

# Temperature-sensitive smart polymer with self-controlled glass transition temperature

Naoya Tsugawa<sup>1,2</sup>, Panitha Phulkerd<sup>1</sup>, Ayumi Kiyama<sup>1</sup> and Masayuki Yamaguchi<sup>1\*</sup>

<sup>1</sup>School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

<sup>2</sup>TOSOH Analysis and Research Center Co., 1-8 Kasumi, Yokkaichi, Mie 510-8540, Japan

\*Corresponding author

DOI: 10.5185/amlett.2018.2128

www.vbripress.com/aml

## Abstract

We evaluated the effect of adding a small amount of poly(*N*-isopropylacrylamide) (PNIPAM), which is a temperature-sensitive polymer, on the glass transition temperature ( $T_g$ ) of poly(vinyl acetate) (PVAc). The  $T_g$  of a blend comprising 5wt.% PNIPAM was affected by the ambient temperature; the  $T_g$  was low when the blend was stored at low temperatures and high when it was stored at high temperatures. This phenomenon can be attributed to the hydrophilic–hydrophobic transition of the PNIPAM. At low temperatures, the moisture content of the blend increased, resulting in a low  $T_g$  because of the plasticizing effect of water molecules on the PVAc. Because the material becomes soft at low temperatures, this unique property can be exploited in the design of smart materials. Copyright © 2018 VBRI Press.

**Keywords:** Poly(*N*-isopropylacrylamide), poly(vinyl acetate), smart polymer, polymer blend.

## Introduction

One of the recent trends in polymer science is the development of smart materials. In general, a smart polymer material changes its properties according to the ambient conditions - including temperature, pH, electric/magnetic field, and mechanical response/damage - as if it has intelligence [1-6]. Among such polymers, poly(*N*-isopropylacrylamide) (PNIPAM) is known to undergo conformational change at specifically 32°C, as clarified by several pioneering studies [7-12]. Below that temperature, PNIPAM behaves as a hydrophilic material, and is therefore soluble in water. Above 32°C, it becomes hydrophobic owing to the coil-globule transition. This specific property of PNIPAM has been detected in various block copolymers with PNIPAM segments [13]. These block copolymers have various applications including cell culture membranes [14,15], drug delivery systems [16,17], and chromatograms [18]. However, to the best of our knowledge there have been no studies on the temperature sensitivity of polymer blends containing PNIPAM. Because the coil-globule transition of PNIPAM causes a marked change in many of its properties, interesting responses to temperature change are also expected even in blends containing it. We used poly(vinyl acetate) (PVAc) in the present study because the glass transition temperature ( $T_g$ ) of PVAc is closed to the coil-globule transition temperature of PNIPAM.

## Experimental

### Materials

We purchased PVAc and PNIPAM from Sigma-Aldrich Japan. The weight-average molecular weights were 100,000 for PVAc and 20,000–40,000 for PNIPAM.

The PVAc and PNIPAM were dissolved in a mixed solvent comprising dichloromethane and methanol in a 9:1 weight ratio, and stirred for 8 h. The solution was poured onto a poly(tetrafluoroethylene)-coated tray and dried at 25°C for 4 h under vacuum. The dried mixtures were compressed into flat 1-mm thick sheets using a compression-molding machine at 115°C for 3 min. The sheets were kept in a temperature- and humidity-controlled chamber at either 15°C and 50% relative humidity (RH) or 50°C and 50%RH for 3 days. The measurements were obtained immediately after this procedure.

### Measurements

The morphology was characterized using a scanning electron microscope (SEM) (JSM-7100F, JEOL, Japan) with a field emission gun operating at 5 kV. Prior to the observation, the cryogenically fractured surface was coated with osmium.

The temperature dependencies of the oscillatory tensile moduli—i.e., the storage modulus  $E'$  and the loss modulus  $E''$ —were investigated using a dynamic mechanical analyzer (Rheogel-E4000, UBM, Japan)

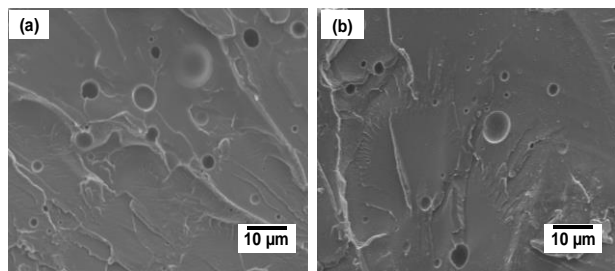
from -30 to 100°C. Rectangular specimens (width 5mm; length 10mm) were cut from the sheets.

The thermal properties were evaluated using a differential scanning calorimeter (DSC) (DSC 8500, PerkinElmer, MA, USA). Approximately 10 mg of the sample encapsulated in an aluminum pan was heated from -50°C at a heating rate of 10°C/min.

The water content was measured using a 860 KF (Karl Fischer) coulometric titrator (Metrohm AG, Switzerland). The measurements were performed three times and its average value was calculated.

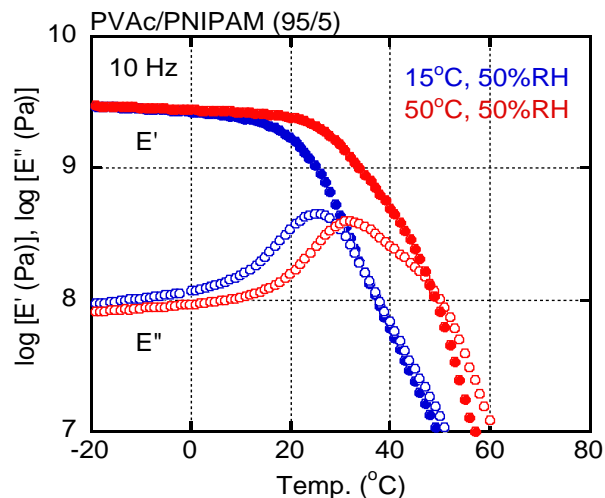
## Results and discussion

The morphology of the blend sheets was characterized using SEM as shown in **Fig. 1**. The observation was carried out using two samples with the same blend ratio, i.e., PVAc/PNIPAM (95/5); one was stored at 15°C and 50%RH and the other was stored at 50°C and 50%RH, each for 3 days. Both samples exhibited a similar morphology, i.e., a sea-island structure, in which the diameter of the dispersed PNIPAM droplets (1–10 μm) was not affected by the storage conditions. The results revealed that the PVAc was immiscible with PNIPAM, and the dispersed PNIPAM droplets were surrounded by the PVAc matrix.



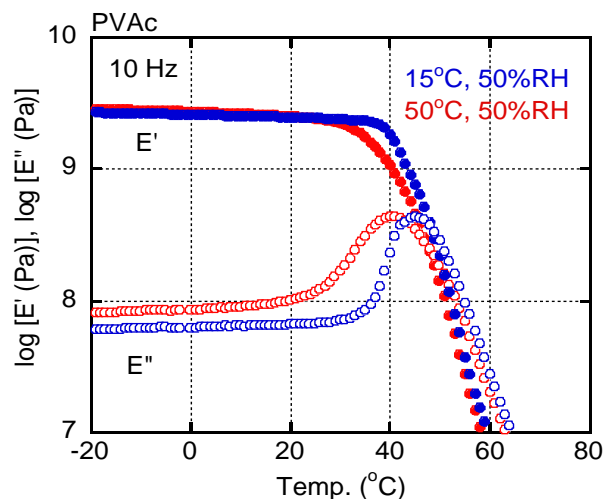
**Fig. 1.** Scanning electron microscope (SEM) images of PVAc/PNIPAM (95/5) stored at (a) 50°C and 50%RH and (b) 15°C and 50%RH.

The temperature dependencies of the dynamic tensile moduli of the PVAc/PNIPAM (95/5) sheets stored at either 15°C and 50%RH or 50°C and 50%RH are shown in **Fig. 2**. Considering that the  $T_g$  of pure PNIPAM is reported to be 115–150°C [19], the peak in the loss modulus ( $E''$ ) curve can be ascribed to  $\alpha$ -relaxation - i.e., the glass-to-rubber transition - of PVAc. The peak temperatures, defined as  $T_g$  in this study, were 24.9°C for the sheet stored at 15°C and 50%RH and 31.2°C for the sheet stored at 50°C and 50%RH, demonstrating that the  $T_g$  of the sample is dependent on the storage condition. This is an attractive property, because the material becomes soft at low temperatures and hard at high temperatures. In other words, the addition of PNIPAM confers “intelligence” on the PVAc, enabling it to adjust its modulus and flexibility according to the ambient temperature. Except for our previous studies [20,21], to the best of our knowledge, such smart materials have never been reported before.



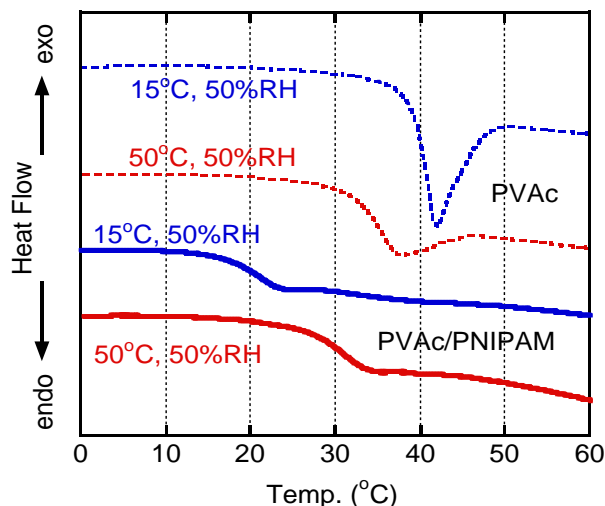
**Fig. 2.** Temperature dependence of the tensile storage modulus  $E'$  and loss modulus  $E''$  at 10 Hz of PVAc/PNIPAM (95/5) stored at 15°C and 50%RH and 50°C and 50%RH.

The effect of the storage temperature on  $T_g$  was also investigated for pure PVAc, as shown in **Fig. 3**. We confirmed that the storage conditions affected the  $T_g$  of PVAc. However, after storing at a low temperature, the  $T_g$  increased. This contradicted the result for the blend. In general, this result is an undesirable phenomenon, because low-temperature toughness is lost.



**Fig. 3.** Temperature dependence of the dynamic tensile moduli at 10 Hz of PVAc stored at 15°C and 50%RH and 50°C and 50%RH.

It has been reported that PVAc and poly(methyl methacrylate) (PMMA) exhibit an association state that affects the rheological properties including the  $T_g$  [22-28]. In particular, it has recently been reported that even a small amount of solvent (< 1%) greatly reduces the  $T_g$  of PMMA [29]. A similar phenomenon is expected for PVAc, as suggested by Onogi et al. [30]. Therefore, we deduce that the  $T_g$  shift to a lower temperature can be attributed to moisture absorption, which generally increases at high temperatures. In fact, Bair et al. reported that water acts as a plasticizer for vinyl acetate unit [31].



**Fig. 4.** DSC heating curves of PVAc and PVAc/PNIPAM (95/5), both stored at 15°C and 50%RH and 50°C and 50%RH.

We also performed DSC measurements to confirm the effect of the storage conditions on the glass transition temperatures of the blend and pure PVAc. As can be seen in **Fig. 4**, the  $T_g$  was affected by the storage temperature. Furthermore, the PVAc sheet stored at 15°C had a higher  $T_g$  than the sheet stored at 50°C. In contrast, the  $T_g$  order was reversed for the blend sample. These DSC results agreed well with the dynamic mechanical properties.

Considering that the  $T_g$  of PVAc is sensitive to moisture, the  $T_g$  of the blend must also be determined by the content of absorbed moisture. After storage at 15°C and 50%RH—under which conditions PNIPAM behaves as a hydrophilic material—the blend sheet absorbed more water, even though the PNIPAM dispersion was surrounded by the PVAc matrix. As a result, the  $T_g$  decreased. When stored at 50°C and 50%RH, in contrast, the blend sheet became “dry” owing to the hydrophobic character of PNIPAM. To confirm this, we evaluated the moisture content in the sheets after storage at each condition using a Karl Fischer coulometric titrator, as summarized in **Table 1**.

Although the water content of the PVAc sheet increased with the storage temperature, which is a general phenomenon, that trend was reversed in the PVAc/PNIPAM sheets. This suggests that the PNIPAM underwent a coil-globule transition—i.e., hydrophilic–hydrophobic change—even in the blend with PVAc. These results suggest that the “smart” behavior of the PVAc/PNIPAM blend—i.e.,  $T_g$  control according to ambient temperature—can be attributed to the hydrophilic–hydrophobic change in the PNIPAM, which changed the amount of moisture in the sample.

**Table 1.** Water content of the sheets.

Sample sheets	Storage conditions	Water content (wt.%)
PVAc	15°C, 50%RH	0.25
	50°C, 50%RH	0.42
PVAc/PNIPAM (95/5)	15°C, 50%RH	1.05
	50°C, 50%RH	0.80

## Conclusion

We investigated changes in the  $T_g$  of a PVAc blend containing 5 wt.% PNIPAM by examining its dynamic mechanical properties and obtaining DSC heating curves. In particular, we studied the effect of storage conditions on the  $T_g$ . The blend underwent distinct phase separation, following which PNIPAM droplets were dispersed in the PVAc matrix. We found that the  $T_g$  of the blend sample stored at 15°C and 50%RH was lower than that of the blend sample stored at 50°C and 50%RH; in contrast, pure PVAc had a lower  $T_g$  after storage at 50°C and 50%RH. This anomalous  $T_g$  shift is an attractive property because the material becomes soft at low temperatures. The  $T_g$  change can be attributed to moisture absorption. The water content of the blend increased at low temperatures because of the hydrophilic property of PNIPAM.

## Author’s contributions

Conceived the plan: NT, PP, AK, MY; Performed the experiments: NT, PP; Data analysis: NT, PP; Wrote the paper: NT, MY. Authors have no competing financial interests.

## References

- Zwaag, S. V. D.: Self-healing materials, Springer, **2008**.
- Eds. Aguilar, M. R.; Roman, J. S., Smart polymers and their applications, Woodhead Publishing, **2014**.
- Kuhakongkiat, N.; Sugiyama, M.; Guesnier, M.; Azaman, F. A.; Yoshida, K.; Yamaguchi, M.; *J. Appl. Polym. Sci.*, **2017**, *135*, 45927.  
DOI: [10.1002/app.45927](https://doi.org/10.1002/app.45927)
- Watanabe, R.; Sako, T.; Korkiatithaweechai, S.; Yamaguchi, M.; *J. Mater. Sci.*, **2017**, *52*, 1214.  
DOI: [10.1007/s10853-016-0419-1](https://doi.org/10.1007/s10853-016-0419-1)
- Eds. Ponnamma, D.; Sadasivuni, K. K.; Kabibihan, J. J.; Al-Maadeed, M. A.; Smart polymer nanocomposites: Energy harvesting, self-healing and shape memory applications, Springer, **2017**.
- Ed. Nasar, A.; Smart polymers and composites, Materials Research Forum LLC, **2018**.
- Heskins, M.; Guillet, J. E.; *J. Macromol. Sci., Part A, Chem.*, **1968**, *2*, 1441.  
DOI: [10.1080/10601326808051910](https://doi.org/10.1080/10601326808051910)
- Schild, H. G.; *Prog. Polym. Sci.*, **1992**, *17*, 163.  
DOI: [10.1016/0079-6700\(92\)90023-R](https://doi.org/10.1016/0079-6700(92)90023-R)
- Winnik, F. M.; Ottavani, M. F.; Bossmann, S. H.; Garcia-Garibay, M.; Turro, N. J.; *Macromolecules*, **1992**, *25*, 6007.  
DOI: [10.1021/ma00069a025](https://doi.org/10.1021/ma00069a025)
- Okada, Y.; Tanaka, F.; *Macromolecules*, **2005**, *38*, 4465.  
DOI: [10.1021/ma0502497](https://doi.org/10.1021/ma0502497)
- Kujawa, P.; Aseyev, V.; Tenhu, H.; Winnik, F. M.; *Macromolecules*, **2006**, *39*, 7686.  
DOI: [10.1021/ma061604b](https://doi.org/10.1021/ma061604b)
- Tanaka, F.; Koga, T.; Kojima, H.; Winnik, F. M.; *Macromolecules*, **2009**, *42*, 1321.  
DOI: [10.1021/ma801982e](https://doi.org/10.1021/ma801982e)
- Ding, Z.; Chen, G.; Hoffman, A.; *Bioconjugate Chem.*, **1996**, *7*, 121.  
DOI: [10.1021/bc950087r](https://doi.org/10.1021/bc950087r)
- Nakayama, M.; Okano, T.; Winnik, F. M.; *Mater. Matt.*, **2010**, *5*, 56.
- Akiyama, Y.; Kikuchi, A.; Yamato, M.; Okano, T.; *Langmuir*, **2004**, *20*, 5506.  
DOI: [10.1021/la036139f](https://doi.org/10.1021/la036139f)
- Hoare, T. R.; Kohane, D. S.; *Polymer*, **2008**, *49*, 1993.  
DOI: [10.1016/j.polymer.2008.01.027](https://doi.org/10.1016/j.polymer.2008.01.027)
- Schmaljohann, D.; *Adv. Drug Delivery Rev.*, **2006**, *58*, 1655.  
DOI: [10.1016/j.addr.2006.09.020](https://doi.org/10.1016/j.addr.2006.09.020)

18. Alem, H.; Jonas, A. M.; Champagne, S. D.; *Polym. Deg. Stab.*, **2010**, *95*, 327.  
DOI: [10.1016/j.polymdegradstab.2009.11.004](https://doi.org/10.1016/j.polymdegradstab.2009.11.004).
19. Ito, M.; Ishizone, T.; *J. Polym. Sci., Part A: Polym. Chem.*, **2006**, *44*, 4832.  
DOI: [10.1002/pola.21583](https://doi.org/10.1002/pola.21583)
20. Kuhakongkiat, N.; Wachteng, V.; Nobukawa, S.; Yamaguchi, M.; *Polymer*, **2015**, *78*, 208.  
DOI: [10.1016/j.polymer.2015.09.079](https://doi.org/10.1016/j.polymer.2015.09.079)
21. Kuhakongkiat, N.; Nobukawa, S.; Yamaguchi, M.; *J. Macromol. Sci., Part B, Phys.*, **2016**, *55*, 262.  
DOI: [10.1080/00222348.2016.1138182](https://doi.org/10.1080/00222348.2016.1138182)
22. Masuda, T.; Kitagawa, K.; Onogi, S.; *Polym. J.*, **1970**, *1*, 418.  
DOI: [10.1295/polymj.1.418](https://doi.org/10.1295/polymj.1.418)
23. Masuda, T.; Toda, N.; Aoto, Y.; Onogi, S.; *Polym. J.*, **1972**, *3*, 315.  
DOI: [10.1295/polymj.3.315](https://doi.org/10.1295/polymj.3.315)
24. Plazek, D. J.; Tan, V.; O'Rourke, V. M.; *Rheol. Acta*, **1974**, *13*, 367.  
DOI: [10.1007/BF01521729](https://doi.org/10.1007/BF01521729)
25. Bercea, M.; Peiti, C.; Simionescu, B.; Navard, P.; *Macromolecules*, **1993**, *26*, 7095.  
DOI: [10.1021/ma00077a061](https://doi.org/10.1021/ma00077a061)
26. Osaki, K.; Takatori, E.; Watanabe, H.; Kotaka, T.; *Rheol. Acta*, **1993**, *32*, 132.  
DOI: [10.1007/BF00366676](https://doi.org/10.1007/BF00366676)
27. Fuchs, M.; Friedrich, C.; Weese, J.; *Macromolecules*, **1996**, *29*, 5893.  
DOI: [10.1021/ma951385m](https://doi.org/10.1021/ma951385m)
28. Xue, L.; Agarwal, U. S.; Zhang, M.; Staal, B. B. P.; Muller, A. H. E.; Bailly, C. M. E.; Lemstra, P. J.; *Macromolecules*, **2005**, *38*, 2093.  
DOI: [10.1021/ma0484936](https://doi.org/10.1021/ma0484936)
29. Ito, A.; Ayerdurai, V.; Miyagawa, A.; Matsumoto, A.; Okada, H.; Courtoux, A.; Yamaguchi, M.; *J. Soc. Rheol. Jpn.*, **2018**, *46*, 117.
30. Onogi, S.; Masuda, T.; Ibaragi, T.; *Kolloid Z.*, **1968**, *222*, 110.
31. Bair, H. E.; Johnson, G. E.; Anderson, E. W.; Matsuoka, S.; *Polym. Eng. Sci.*, **1981**, *21*, 930.  
DOI: [10.1002/pen.760211410](https://doi.org/10.1002/pen.760211410)