

# Binary Blends Based on Poly(*N*-isopropylacrylamide): Miscibility Studies with PVA, PVP, and PAA

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Received 8 October 2002; accepted 26 September 2003

**ABSTRACT:** Blends of poly(vinyl alcohol) (PVA), poly(acrylic acid), (PAA), and poly(vinyl pyrrolidone) (PVP), with poly(*N*-isopropylacrylamide) (PNIPAM), were prepared by casting from aqueous solutions. Mechanical properties of PNIPAM/PVA blends were analyzed by stress-strain tests. Differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) were employed to analyze the miscibility between the polymeric pairs. The results revealed that PNIPAM is not miscible with PVA and

PVP in the whole range of composition. On the other hand, PNIPAM interacts strongly with PAA forming interpolymer complex due to the formation of cooperative hydrogen bonds. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 743–748, 2004

**Key words:** poly(*N*-isopropylacrylamide); poly(vinyl alcohol); poly(acrylic acid); poly(vinyl pyrrolidone); miscibility; blends

## INTRODUCTION

In past decades, blends have been intensively investigated mainly to satisfy the need of specific sectors of the polymer industry.<sup>1,2</sup> Frequently, polymer blends show superior performance in relation to the individual components and, consequently, the range of applications grows continuously for this class of materials.

An important factor in the development of new materials based on polymeric blends is the miscibility between the polymers in the mixture.<sup>3</sup> The degree of miscibility is directly related to the final properties of polymeric blends. However, from a thermodynamic point of view, miscibility is known to be a rare phenomenon occurring when the constituents present functional groups capable of forming strong interactions. On the other hand, from a technological stance, it is sufficient for a blend to behave as a single phase material. In this case, the material is categorized as “compatible” and a certain degree of compatibility is indispensable for practical purposes.

Actually, many studies have been focused on “smart” or “intelligent” polymers. These are stimuli-responsive materials with the ability to change drastically some properties in water solution even at small changes in environmental conditions such as temper-

ature, pH, magnetic field strength, etc.<sup>4–9</sup> Poly(*N*-isopropylacrylamide) (PNIPAM) is a thermoresponsive polymer, i.e., it dissolves in water at room temperature but undergoes a phase separation when heated at about 32°C, exhibiting a lower critical solution temperature (LCST).<sup>10,11</sup> This property has attracted great interest and numerous investigations have been reported on the thermosensitive swelling behavior of PNIPAM in fields such as drug delivery,<sup>5,12</sup> regulation of enzyme activity,<sup>13</sup> mass separation,<sup>7,14–18</sup> artificial muscles,<sup>19,20</sup> etc.

The properties of the solid PNIPAM have received little attention since most of the applications of polyacrylamides are based on their behavior in aqueous solution.<sup>21,22</sup> However, PNIPAM shows great potential in the preparation of miscible blends because it contains a proton-acceptor moiety (amide) and can interact with polymers containing proton-donating units, such as carboxylic, phenolic, or alcoholic hydroxyl groups. Miscibility was observed with poly(*N,N*-dimethylacrylamide), another proton acceptor polymer, with poly(vinyl alcohol) (PVA)<sup>23</sup> and poly(2-hydroxypropyl methacrylate).<sup>24</sup> Ribeiro e Silva et al.,<sup>25</sup> by the measurement of the melting temperature depression, verified that poly(ethylene oxide) (PEO), a highly crystalline polymer, is miscible with PNIPAM and poly(*N-tert*-butylacrylamide). Staikos et al.<sup>26</sup> reported the formation of a very compact structure, frequently named “interpolymer complexes,” between PNIPAM and poly(acrylic acid) (PAA) in an aqueous acid conditions.

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In the present article, we relate the characterization state of miscibility in binary blends of PNIPAM with PVA, PAA, and PVP.

## EXPERIMENTAL

### Materials

PNIPAM was synthesized via free radical mechanism, under nitrogen atmosphere, according to the method described by Freitas.<sup>27</sup> The monomer (NIPAM, Aldrich) and the initiators (ammonium persulfate and sodium metabisulfite, Reagen), analytical grade, were used as received. PVA (Rhodia,  $M_w$  127,000 and 87.7% hydrolyzed), PAA (Aldrich,  $M_w$  450,000), and PVP (Merck,  $M_w$  25,000) were used without further purification.

### Casting blends

Aqueous solutions of the individual polymers (2%) were mixed to obtain the desired proportions and stirred for 30 min at room temperature. Homopolymers and blends films (PNIPAM/PVA, PNIPAM/PAA, and PNIPAM/PVP) were cast on petri dishes by water evaporation at 25°C. The films were stored in a desiccator.

### Mechanical tests

Stress–strain tests were performed on an INSTRON 5542 using a 5 N cell detector and a cross-head speed of 1 mm/min. The rectangular samples with dimensions at 30 mm × 1.5 mm × 40 μm were analyzed at room temperature.

### Thermal analysis

Differential scanning calorimetry (DSC) experiments were performed using Perkin–Elmer DSC 7 equipment. Samples at about 5 mg, aluminum pans, nitrogen flow, and a scan rate of 10°C/min were used. The results reported here correspond to the second heating scan.

### Morphological studies

Scanning electron microscopy (SEM) was carried out on a JEOL JSM-T300 (at 15 kV) or JEOL JSM-5600 (at 12 kV) using samples that were ripped at ambient temperature and sputter coated with gold.

## RESULTS AND DISCUSSION

### Preliminary observations

By casting from aqueous solutions, pure PNIPAM rendered slightly opaque and brittle films. PVA, PAA, and PVP gave transparent and colorless films, which are flexible in the case of PVA and brittle for PAA and PVP.

In general, blends of PNIPAM/PVA showed flexibility and transparency that are roughly a combination of those properties of the pure components, being more rigid the higher the content of PNIPAM is. The films of PNIPAM/PVP blends were brittle in all ranges of composition studied, while, for PNIPAM/PAA blends, no films were obtained due to the formation of an interpolymer complex that precipitates in aqueous solutions.

### PNIPAM/PVA blends

The results of the stress–strain measurements of PNIPAM/PVA blends are presented in Figure 1.

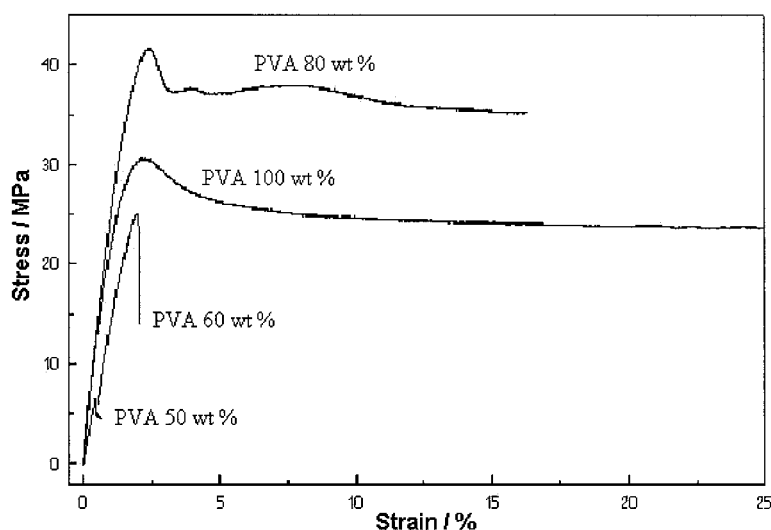


Figure 1 Stress–strain curves for PVA homopolymer and for PNIPAM/PVA blends.

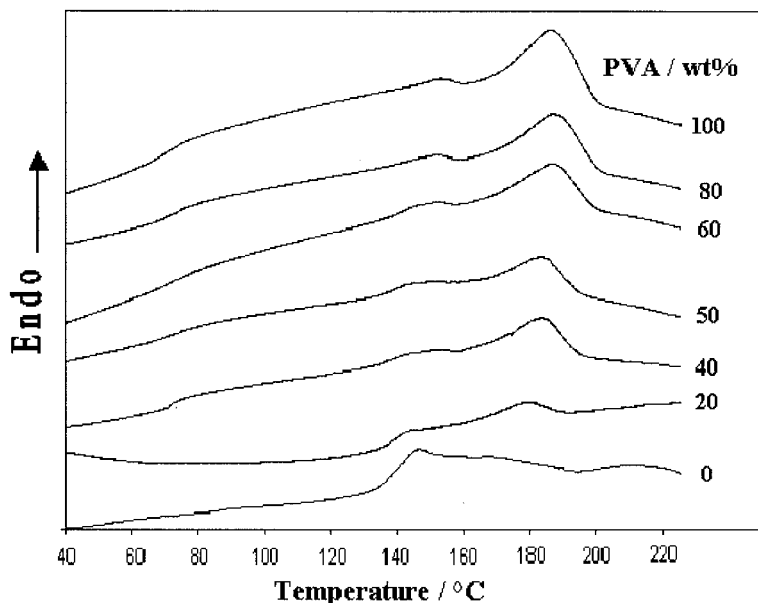


Figure 2 DSC curves for PNIPAM/PVA blends cast from aqueous solutions.

Pure PVA presents the typical behavior of plastic materials with a great elongation at break (ca. 120%, not completely shown in the figure). PNIPAM, on the other hand, is a very brittle material and it was not possible to measure its mechanical properties. For the blends, the incorporation of PNIPAM up to 20% made the films stronger, with an increase in the Young modulus and in the stress at yield, but with a considerably decrease in the elongation at break. With the increase in the PNIPAM concentration, the blends became more brittle, reflecting the PNIPAM behavior and reducing the plastic effect due to PVA.

In Figure 2 we present the DSC curves obtained for homopolymers and PNIPAM/PVA cast films. Here, we show the second heating scan for the samples with exactly the same thermal history. Glass transition temperatures ( $T_g$ ) and melting parameters (melting point,  $T_m$ , and heat of fusion,  $\Delta H_f$ ) are reported in Table I.

By analyzing the thermograms in Figure 2, we can see the  $T_g$  of PVA at 68.6°C and an endothermic peak at 186.7°C due to the melting of its crystalline phase. The area related to the melting peak is associated to the enthalpy of fusion ( $\Delta H_f$ ) of the crystalline region of PVA. For this polymer, with 12.3% of acetate groups, the degree of crystallinity is about 20%.<sup>28</sup> In the same figure it is possible to see the  $T_g$  of pure PNIPAM at 136.9°C.

It is well known that miscible blends show a single  $T_g$  intermediate to those of the pure components; for immiscible blends, however, the  $T_g$ s of each component are present. The calorimetric results presented in Figure 2 clearly show that the PNIPAM/PVA blends are immiscible in the amorphous regions. For all compositions tested, two distinct values of glass transition

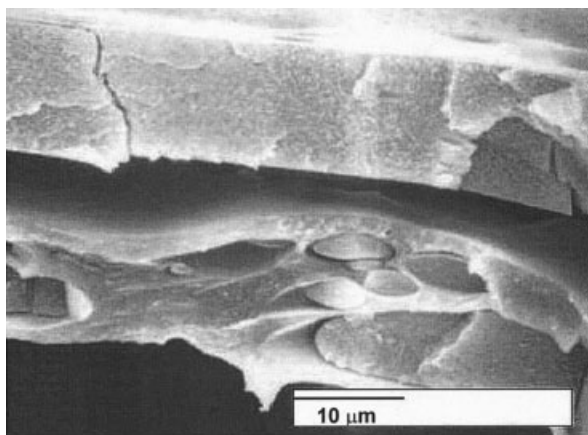
temperatures were observed ( $T_g^1$  and  $T_g^2$ ), each close to the  $T_g$  of the corresponding homopolymer. At a blend composition of 20 wt % in PVA it was difficult to detect the  $T_g$  of the semicrystalline polymer, although the melting endotherm of the crystalline region had been easily observed. The blends with high concentrations in PVA also exhibit exothermic peaks between the  $T_g$  and the  $T_m$ . This indicates that recrystallization occurs during the DSC experiments. For these blends, the cooling time was not sufficient to allow complete crystallization and, consequently, a recrystallization takes place during the second scan. For the blend at 80 wt % in PVA this thermal event seems to overlap the  $T_g$  of PNIPAM, which is not mentioned in Table I. All blends also show a single endothermic peak corresponding to the melting of the PVA crystalline phase, which is not depressed significantly by the PNIPAM incorporation, indicating that the homopolymers are not miscible in the molten state.

Other evidence for the immiscibility between PNIPAM and PVA is provided by SEM (Fig. 3). In all

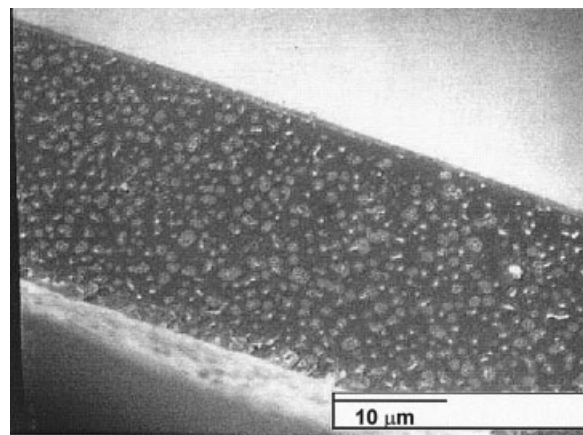
TABLE I  
DSC Results for PNIPAM/PVA Blends

PVA (wt %)	$T_g^1$ (°C)	$T_g^2$ (°C)	$T_m$ (°C)	$\Delta H_f$ (J/g)
100	68.6	—	186.7	31.8
80	71.5	—	187.5	33.0
60	72.4	139.3	187.2	36.2
50	72.2	138.1	183.7	30.5
40	71.7	137.9	183.5	40.5
20	—	138.7	179.5	29.2
0	—	136.9	—	—

$T_g^1$ , related to PVA;  $T_g^2$ , related to PNIPAM.



**Figure 3** SEM micrograph of fractured surface of PNIPAM/PVA 50/50 blend.



**Figure 5** SEM micrograph of fractured surface of PNIPAM/PVP 50/50 blend.

compositions studied here, we observed a significant phase separation due to the immiscibility among the constituents. The direct observation of two distinct layers for the blend at 50 wt % in PVA demonstrates, beyond the immiscibility, a high degree of incompatibility among PVA and PNIPAM. Although PNIPAM and PVA present, respectively, proton-accepting and proton-donating units, there are no effective interactions, probably due to the steric hindrance of the isopropyl groups that makes the contact between the amide and the alcoholic hydroxyl moieties difficult.

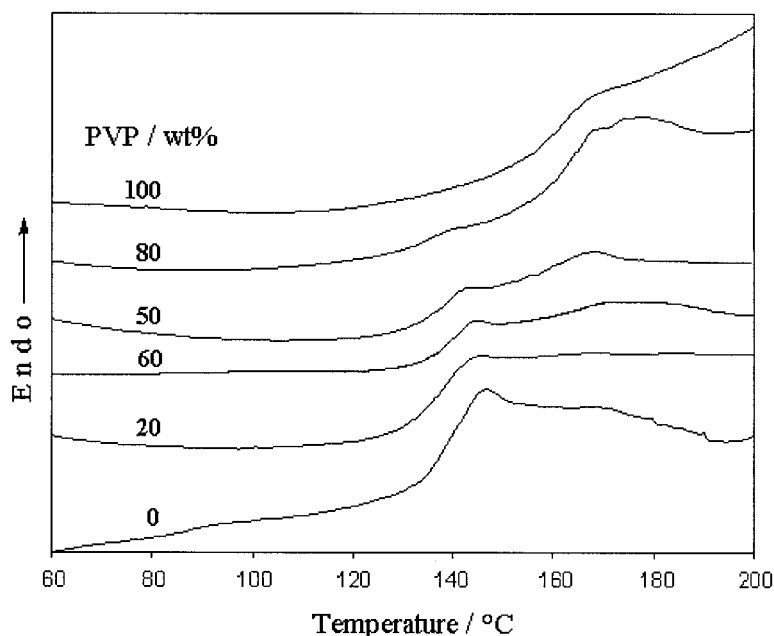
#### PNIPAM/PVP blends

Investigations into the miscibility of the PNIPAM/PVP blends using DSC and SEM showed that the

constituents are immiscible in the whole range of composition.

Although PVP and PNIPAM have polar side groups, with the possibility to interact through dipole-dipole attractions, in Figure 4 we can easily identify their  $T_g$ s as a result of phase separation. The values of the  $T_g$ s are independent of the composition and similar to those of the respective homopolymers.

By the morphological analysis performed through SEM (Fig. 5) it is possible to see two distinct phases constituted by the globular structures dispersed in a compact matrix. As reported for the PNIPAM/PVA blends, the immiscibility can be explained by the weak interactions among the polymers due to the spatial hindrance. As expected, hydrogen bonding does not take place in this system because PVP, as well as



**Figure 4** DSC curves for PNIPAM/PVP blends.

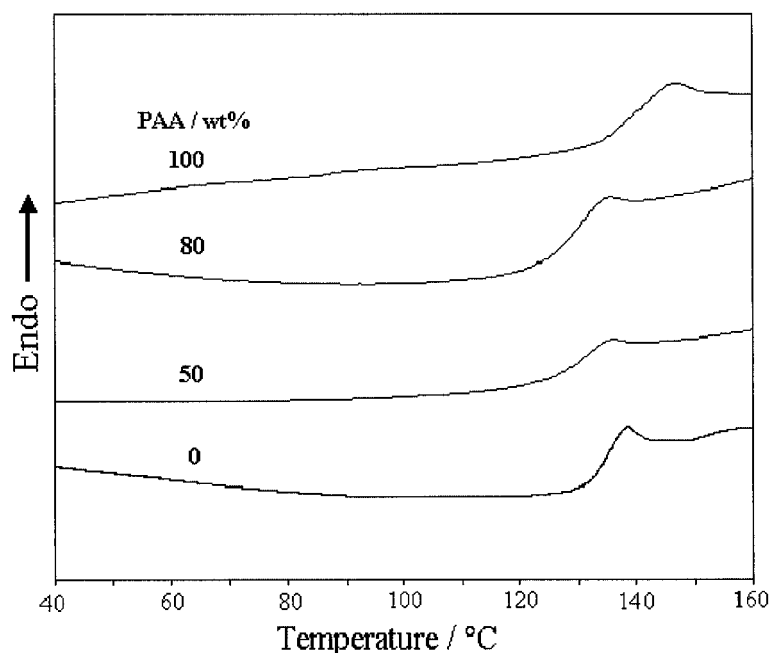


Figure 6 DSC curves for PNIPAM/PAA interpolymer complexes.

PNIPAM, is a Lewis base and acts as a proton acceptor.

#### PNIPAM/PAA complexes

PNIPAM forms strong and compact hydrogen-bonding interpolymer complexes (ICP) with PAA that precipitate at lower pH values.<sup>29</sup> Stoichiometric ICP stabilized by hydrogen bonds are the products of interaction between proton-donating, such as poly(carboxylic acids), and proton-accepting polymers in solutions. A great number of studies have been performed with PAA on the subject.<sup>26,30,31</sup> PNIPAM presents amide groups that are proton acceptor and interact with the carboxylic groups of PAA by the formation of hydrogen bonds. When the water solutions of PNIPAM and PAA are mixed, a complex is rapidly formed and precipitates in solution, making it impossible to obtain films. After they were dried, these complexes were analyzed by DSC and the results are presented in Figure 6, where we can observe only one  $T_g$  as a result of the effective interactions between the homopolymers. In the two compositions studied (50 and 80 wt % in PAA), the  $T_g$  of the blend is lower than the average  $T_g$  of the pure components. This negative deviation from additivity of the glass transition temperatures was also observed by Parada et al.<sup>23</sup> in blends composed by poly(vinyl acetate-co-vinyl alcohol) and poly(*N,N*-dimethylacrylamide) and they attributed this behavior to deviations with respect to free volume linearity in the blends. Changes in the free volume are related with specific interactions between chains: the free volume diminishes with increases in the specific interactions. For

the PNIPAM/PAA blends, the mobility of the chains decreases due to the presence of hydrogen bonds that act as crosslinks. To solve this problem, at present, we are studying the thermal properties and the miscibility of PNIPAM/PAA blends as a function of pH of the solution, aiming to avoid phase separation, which would allow us to prepare blends by casting.

#### CONCLUSION

By casting from water solutions we were able to prepare binary blends composed of PNIPAM/PVA and PNIPAM/PVP and ICPs between PNIPAM and PAA. By the stress-strain tests it was possible to observe that the mechanical behavior of the PNIPAM/PVA blends is strongly influenced by the PNIPAM content. Miscibility in these systems was studied by DSC and SEM and the results showed that PNIPAM/PVA and PNIPAM/PVP blends are immiscible in all compositions studied, reflecting the weak interactions among the polymeric pairs. This behavior can be explained by the steric effects of the isopropyl groups that make the contact between the polar side groups difficult. On the other hand, the interactions between PNIPAM and PAA are very strong, originating an interpolymer complex. In this case, the amide and the acid carboxylic groups form hydrogen bonds that are responsible for the stabilization of the stoichiometric interpolymer complexes.

Valdir Mano thanks Coordenadoria de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil) for awarding a research fellowship.



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