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Thermoplastic Elastomers Based on Ionic Liquid and Poly(vinyl alcohol)

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ABSTRACT: We report a new kind of thermoplastic elastomer using poly(vinyl alcohol) (PVOH) and a high-melting ionic liquid (IL), 1-ethylpyridinium bromide. Wide angle X-ray scattering results indicate that the IL is highly miscible with PVOH for PVOH-rich mixtures (up to 40% by mass of IL) while IL-rich mixtures exhibit diffraction peaks from IL crystals that are precipitated in the amorphous phase of the mixture. Thermal analysis shows that both the melting temperature (T_m) and the glass transition temperature (T_{σ}) of the "as-cast" mixtures decrease noticeably as IL content increases, indicating good miscibility of IL with PVOH. Physical aging of the mixtures for 1 week at room temperature led to the appearance of a secondary endothermic peak at almost constant tempera-



ture irrespective of the mixture composition, suggesting the formation of an IL-PVOH complex. FT-IR analysis shows that the O-H stretching vibration band shifts to higher frequency as IL content increases. This result implies that the IL interacts with the hydroxyl groups of PVOH, forming IL-PVOH complexes that act as physical junctions. The tensile modulus decreases significantly as IL content in the mixture increases, indicating that the IL not only promotes the physical association of PVOH but also acts as a plasticizer. The highly elastic behavior of these mixtures suggests a network structure of PVOH in the presence of IL, in which both the crystalline phase of PVOH and IL-PVOH complexes act as physical cross-links that bridge the IL-swollen PVOH amorphous phase. These observations demonstrate that simple mixtures of a polar polymer and a compatible high-melting ionic liquid can yield thermoplastic elastomers with widely tunable thermal and mechanical properties.

INTRODUCTION

Thermoreversible physical gels from synthetic polymers have received considerable attention due to their ability to respond to very weak external perturbations such as temperature, pH and solvent.¹ While *chemical gels* are comprised of three-dimensional networks with point-like junctions formed by robust, irreversible covalent bonds that are stable under ambient conditions, physical gels are typically composed of supramolecular networks based on noncovalent van der Waals interactions.² Stable physical gels can be formed when there is cooperativity in the weak van der Waals interaction, which implies that the junction domains are not point-like but extend into space. Since the energy involved in van der Waals interaction is of the order of kT, these gels are "heatreversible".³ While polymers possessing bulky side groups tend to form physical gels by solvent induction, those without bulky side groups often form physical gels by crystallization.³

Poly(vinyl alcohol) (PVOH) hydrogels are formed by crystallization-induced physical gelation and have been studied intensively for the past few decades. The microstructure of PVOH hydrogels prepared through freeze/thaw cycling was investigated by Willcox et al.4 to understand the reversible gelation and subsequent aging effects. They found that a few percent (ca. 0.5%) of chain segments crystallize in the first cycle to form primary crystallite junctions that lead to liquid-like microstructure, which transforms into a fibrillar network with increased crystallinity (ca. 5%) by aging or additional freeze/thaw cycles. Ricciardi et al.⁵ investigated the rheological properties of atactic PVOH hydrogels prepared by freeze/thaw cycles and found that

the first few freeze/thaw cycles significantly affect the hydrogel structure and rheological properties, and the storage modulus is mainly controlled by the crystallinity of atactic PVOH rather than hydrogen bond interactions. Miyazaki et al.⁶ studied the structural changes in PVOH films during uniaxial stretching in water by in situ small-angle X-ray scattering measurements. They observed a transition from lamellar to microfibrillar structures above a strain of 180% and a strain-induced hardening accompanied by the development of the network of extended amorphous regions that bear the large stress in the network. On the basis of their observations, a structure model reflecting elastic expansion of the interlamellar amorphous regions, lamellar breakup, fibrillation, and expansion of interfibrillar amorphous regions under stretching conditions was proposed, which also contained strain-induced crystallization in the interfibrillar amorphous regions.7

As can be inferred from the effect of freeze/thaw cycles or prolonged aging on the properties of PVOH gels, the equilibrium state of PVOH hydrogels cannot be reached immediately. Aging of PVOH hydrogels is likely due to the hydrogen bonding interaction between water and hydroxyl groups in PVOH as well as the PVOH's tendency to crystallize, which is supported by the observation that aged PVOH gels show higher crystallinity than as-cast ones.⁴ Water molecules weakly bound to PVOH via

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hydrogen bonding can be squeezed out of the hydrogels as PVOH undergoes crystallization during aging, which leads to phase-separated, milky white physical gels composed of expelled water phase and PVOH-rich phase with few water molecules between polymer chains.

The motivation of this work is to prepare physical gels of PVOH in which the volatile water is replaced with a nonvolatile, high-melting ionic liquid (IL) so that the resulting materials may form stable, solid-like elastomers. Because of their unique properties such as negligible vapor pressure, good thermal stability, extremely high ionic conductivity and facile variation in properties by virtually unlimited combinations of anions and cations, ILs have recently attracted a lot of interest from both academia and industry, finding applications as alternative solvents for synthesis and extraction, diluents in polymer membranes, nonvolatile plasticizers and components for polymer gel electrolytes.⁸⁻¹¹ While the electrochemical properties of polymer - ionic liquid gels have been extensively studied to develop new kinds of electrolytes, ^{10,12,13} relatively little effort has been expended to elucidate the physical properties of such systems. Scott et al.¹⁴ showed that the room temperature IL, 1-butyl-3methylimidazolium hexafluorophosphate, could be used as an efficient plasticizer for poly(methyl methacrylate) (PMMA), prepared by in situ radical polymerization in the IL medium. They observed a linear decrease in T_{g} and a dramatic decrease in elastic modulus of PMMA containing up to 50% by mass of the IL. Brown et al.¹⁵ investigated the interaction of the IL, 1-ethyl-3methylimidazolium ethylsulfate, with low- T_{g} zwitterionomers in the presence of moderate amount of dipolar sulfobetaine-based zwitterions. They found that the IL preferentially swelled the ionic domains without affecting the morphology of the nonpolar matrix of the two-phased zwitterionic copolymer membrane, which resulted in a significant decrease in $T_{\rm g}$ of the zwitterionic phase as well as a drastic increase of ionic conductivity at high swelling levels. Eastman et al.¹⁶ showed that ILs could be used as viable solvents for the modification of PVOH under simple reaction conditions. They demonstrated rapid esterification of PVOH using four different acid chlorides in both 1-butyl-3methylimidazolium chloride and tri-n-butylethylphosphonium diethylphosphate, as well as urethanation of PVOH with appropriate IL solvent. He et al.¹⁷ investigated the gelation behavior, ionic conductivity, rheological properties and microstructures of the ionic gels prepared by swelling a triblock copolymer, poly-(styrene-block-ethylene oxide-block-styrene), with a room temperature IL, 1-butyl-3-methylimidazolium hexafluorophosphate $([BMIM][PF_6])$. They observed a transition from a liquid-like state to a solid-like state as the polymer content increased, weak concentration dependence for ionic conductivity and two relaxation modes of the triblock copolymer network. More recently, Harner et al.¹⁸ described the thermoreversible gelation of a room-temperature ionic liquid, 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][EtSO₄]), by crystallization of a dissolved poly(ethylene glycol). They showed that the polymer concentration and molar mass affect the gelation process, which proceeds by kinetically frustrated polymer crystallization.

We investigate here the interaction between a polar polymer (PVOH) and a high-melting ionic liquid (1-ethylpyridinium bromide) that exhibit elastomeric behavior analogous to PVOH hydrogels. A high-melting IL having Br⁻ counterion was chosen since the hydrogen-bond accepting Br⁻ can enhance miscibility with PVOH while the high melting temperature of the IL can lead to solid-like mixtures at room temperature. Polymers

modified with high-melting organic compounds were shown to exhibit unique morphologies and mechanical properties by Yoon et al.^{19,20} and this work is motivated by those observations. Although systems wherein the solvent represents the major component are typically considered as gels,³ a wider composition range was considered for IL—PVOH mixtures. It is expected that our results will lead to the development of thermo-reversible elastomers such as stimuli-responsive physical gels.

EXPERIMENTAL SECTION

General Information. 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.

Materials. PVOH (98% to 99% by saponification and 85k to 114k in mass average relative molecular mass, as quoted by the supplier) was obtained from Sigma-Aldrich and used as received. 1-Ethylpyridinium bromide (melting point of 117 to 120 $^{\circ}$ C, as quoted by the supplier) was purchased from Fisher Scientific. Since the IL used in this study is highly susceptible to ambient moisture, the IL was dried at 90 $^{\circ}$ C in a vacuum oven for 1 h before using.

Sample Preparation. Aqueous solutions of PVOH (5% by mass) were prepared by mixing polymer powder with deionized water (18 M $\Omega \cdot cm$) at 90 °C for 5 h with constant stirring. Mixtures of IL and PVOH were made by adding IL into the aqueous PVOH solution, followed by mixing at 90 °C for 30 min with constant stirring to yield homogeneous aqueous solutions in various compositions. Each mixture was transferred to a Petri dish, covered by perforated aluminum foil and placed on a flat table for 3 d to allow slow evaporation of water, which was used as a cosolvent for both IL and PVOH. Film samples thus prepared were dried further under the hood with gentle air flow for 1 d, followed by vacuum drying at 50 °C overnight. Dried film samples were detached from the Petri dishes and denoted as "*as-cast*" samples. "*Aged*" samples were prepared by keeping the as-cast samples inside a desiccator under vacuum at room temperature for a predetermined period of time.

Thermal, Mechanical, and Structural Characterization. Differential scanning calorimetry (DSC) data were acquired using a TA Instrument (DSC Q2000) with a scan rate of 10 °C/min during heating and 5 °C/min during cooling to determine the melting temperature, glass transition temperature and crystallization temperature. Thermal gravimetric analysis (TGA) data were obtained using a TA Instrument (TGA Q500) with a heating rate of 10 °C/min under dry nitrogen environment to estimate thermal stability and moisture contamination. Room temperature uniaxial tensile stress-strain curves were collected with a Texture Analyzer (TA-XT2i) at a cross-head speed of 10 mm/min using 3 to 5 replicates of rectangular film specimens (4 mm in width, 40 mm in length, $30-50 \,\mu$ m in thickness) which were cut from the dried bulk films. In cyclic loading/unloading tests, film specimens were stretched to predetermined strain levels, and the cross-head was immediately reversed and returned to its initial position, all at a cross-head speed of 10 mm/min. Fresh rectangular samples were used for each strain level. Wide angle X-ray scattering (WAXS) patterns were acquired using a copper source for 11 h at room temperature. The source-to-sample distance (SSD) was fixed at 122.5 cm and the sample-to-detector distance (SDD) was fixed at 21.5 cm. Intensities are presented against the scattering vector q = $(4\pi/\lambda)\sin(\theta)$, where 2θ is the scattering angle and λ is the wavelength of the radiation (Cu K_{α}: λ = 1.54 Å). Fourier transform infrared (FT-IR) spectra were collected using a Nicolet NEXUS 670 with an ATR fixture in the wavenumber range from 650 to 4000 cm⁻¹ under atmospheric conditions.



Figure 1. TGA thermograms for selected mixtures of PVOH and 1-ethylpyridinium bromide. Samples containing PVOH were prepared from aqueous solution, followed by slow evaporation of water and vacuum drying at 50 $^{\circ}$ C overnight. Neat IL was dried at 90 $^{\circ}$ C under vacuum overnight. (a) TGA thermogram in full scale. (b) TGA thermogram in temperature range between 0 and 250 $^{\circ}$ C to evaluate moisture contamination.

RESULTS AND DISCUSSION

Homogeneous mixtures of a high-melting ionic liquid (1ethylpyridinium bromide) and a polar polymer (PVOH) were prepared using deionized water as a cosolvent, since the direct thermal mixing of the polymer and IL often led to an inhomogeneous mixture due to relatively high viscosity and thermal stability limit of PVOH, which undergoes rapid decomposition above its melting temperature. Optically transparent films composed of IL and polymer could be easily obtained after removing water by slow evaporation. Prepared compositions ranged from 0% up to 70% by mass of IL in 10% intervals, above which homogeneous binary mixtures could not be formed after drying. Samples are named as "IL/PVOH (x/y)" where x/y is a mixing ratio of IL (x) to PVOH (y) by mass in the mixture. TGA analysis indicates that the dried mixtures still contain 2% to 5% by mass of water when exposed to atmospheric conditions for characterization (which takes up to 30 min) due to the hygroscopic nature of the IL (Figure 1). The water content tends to increase as the IL content in the mixture increases, which could provide further plasticizing effect for IL-rich mixtures.

PVOH, which is prepared by hydrolysis of radically polymerized poly(vinyl acetate), is atactic yet crystalline.²¹ As the IL content increases from 0% to 70% by mass, the melting temperature of the as-cast mixtures (no aging) decreases from 224 to 123 °C as determined at the minimum endothermic peak position from reheating scans (Figure 2a, 2e). The significant depression of the melting temperature implies that the chosen IL is a good solvent for PVOH. In addition to the decrease in melting temperature, the endothermic peak becomes broader in width and weaker in intensity as the IL content increases. The crystallization temperature of the as-cast mixtures also decreases from 119 to 63 °C with broadening width and weakening intensity of the exothermic peak as the IL content increases from 0% to 70% by mass (Figures 2b, 2f). These results indicate that the initial crystallization of PVOH is affected by the IL, which could provide a medium in which PVOH chains are dispersed and then crystallize,18 leading to the formation of crystals with broad size distribution as well as a reduced overall crystallinity of the mixture. The T_{g} of the as-cast mixtures shows a similar trend: as the IL content increases from 0% to 70% by mass, the T_{g} decreases from +82 to -59 °C (Figures 2a, 2f). The significant drop in T_g demonstrates that the IL used in this study is an efficient plasticizer for PVOH. Samples that were aged inside DSC pans for 1 week under ambient conditions show a secondary endothermic peak at around 50 to 60 °C independent of the composition of the mixtures, in addition to the primary endothermic peak (Figures 2c,e). The secondary peak is most likely associated with the formation of IL-PVOH complexes during the aging period, which is typically observed for solvent-induced gels and act as physical junctions.³ Polymer-solvent molecular compound (IL-PVOH complex) is formed through "weak" bonds such as van der Waals or hydrogen bonds.²² Although the interaction of individual pair of polymer and solvent is weak, aggregates of such interactions form physical junction "domains" (in contrast to "point-like" junctions in chemical cross-links) that are strong enough to act as physical junctions. When aged for one month, those two endothermic peaks become closer to each other and form a huge endothermic peak with extremely broad width and strong intensity as the IL content in the mixture increases (Figure 2d). These observations indicate that IL interacts slowly with PVOH at room temperature, facilitating the crystallization of PVOH as well as the formation of IL-PVOH complexes, both with wide size distribution. The slow interaction kinetics is presumably due to the solid-like nature of the mixtures that hinders the diffusion of free IL molecules to reach free hydroxyl groups of PVOH and/or molecular rearrangement in the mixtures. It should be noted that the likely formation of IL-PVOH complex suggests a strong dependence of the properties of IL-PVOH mixture on the IL identity, since the properties of most solvent-induced gels strongly depend on the solvent type.

Circularly averaged 1-D scattering profiles from the 2-D WAXS patterns for one month old samples are shown in Figure 3. Each scattering pattern is deconvoluted into Gaussian peaks using the multipeak fit module of Igor Pro (Version 6.1.2.1). The WAXS spectrum of neat PVOH shows a diffraction peak of amorphous halo centered at $q = 14.2 \text{ nm}^{-1}$, consistent with data reported in the literature,^{23,24} along with a crystalline peak centered at $q = 13.9 \text{ nm}^{-1}$ from the (101) diffraction of the PVOH semicrystalline phase, which is due to the intermolecular interference between the PVOH chains in the direction of the intermolecular hydrogen bonding.²⁴ The WAXS spectrum of neat IL, on the other hand, is composed of many diffraction peaks, reflecting the polymorphism of the IL caused by the inhibition of crystallization through provision of a large number of similarly stabilized solid state structures.²⁵ WAXS spectra of mixtures exhibits systematic changes as a function of the mixture



Figure 2. Thermal properties of IL–PVOH mixtures. (a) DSC thermograms from reheating scan at 10 °C/min for selected as-cast samples. (b) DSC thermograms from cooling scan at 5 °C/min for selected as-cast samples. (c) DSC thermograms for selected samples aged inside DSC pans for 1 week at room temperature. Samples were cooled to -90 °C before heating at 10 °C/min. (d) DSC thermograms for selected samples aged inside DSC pans for one month at room temperature. Samples were cooled to -90 °C before heating at 10 °C/min. (e) Melting temperature as a function of IL content in the mixture. Aging condition is noted in the legend. (f) Glass transition temperature and crystallization temperature as a function of IL content in the as-cast mixture.

composition. As the IL content in the mixture increases (up to 40% by mass), the peak from the amorphous halo increases in intensity and shifts to higher q values while the crystalline diffraction peak position of PVOH is not affected (Figure 3a). This result indicates that the gradual structural change in the mixture occurs mainly in the amorphous phase of PVOH. A shifting of the peak to higher q values implies that the characteristic Bragg spacing (d) associated with the amorphous halo, calculated by $d = 2\pi/q_{\text{max}}$ where q_{max} is the scattering vector at

the peak's maximum, decreases as the IL content increases. The low-angle amorphous halo $(2\theta < 20^{\circ} \text{ for Cu } K_{\alpha})$ is mainly due to intermolecular scattering (in contrast to the intramolecular scattering from covalently bonded scattering centers) and the corresponding value of *d*, which reflects an order of magnitude of the distance of closest approach of the scattering entities, may be used to estimate the intermolecular spacing.^{26–29} Since the amorphous halo of our mixtures is located in the range of 20.02° < 2 θ < 23.19°, which is slightly outside of the typical



Figure 3. Circularly averaged 1-D scattering profiles from the 2-D WAXS patterns. Samples were aged at room temperature under vacuum for one month. (a) PVOH-rich mixtures. Dashed curves represent deconvoluted Gaussian curves and symbols represent experimental data. Solid curves are best-fit of the experimental results constructed from the addition of each Gaussian curve. Inset is 1-D scattering pattern for neat IL. (b) IL-rich mixtures. Each curve is from experimental data and shifted in the intensity axis (*y*-axis) for clarity. Inset is 1-D scattering pattern of IL–PVOH (5/5) mixture.

intermolecular scattering regime, it is likely that both intermolecular and intramolecular scattering may affect the amorphous halo. In this case, intramolecular scattering is most likely from the neighboring IL molecules associated with the neighboring hydroxyl groups of PVOH (e.g., closely packed IL molecules in IL— PVOH complex), and thus the corresponding intrachain correlation distance is expected to be shorter than interchain correlation distance. As the IL content in the mixture increases, influence from the intramolecular scattering would become stronger and the corresponding *d*-spacing in amorphous phase should decrease. However, further study is required to clarify the change in *d*-spacing in the amorphous phase.

It should be noted that, in case of binary mixtures of PVOH and IL, the total scattering intensity (I_{tot}) is composed of the contributions from PVOH (I_{PVOH}), IL (I_{IL}) and the interference between PVOH and IL (I_{int}). Our results show that the diffraction peaks from IL crystals, if any, are practically absent for PVOH-rich mixtures (up to 40% by mass of IL). IL crystals would lead to very strong diffraction peaks due to their electronrich structure, since the electron density difference provides the



Figure 4. FT-IR spectra of hydroxyl vibration region. Samples were aged for 1 month at room temperature under vacuum.



Figure 5. Tensile properties of the mixtures of IL and PVOH. (a) Representative stress—strain curves from uniaxial tension tests. Inset is for small strain region. Samples were aged at room temperature under vacuum for 2 weeks. Extensibility of IL—PVOH mixtures is often governed by defects in film samples and cannot be interpreted as a true material property. (b) Young's modulus as a function of IL content in the mixture. Samples were aged at room temperature under vacuum for predetermined time period as noted in the legend. The modulus was calculated from the slope of the stress—strain curve in the small strain (less than 2% of strain) region that exhibits linear response. The error bars represent one standard deviation of the data, which is taken as the uncertainty of the measurement.



Figure 6. Representative stress—strain response for selected mixtures of IL and PVOH with different aging time. Samples were aged at room temperature under vacuum. (a) IL/PVOH = 1/9 mixture by mass. (b) IL/PVOH = 3/7 mixture by mass. (c) IL/PVOH = 5/5 mixture by mass. (d) IL/PVOH = 7/3 mixture by mass.

contrast for X-ray scattering. The absence of such peaks in the mixture suggests that IL cannot crystallize itself readily in the PVOH-rich mixtures and the interaction between PVOH and IL does not yield new crystals of well-defined size and structure, either. Instead, it is likely that IL is almost completely miscible with PVOH, causing changes in the amorphous structure of the mixture. While the ordered segments in the amorphous phase of neat PVOH could be established mainly by hydrogen-bonding between chains as well as the nonbonding (van der Waals) interactions between hydrogen-bonded chains,²⁶ incorporation of IL into PVOH is likely to generate an additional interaction between IL and PVOH, possibly forming IL—PVOH complex dispersed throughout the amorphous phase of the mixture that could act as physical junctions.

WAXS patterns for IL-rich mixtures are noticeably different from PVOH-rich mixtures (Figure 3b). As the IL content increases, the contribution from the IL on the diffraction pattern becomes more evident while the influence from the PVOH becomes less, as expected. The 1-D scattering profile of PVOH mixed with 50% by mass of IL still exhibits the amorphous halo as well as the crystalline diffraction peak from PVOH overlapped with a few additional diffraction peaks from IL crystals, indicating that IL that is not closely associated with PVOH chains begins to precipitate in the amorphous phase of the mixture and form its own crystals. At higher content of IL, characteristic diffraction peaks from IL crystals appear more clearly in the scattering profiles of the mixtures. However, q values of some peaks in the mixture do not match exactly to those in the neat IL, indicating that some of the solid-state structure of the IL is destroyed and/ or new ordered structures are formed. It is also evident that diffraction peaks for IL-rich mixtures show broader width compared to those for neat IL, indicating higher heterogeneity in crystal size for the mixtures. It appears that IL is completely miscible with amorphous phase of PVOH up to ca. 40% by mass of IL while further increase in IL content leads to a formation of small crystallites with a broad size distribution. It should be noted that the expected melting peak from small crystallites of IL in ILrich mixtures in DSC thermogram is likely to be overshadowed by a huge, broad melting peak of the aged mixtures (Figure 2d).

Chemical interaction between the IL and PVOH was investigated by FT-IR. The IR peak associated with hydroxyl (O–H) stretching vibration shifts to higher wavenumber as IL content increases (Figure 4). According to the energy potentials, the wavenumber (or frequency) at which broad O–H stretching vibration occurs increases as the O–H bond strength increases.^{30,31} From this viewpoint, the O–H bond in PVOH becomes stronger as IL is added. The change in O–H bond strength of PVOH in the presence of IL suggests that IL interacts with the hydroxyl group of PVOH, forming IL–PVOH complex.³² The resulting IL–PVOH complex is likely to exist as aggregates with low degree of order, considering the asymmetric, bulky structure of the IL.

Mechanical properties of the mixtures were investigated by uniaxial tension tests together with loading/unloading tests. As the IL content in the mixture increases, the stiffness (modulus) of the material decreases sharply while the extensibility (elongation



Figure 7. Loading/unloading cyclic test results for selected mixtures of IL and PVOH. Samples were aged at room temperature under vacuum for 1 month. (a-c) Stress-strain response. Strain ($\Delta L/L_0$) is defined as the ratio of the change in length (ΔL) to the initial length (L_0) of the film sample. (d-f) elastic strains (ε_e) and plastic strains (ε_p) as decomposed from the total true strains (ε_t). True strain is defined as a differential form (d $\varepsilon_t = dL/L$) in terms of specimen length (L).

at break) increases significantly with no yield point, exhibiting rubber-like elasticity (Figure 5). It should be noted that the extensibility is often governed by defects in the film samples and cannot be regarded as a true material property. However, most of the mixtures containing more than 20% by mass of IL showed higher than 300% of elongation at break while neat PVOH failed at the early stage of deformation (ca. 10% of elongation). Because of the good miscibility between PVOH and IL as inferred from the X-ray scattering results at low to moderate concentrations of IL in the mixture, IL acts as an efficient plasticizer. Young's modulus changes by 3 orders of magnitude over the range of IL concentrations (Figure Sb). The soft, elastic properties of the mixtures imply that IL has dual functionalities: one as a plasticizer through good miscibility and the other as a physical junction promoter through specific interaction with PVOH. Unlike the PVOH hydrogels, which exhibit stress-whitening caused by phase separation under tension due to the squeezing of water molecules from the gels and associated strain-induced crystallization of the PVOH,⁶ mixtures of IL and PVOH do not show stress-whitening up to 300% strain. This result suggests that IL forms more uniformly distributed junctions than PVOH hydrogels and is not expelled from the gels easily.

Effect of aging at room temperature on tensile properties is shown in Figure 6. While the stiffness of PVOH hydrogel slowly increases as the hydrogel undergoes phase separation driven by slow but gradual crystallization of PVOH,⁴ aging effect of IL-PVOH mixtures on the mechanical properties seems to be affected by the mobility of the system characterized by $T_{\rm g}$. As the IL content in the mixture increases, T_{g} decreases and the aging process is facilitated by the enhanced mobility. Although DSC results suggest increasing overall crystallinity for IL-rich mixtures as aging time increases (as estimated by the area under the endothermic peak in Figure 2, parts a, c, and d), stiffness of those mixtures does not increase much while extensibility shows an increasing trend. Although the reason for this apparently contradictory observation is not clear, it is likely that the increasing overall crystallinity is mainly due to the increasing number of physical junctions instead of PVOH crystallization. Those physical junctions are probably too weak to increase the stiffness of the IL-PVOH mixtures, but the increased number of such junctions would be effective to hold the polymer chains together and the extensibility would increase as a result. This observation is in contrast to chemically cross-linked polymers, in which the stiffness of the materials increases as the molecular



Figure 8. Schematic description of the PVOH mixed with the IL. Physical cross-links are represented by the crystalline phase of the PVOH as well as the IL–PVOH complex composed of a great number of individual IL–PVOH interactions.

Table 1. Properties of the IL-PVOH Mixtures^a

mass between cross-links decreases. Apparently IL's role as a plasticizer dominates the stiffness of the material while the increasing number of physical junctions contributes to the enhanced extensibility.

The elastic recovery properties were evaluated by decomposing the total strain into plastic strain and elastic strain from the loading/unloading test.⁶ The free-standing film was subject to uniaxial tension with a constant crosshead speed of 10 mm/min until a predetermined strain was achieved, followed by an instant invert of the crosshead movement to contract the sample until a stress of zero was achieved. The unrecovered strain at zero stress was assigned as the plastic strain, $\varepsilon_{\rm p}$, and the difference between the total strain and the plastic strain was assigned as the elastic strain, ε_{e} . True strain (ε_{t}) was used as the total strain to compare our result with that of PVOH swollen by water in the literature.⁶ Figure 7 shows that elastic strain is dominant at low strain levels while plastic strain eventually becomes larger than elastic strain at high strain levels. The intersection point shifts to higher strain as the IL content increases, indicating the elasticity increases as the IL content increases. Unlike PVOH hydrogels which show constant elastic strain after the onset of strain induced hardening,⁶ mixtures of IL and PVOH do not show noticeable strain hardening and the elastic strain keeps increasing within the strain range in our experiment. According to Miyazaki et al,⁶ strain-induced crystallization in PVOH hydrogels occurs in the interfibrillar extended amorphous regions. Although IL-PVOH mixtures are expected to be similar to PVOH hydrogels except that water is replaced with IL, the absence of strain hardening in IL-PVOH mixtures indicates that the amorphous phase formed by the interaction between IL and PVOH could be fundamentally different from that of PVOH swollen by water.

On the basis of the aggregated results of DSC, FT-IR, WAXS and mechanical properties, we propose a schematic description of the PVOH mixed with the IL as shown in Figure 8. Both the crystalline regime of the PVOH and the group of IL—PVOH complex in the amorphous phase represent physical junctions. It should be noted that a large number of IL—PVOH complex would be required to form a stable physical junction due to the weak interaction strength of the individual pair. PVOH chains in the amorphous phase form homogeneous mixture with the IL,

properties	aging time	PVOH	IL/PVOH (1/9)	IL/PVOH (2/8)	IL/PVOH (3/7)	IL/PVOH (4/6)	IL/PVOH (5/5)	IL/PVOH (6/4)	IL/PVOH (7/3)
modulus (MPa)	1 week	4012 ± 128.5	3578 ± 207.2	1938 ± 371.3	48 ± 7.0	32 ± 5.1	19 ± 5.5	14 ± 0.9	4 ± 1.0
	2 weeks	4231 ± 167.2	3710 ± 107.3	161 ± 20.1	59 ± 4.3	36 ± 5.1	26 ± 4.5	15 ± 1.6	5 ± 0.7
	1 month	4190 ± 306.8	160 ± 52.8	66 ± 5.6	50 ± 3.7	32 ± 5.2	25 ± 5.5	15 ± 1.4	7 ± 1.0
$T_{\rm m}$ (°C)	as-cast	224	215	192	185	163	166	133	123
	1 week	220	213	190 48	181 56	159 60	164 55	134 60	124 60
	1 month	224	217	201 85	183 121	186 147	144	133	140
$T_{\rm g}$ (°C)	as-cast (heating)	82	62	36	28	0	9	-21	-59
	as-cast (cooling)	68	55	29	20	-9	2	-30	N/A
$T_{\rm c}$ (°C)	as-cast	199	192	164	150	121	124	66	63
d-spacing in amorphous	1 month	0.443	0.417	0.414	0.407	0.403	0.382	N/A	N/A
phase (nm)									
d-spacing in crystalline	1 month	0.452	0.453	0.453	0.452	0.452	0.453	N/A	N/A
phase (nm)									

^{*a*} Uncertainty of the modulus corresponds to one standard deviation of the data collected from 3 replicates of samples.

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thereby being plasticized efficiently. Table 1 summarizes the properties of the PVOH mixed with the IL.

CONCLUSIONS

Binary mixtures of poly(vinyl alcohol) (PVOH) and highmelting ionic liquid (IL), 1-ethylpyridinium bromide, were prepared using water as a cosolvent. After removal of water, the resulting binary mixtures form soft elastic materials akin to PVOH hydrogels. While neat PVOH is relatively stiff and breaks at small strain, incorporation of IL into PVOH lowers the stiffness dramatically and enhances the extensibility significantly. Both the melting temperature and glass transition temperature of the fresh samples decrease noticeably as the IL content in the mixture increases, indicating that the IL is an efficient plasticizer for PVOH. Aged samples show a secondary endothermic peak at almost constant temperature independent of the composition, indicating the formation of IL-PVOH complexes. Those IL-PVOH complexes, together with PVOH crystals, are expected to act as physical junctions that prevent viscous flow upon deformation, thus promoting an elastic response. WAXS results indicate that the introduction of IL into PVOH affects the amorphous phase of the mixtures, possibly by forming an IL-PVOH complex. FT-IR results show that the inherent hydrogen bonding in PVOH is at least partly replaced with the interaction between IL and PVOH to form junction domains. Although the chosen IL is apparently a good solvent for PVOH, the resulting mixtures form soft elastomers instead of polymer solutions at room temperature due to the high melting temperature of the IL and the propensity to form specific interactions between IL and the hydroxyl group of PVOH. The dual functionality of the IL (good solvent and physical junction promoter) changes the structure of PVOH dramatically by forming junction domains that tie the PVOH chains in the amorphous phase swollen by the IL molecules, leading to a network structure similar to physical gels. These observations suggest that mixtures of polar polymers and compatible high-melting ionic liquids could provide a simple method to prepare thermoplastic elastomers with widely tunable thermal and mechanical properties.

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DISCLOSURE

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