

Mechanical Property and Swelling Behavior of Semi-Interpenetrating Polymer Networks Based on Polyvinyl Alcohol and Polyurethane

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Received 20 March 1997; accepted 29 May 1997

ABSTRACT: We have studied the mechanical property and swelling behavior of semi-interpenetrating polymer networks (semi-IPNs) of poly(vinyl alcohol) (PVA) and polyurethane (PU) with reactive groups under different experimental conditions. Tensile strength and elongation of these semi-IPNs are strongly dependent on the composition of IPNs and degree of PU crosslinking. It is clear that the composition of PVA and PU forms different IPNs morphology, which would determine the final mechanical property. The experimental results also demonstrate that the degree of crosslinking, which is controlled by heat treating temperature time, and amount of reactive groups, affects the swelling behavior of IPNs. With a change in the degree of crosslinking, the degree of swelling of IPNs is also different. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 473–479, 1998

Key words: swelling; semi-IPNs; aqueous polyurethane; poly(vinyl alcohol)

INTRODUCTION

Interpenetrating polymer networks (IPNs) are one of the types of polymer composite materials that combine the properties of the component-forming networks.¹ We synthesized and characterized aqueous polyurethane (APU),^{2–4} which can be mixed with aqueous poly(vinyl alcohol) (PVA) to form aqueous mixtures of APU and PVA. One of synthesized APUs contains epichlorohydrin (ECH) and diethylenetriamine (DTA), which supply the APU molecule chloromethyl and amino groups; when heated, these groups can react each other, and then extended molecular weight of polyurethane can be produced. Upon

heating mixtures of PU and PVA, the PU component of mixture will form the crosslinking networks; and PVA can easily crystallize to form physical crosslinking points, and then semi-IPNs are obtained. These semi-IPNs materials can be used for producing the hydrophilic polymer films with good toughness, which are important in the fields of membrane separation and adsorption. PVA component of mixture possesses strong hydrophilicity and APU supply semi-IPNs excellent toughness. This article focuses on the mechanical property and swelling behavior of semi-IPNs of PU and PVA.

EXPERIMENTAL

Methyl ethyl ketone (MEK), polypropylene glycol (PPG), epichlorohydrin (ECH), diethylenetriamine

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Journal of Applied Polymer Science, Vol. 67, 473–479 (1998)
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(DTA), and tolylene diisocyanate (TDI) were commercial pure reagents. Polyvinyl alcohol (PVA, 88% hydrolyzed) was purchased in industrial products. Aqueous polyurethane was synthesized as the method² in this laboratory. For future reference, PU means aqueous polyurethane in this article.

The structure of IPNs was determined by infrared (IR) spectra on a SDX-type (Nicolet, U.S.A.).⁵ The swelling behavior of IPNs was investigated on a auto-detector of swelling behavior,⁶ which was made in Department of Chemistry, Nankai University, People's Republic of China. (PRC) Aqueous PVA and PU were mixed to obtain the mixtures, then the films were placed in a vacuum oven of 10^5 Pa at 40°C for another week to completely remove the water. Careful effort to dry the films under 40°C to must be made to avoid crosslinking. Tensile samples were prepared from the casting films to cut into rectangle shape (60

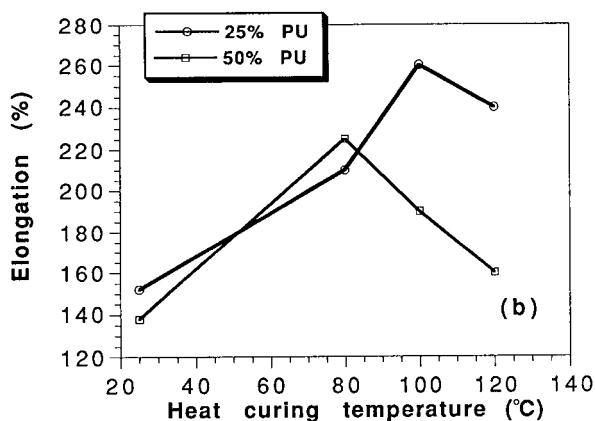
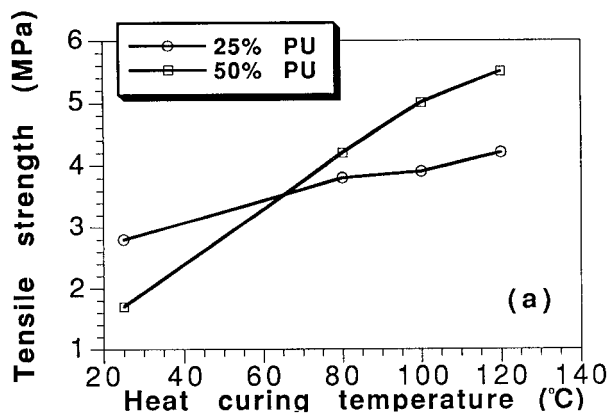


Figure 1 Tensile strength (a) and elongation (b) of IPNs with 25% and 50% PU versus heat curing temperature when holding the heat curing time at 20 min.

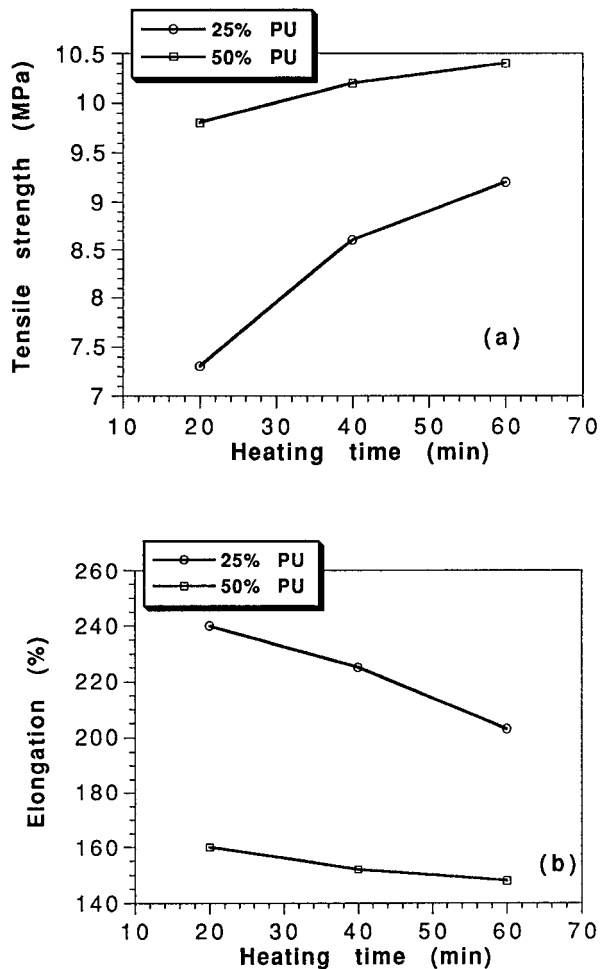


Figure 2 Tensile strength (a) and elongation (b) of IPNs with 25% and 50% PU versus heat curing time holding heat curing temperature at 120°C.

$\times 6 \times 1$ mm). Stress-strain measurements were performed on a tensile tester at a crosshead speed 1 cm min and 23°C (WD-1, PRC).

RESULTS AND DISCUSSION

As mentioned above, synthesized polyurethane contain chloromethyl groups and amino groups. When heated, they will react with each other to produce a crosslinking PU, which will supply IPNs materials with good toughness. If different composite IPNs of PVA and PU are obtained, these materials will present good hydrophilicity, toughness, and mechanical properties. From Figure 1, the tensile strength of IPNs of both 25% and 50% PU content increases with the heat curing

temperature when holding the heat curing at a constant time of 20 min. This can be easily understood when the heat curing time holds a constant value: the higher the heat curing temperature, the higher the reactivity between amino groups and chloromethyl groups; and, of course, the degree of crosslinking increases with increasing heat curing temperature, which will make tensile strength higher. We can also find that the tensile strength of IPNs containing 25% PU is higher than that of IPNs containing 50% PU under room temperature. We may expect that prepolyure-

thane is only a kind of oligomers. If amino and chloromethyl groups don't react at room temperature to extend molecular weight, more oligomers would initiate the cracks significantly. However, when the prepolyurethane oligomer content is higher, the more pre-polyurethane oligomers join the reacting procedure between chloromethyl groups and the amino groups with increasing temperature and then produce the crosslinking polyurethane. Higher tensile strength can be obtained in the 50% PU system, so a crossing point appears; above this temperature, the strength of 50% PU

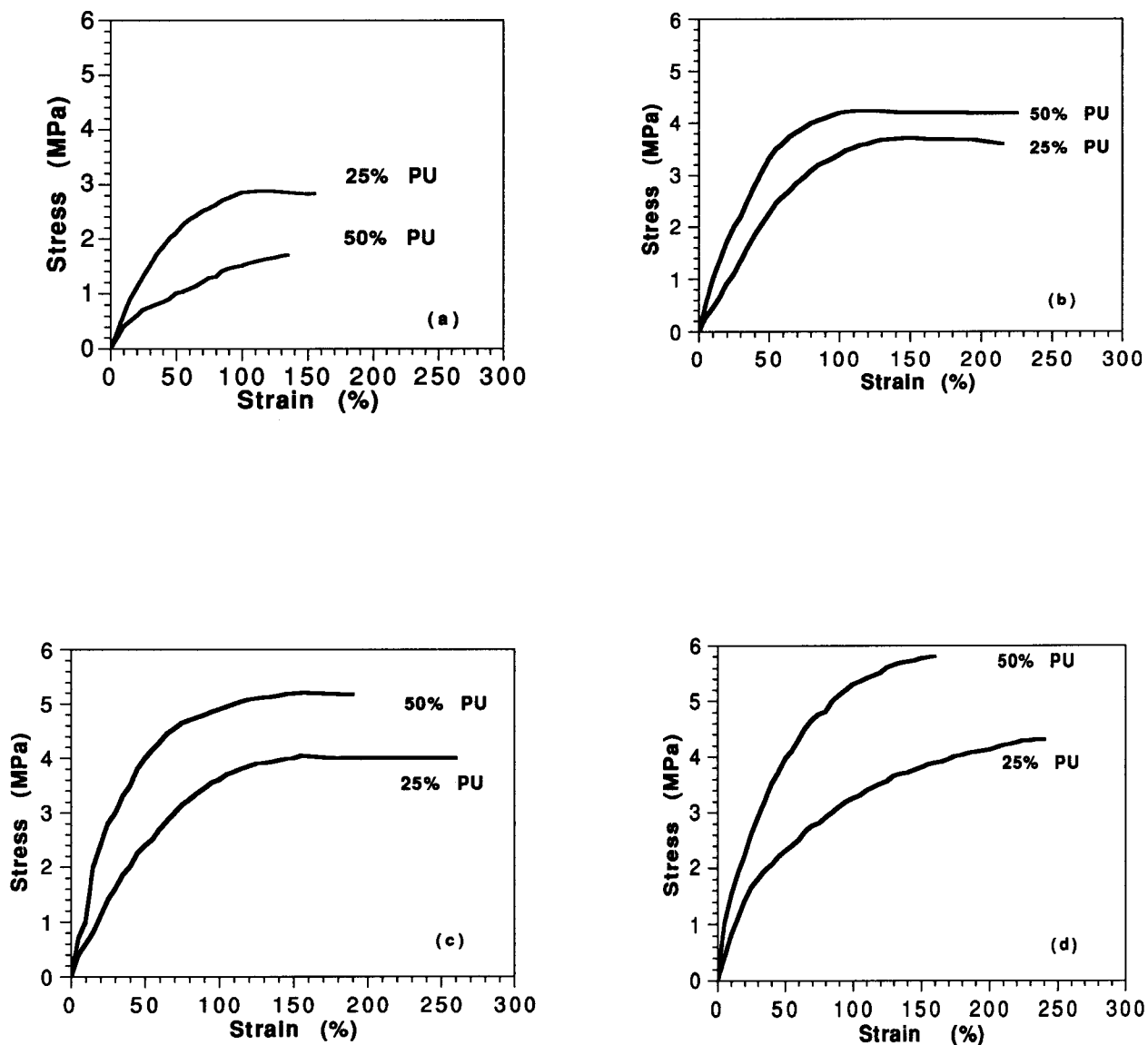


Figure 3 Stress-strain curves of IPNs with different PU content. The tensile samples were treated under (a) 120°C when holding the heat curing time at 20 min.

IPNs material is higher than the 25% PU system's. Theoretically, the crosslinking reaction in PU will occur when temperature is above 50°C. The same explanation can be used in elongation behavior of IPNs. The elongation of IPNs containing 25% PU is higher than that of IPNs containing 50% PU at room temperature because more ends of low-molecular-weight PU will make films of IPNs break much easier.⁷⁻⁸ Again, when heating IPNs films, the elongation of 50% PU films increases quickly and then becomes higher than 25% PU's. However, the maximum elongation values of both 25% and 50% PU films occur when the heat curing temperatures are about 80°C for 50% PU and 100°C for 25% PU. It may be explained by an increase in the degree of crosslinking of PU with temperature. When the crosslinking degree reaches a proper value, at which crosslinked PU presents good rubbery property, if the crosslinking degree increases continually, much higher crosslinking degree will make PU lose the rubbery property. Because 25% PU IPNs contain less reactive groups than 50% PU IPN's, the maximum elongation appears at higher heat curing temperature comparably. The same case occurred in the pure IPNs films.²

As shown in Figure 2, the mechanical properties of IPNs vary with the heat curing time when the heat curing temperature holds as a constant value (120°C). It is similar to the results of Figure 1. The tensile strength of IPNs increase with the heat curing time presenting the degree of crosslinking. Figure 1 indicates that the PVA component takes a main role in tensile strength as the matrix of film where PU exists in that as the oligo-

mer at room temperature. With an increase in the degree of crosslinking with temperature, PU shows a more and more important role in increasing tensile strength. Meanwhile, the elongation of IPNs decreases with heat curing time. The explanation is the same as that in above section.

Figure 3 shows stress-strain curves of IPNs films with different PU content and crosslinking degree. Obviously, higher PU contents and proper crosslinking degree of PU can improve the toughness of IPNs, which is donated mainly by crosslinking PU. It is clear that when prepolyurethane oligomers do not react to form crosslinking PU, these oligomers contain many ends of molecules and reduce both the tensile strength and elongation. One can control the heat curing temperature or time and composition of IPNs to obtain better mechanical property and toughness. With a practical point of view, a better way should be to find the suitable pre-polyurethane's molecular weight supplying soft phase and the reactive group content supplying the degree of crosslinking.

Semi-IPNs of PVA and PU swell strongly in water because PVA is a hydrophilic material. Their swelling behavior is dependent on the composition and the degree of crosslinking of IPNs. An accurate testing method of swelling property for crosslinking materials had been described elsewhere⁶ and was employed to detect the swelling and crosslinking behavior of semi-IPNs of PVA and PU. The details about the work mechanism of the auto-detector of swelling behavior is explained clearly in other articles.⁹⁻¹⁰ The simple principle is schematic in Figure 4.

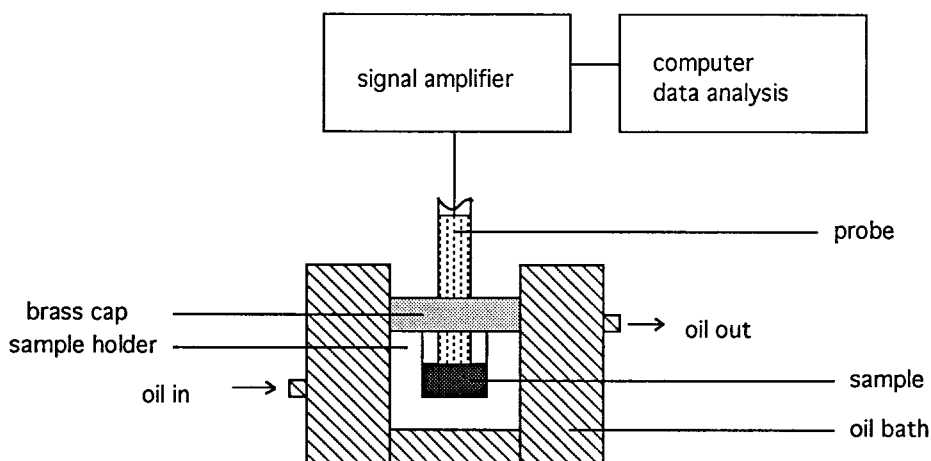


Figure 4 Scheme of the auto-detector of swelling behavior.

This machine can easily detect the swelling behavior of different structures (linear, grafting, or crosslinking). When detected materials are linear polymers, their dissolving rate is fast; the grafting polymer's dissolving rate is slower than linear polymer's. Dissolving can not be found for crosslinking polymers, but swelling behavior is clearly different with the degree of crosslinking. Thus, we can use a probe touching on the detected film surface to determine the polymer dissolving procedure. When detected polymers dissolve or swell, the probe can tell how the swelling stress (F) changes with the swelling procedure, which increases the stress, and the dissolving procedure, which will show a stress reduction. In general, the bigger the F is, the

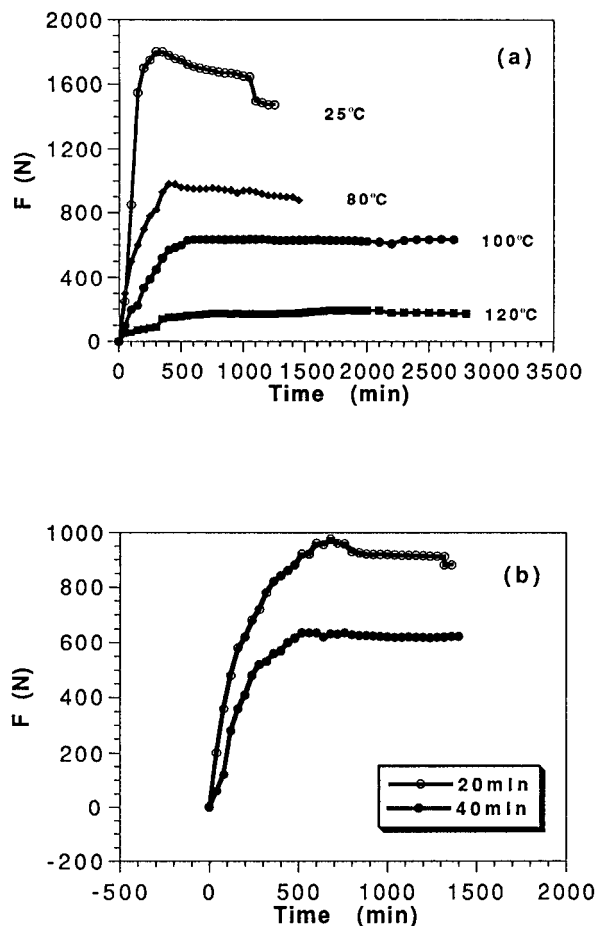


Figure 5 Swelling curves of PU films in water: PU films were prepared under (a) different heat curing temperatures and a holding time of 20 min; (b) different times holding when the temperature at 120°C.

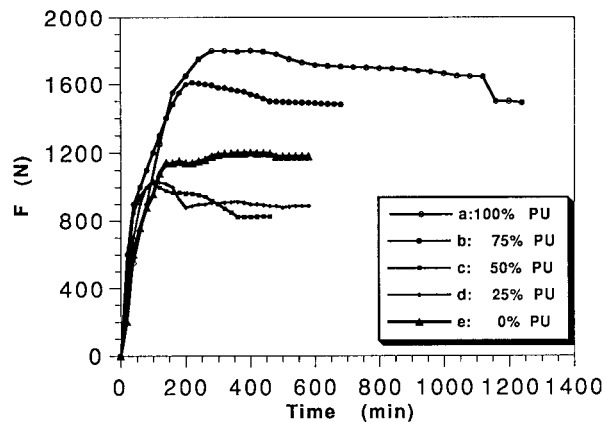


Figure 6 Swelling curves of blends with different composition of PU and PVA in water under room temperature.

easier the swelling of IPNs is. According to this rule, we can figure the structure changing of polymer chains with dissolving or swelling procedure. Figure 5 shows the swelling behavior of PU under different heat curing temperatures. Stress value (F), which was investigated on the swelling surface of IPNs by a detector, varied with heat curing temperature. When PU exists in oligomer, water can easily penetrate into PU matrix to make it swell; then PU dissolves and forms solution so that F reduces after F reaches a maximum value generated due to the swelling. A stress reduction (FD) can be observed from the swelling curve, such as curve 25°C in Figure 5. The FD gradually disappears with increasing heat curing temperature. This means that the degree of crosslinking increases with an increase in the heat curing temperature. When the heat curing temperature is higher than 100°C, no FD is found. It indicates that the crosslinking reaction is completed and that a high crosslinking degree makes swelling behavior different. The same reason can be used to explain the swelling behavior of PU under different heat curing times. With an increase in the heat curing time, F decreases. This shows that more amino groups and chloromethyl groups take part in reaction of crosslinking and that dissolving is impossible because of the high degree of crosslinking.

For blends of PU and PVA, we can investigate the swelling behavior of each component to figure their morphologies. As shown in Figure 6(a), pure PU takes about 280 min to reach maximum

F and then goes down gradually. This means that some of the PU start to dissolve slightly (usually, the PU is a kind of polymer that dislikes water, but the PU studied in this article contains many hydrophilic groups; the molecular weight is small before heated, so it can dissolve in water, and forms a transparency aqueous solution). However, adding some of the PVA to PU shown in Figure 6(b)–(d) has this time significantly shortened. It can also be clearly observed that a FD appears when swelling time is 220, 100, and 100 min for (b), (c), and (d), respectively. No FD appears for pure PVA. We can conclude from these results that the composition will influence strongly the swelling behavior of blends of PU and PVA. Actually, the morphologies and intermolecular interaction of blends determine the swelling procedure of blends. From the micrographic pictures, Fourier transform infrared (FTIR) and dynamic mechanical analysis (DMA) spectra,⁵ we know that PU and PVA blends usually generate the molecular interaction; but they cannot form completely miscible blends, and the phase separation still exists. Especially, when the blend film is immersed in the water, both PU and PVA can form strong hydrogen bonds with water, which will weak the interaction between PU and PVA so that water molecules can penetrate into blends easily. The result is that blends swell and even dissolve easier than both of two pure components do. PVA is one of crystalline polymers; it is hard to dissolve in water under room temperature, and no FD appearing due to dissolving of materials can be observed after the maximum F appearing when materials swell. When the compositions of

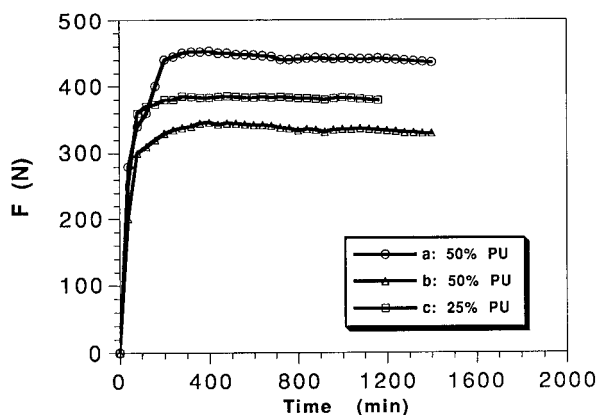


Figure 7 Swelling curves of semi-IPNs under room temperature. Samples were prepared under 120°C and 40 min for (b) and (c) and 120°C, 20 min for (a).

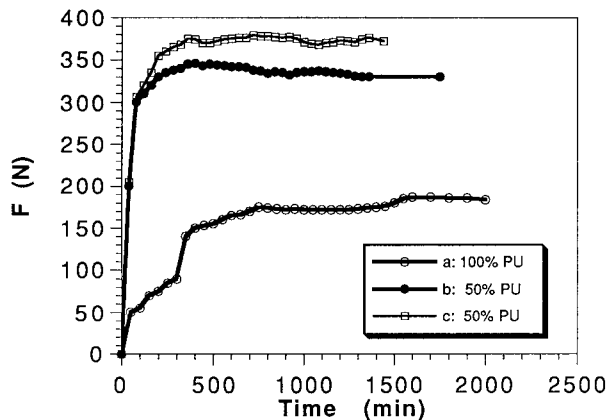


Figure 8 Swelling curves of semi-IPNs at room temperature (a) and (b) and 80°C (c). Samples were prepared under 120°C and 40 min for (a) and (b) and 120°C and 20 min for (a).

blends are 50% and 25% PU (wt %), respectively, the FDs appear so clearly. This means that the blends begin to dissolve quickly. That reason that the values of F of 50% and 25% PU films decrease significantly is because the dissolving of PU begins fast. It is interesting to see when F decreases with swelling time and then reaches a constant value. As mentioned above, PVA cannot dissolve in water under room temperature. Now we can figure out that when the PU in the blends dissolves with swelling time and is finally depleted, the PVA still keep swelling state; this is the reason why F will have a constant value after a reduction. The explanation can also be demonstrated from the results of IPNs swelling curves of crosslinking PU and PVA.

After heated, the composite of PU and PVA becomes the semi-IPNs because of the crosslinking of PU and the crystalline of PVA. Their swelling curves are similar to those before PU crosslinking, but no FD appears for all three curves. As shown in Figure 7(a) and (b), with an increase in the degree of crosslinking of PU, the F value decreases because it is difficult to swell for a high degree of crosslinking PU. When we change the composition of IPNs, the F increases with the PVA content from 50 to 75% [Fig. 7(b) and (c)]; although FD still cannot be seen, the explanation is that the high hydrophilicity of PVA makes the system swell easier. Figure 8 demonstrates this results further: when holding the content of PVA constant, F increases with temperature from room temperature to 80°C. When 50% PU reacts under

120°C and 40 min, we can neglect the effect of reactive temperature on the swelling of crosslinking.

CONCLUSION

Mixing aqueous PU and PVA makes it easy and possible to prepare the mixtures of PU and PVA to form the semi-IPNs, which are usually difficult to make because no cosolvents can be found, and PVA cannot be molten. A new method is used to determine the semi-IPNs swelling behavior and figure their structure. We find that PU improves the toughness of PVA, and PVA supplies systems good hydrophilicity when the experimental temperature increases. Diffusion behavior of water in semi-IPNs is changed due to forming different morphologies of IPNs. The mechanical properties of semi-IPNs can be improved by increasing the degree of crosslinking of PU.

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