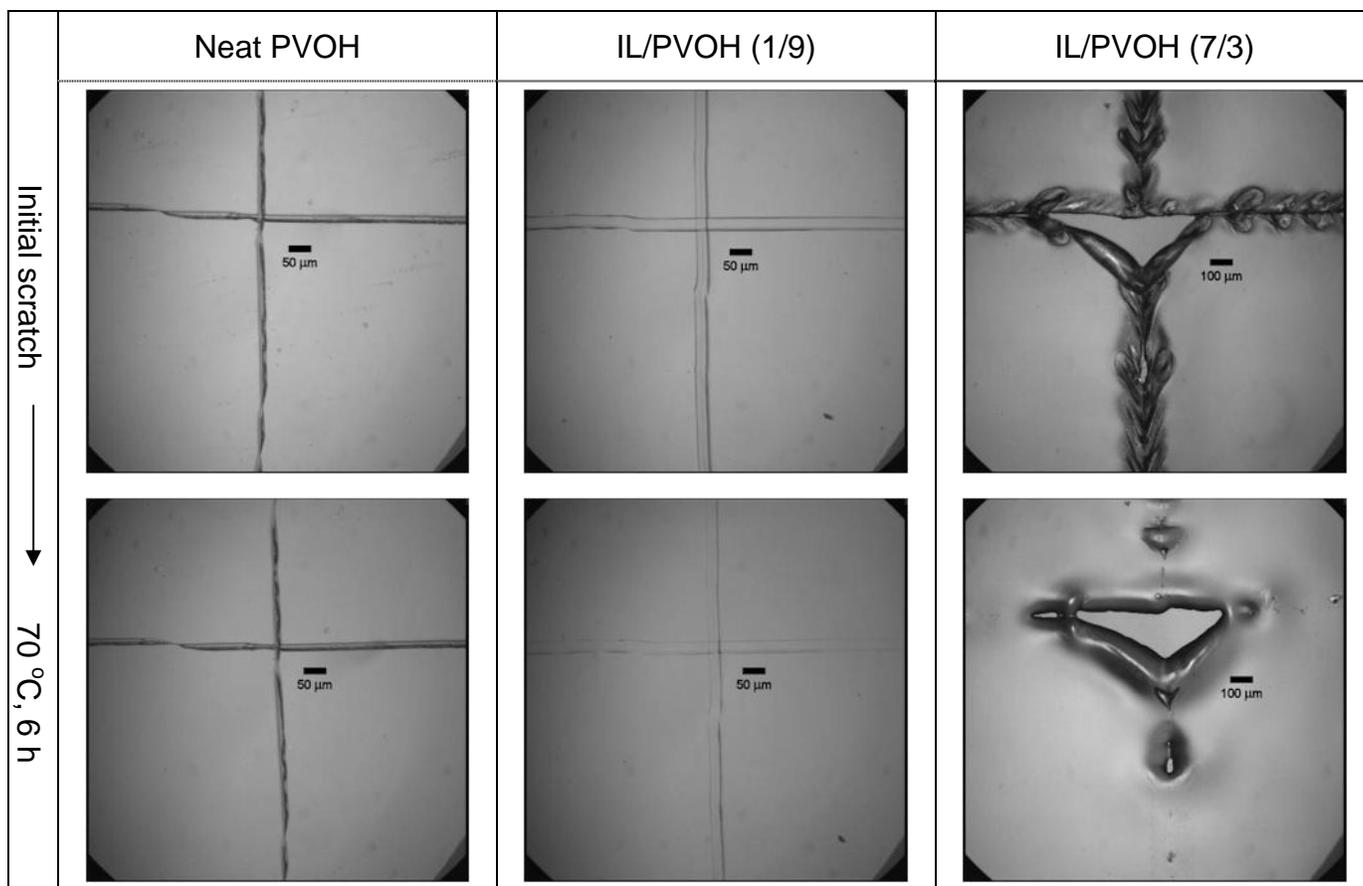


Figure 4. Optical micrographs of scratched films before thermal treatment (upper row) and after thermal treatment (lower row). Thermal treatment was done at 70 °C for 6 h inside a convection oven.

mixture was too soft and severely damaged compared to other samples with lower IL content under the same scratch conditions. Research is in progress to enhance scratch resistance of IL-rich mixtures for practical coating systems with thermal re-mendability.

## Conclusion

Binary mixtures of a high melting ionic liquid (1-ethylpyridinium bromide) and a polar polymer (PVOH) showed widely tunable thermal and mechanical properties as well as highly elastic properties. Interaction between the two components was investigated by X-ray scattering analysis. Due to the reduced glass transition temperature of the mixtures, thermal flow could be triggered under mild heating conditions. Noticeable healing effect was observed for IL-rich mixtures when exposed to 70 °C for 6 h. These observations suggest that such mixtures could provide a simple method to produce thermo-reversible physical gels that can be used for thermally re-mendable coating systems.

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