Thermal and Mechanical Behaviors of Poly(vinyl alcohol)–Lactose Blends

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ABSTRACT: Thermal and mechanical behaviors of poly(vinyl alcohol) (PVA)–lactose blends were studied by differential scanning calorimetry, thermal gravimetric analysis, and stress–strain analysis. The increase in glass transition temperature of the PVA–lactose blends with lactose contents suggests the formation of hydrogen-bonded PVA–lactose complex in the PVA matrix. The hydrogen bonding interactions can improve thermal and mechanical properties of the blends. Results of this study demonstrate that lactose, a byproduct of dairy industry, can be used directly and in substantial quantity (33%) as a modifier to enforce the physical properties of PVA. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 929–935, 2002

Key words: poly(vinyl alcohol); lactose; blends; thermal and mechanical properties

INTRODUCTION

Water-soluble polymers and their blends are subjects of growing interest because these materials are widely used in detergents, paints, textiles, biodegradable plastics, and chemical intermedium.[1] Blends of water-soluble polymers have also been developed into various intermolecular complexes[2–4] that possess new performance; for examples, mechanochemical devices with poly-(methacrylic acid)–poly(ethylene glycol) blends,[5] and temperature-responsive drug delivery systems with poly(acrylic acid) (PAA)–poly(*N,N*-dimethylacrylamide) blends.[6] These unique functions are based on various macromolecular interactions. To date, this concept has been demonstrated by blending PVA with poly(acrylamide),[7] PAA,[8,9]

poly(methacrylic acid),[10] poly(styrenesulfonic acid),[11] and poly(vinyl pyrrolidone);[12] and PAA with poly(styrene sulfonate)[13] and poly(ethylene glycol).[14]

The same concepts have been extended to the intermolecular complexes between polymers and small molecules.[15–17] One advantage of using small organic molecules is that thermodynamic equilibrium at the molecular level can be quickly reached due to smaller sizes of one blending component. Density of hydrogen bonding as physical cross-links in blends can be quantitatively controlled via the strength of electronegativity of the polar groups in small molecules.[18] Unfortunately, only a few works have been reported on these systems.

In this work, we investigated a polymer–small molecular blending system, in which a semicrystalline polymer, PVA, and lactose, a byproduct of dairy industry, were used. Both components are crystallizable and have abundant hydroxyl

Table I   Characteristics of Blend Precursors

Name	Density (g/cm^3)	Hydrolysis Degree (%)	Molecular Weight	T_g (°C)	T_m (°C)
Poly(vinyl alcohol)	1.26[a]	87–89	124,000	71	189
β-D-Lactose	1.59[b]	—	324	—	238

[a] Measured at 23°C by the flotation method in which hexanes and tetrachloride were used.
[b] Reference 19.

groups in their structures. On blending, hydrogen-bonding interactions between the two compounds were expected. As a result, related thermal and mechanical properties could be improved substantially. The research also attempted to clarify the relationship between the morphology of blends and their physical properties.

EXPERIMENTAL

Materials

PVA and lactose (Aldrich) were used as received without any further purification. The characteristics of PVA and lactose are listed in Table I.

Preparation of Blends

PVA and lactose blends containing up to 47% (w/w) lactose were prepared at room temperature. PVA was first dissolved in deionized water by stirring overnight. This procedure was followed by the dropwise addition of lactose, prepared as a 5% aqueous solution, into the vigorously stirred PVA solution. After stirring for 2 h, the clear, homogeneous solution was cast onto a plate. The films were 50 mm in thickness. The samples were dried under vacuum at room temperature for 1 day and then at 60°C for 1 week.

Wide-Angle X-ray Diffraction (WAXD) Measurements

WAXD patterns of PVA–lactose blends were obtained with a Diano-XRD 8000 X-ray diffractometer using nickel-filtered Cu-Kα radiation. The tube current and voltage were 20 mA and 40 kV, respectively. Measurements were scanned between 0 and 50° 2θ angle at 0.04° steps. The counting time was 1 s/step.

Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA)

DSC measurements were performed on a Shimadzu DSC-50Q equipped with a thermal analysis station TA-50WS1. TGA measurements were carried out on a Shimadzu TGA-50Q. Both DSC and TGA measurements were performed in nitrogen at a heating rate of 20°C/min. Both DSC and TGA measurements were duplicated for each sample.

Thermal properties of the PVA–lactose blends were obtained by several heating processes. The melting temperature, T_m, and the enthalpy of melting, ΔH_f, were measured during the initial heating cycle. The glass transition temperature, T_g, was obtained in the second heating process following initial heating to 160°C to remove moisture. Annealing of samples was performed at 100°C for 1 h.

Stress–Strain Test

Uniaxial stress–strain tests of films were conducted (ASTM D 882-91) using an Instron Model 1122 at 25 °C and 65% relative humidity. Samples were 10 mm in width and 50 μm in thickness. A 50-mm gauge length and a 10-mm/min crosshead speed were employed.

RESULTS AND DISCUSSION

DSC thermograms of annealed pure PVA, lactose, as well as PVA–lactose blends are shown in Figure 1. Pure PVA exhibits a clear T_g at 78°C and a prominent melting endotherm at 189°C, indicating a semicrystalline structure. A small endothermic peak at 120°C is unknown. In comparison to PVA, the DSC curve of pure lactose shows a sharp melting peak at 238°C, reflecting its highly crystalline structure. All PVA–lactose blends contain endotherms that are characteristics of both PVA and lactose. The T_ms of the PVA portion in blends are depressed, and the extent of T_m depression increases with increasing lactose content. In the high temperature region >200°C, there exist endotherms that are about the same with the T_m of pure lactose. These peaks are obviously broader
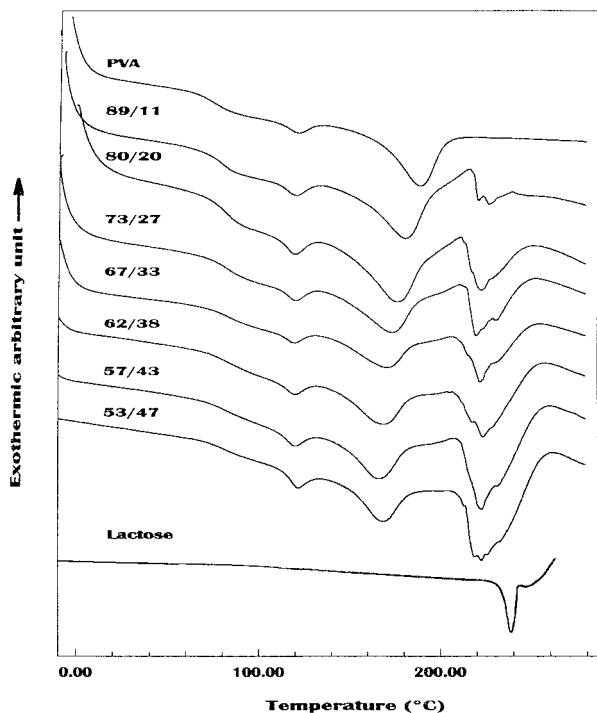
Figure 1 DSC thermograms of annealed films for pure PVA, lactose, and PVA–lactose blends.

than the melting peak of pure lactose. The peak temperature appears to be independent of the amount of lactose in blends, but peak area is proportional to the lactose content.

The onset temperature of degradation is 240°C for both lactose and PVA (Figure 2). Degradation of lactose, indicated by 50% weight loss, occurs ~50°C lower than that of PVA. Onset temperature of degradation of PVA–lactose blends is reduced to 200°C. All blends of PVA–lactose show two weight loss plateaus. The extents of weight loss increase with increasing lactose contents at the first plateau, whereas the opposite is observed at the second plateau. This observation suggests that the first plateau may represent the breakdown of the lactose portion and the second that of PVA in the blends. Based on TGA results, the broad peaks at higher temperatures observed in DSC are thought to be from a combination of melting and degradation of lactose crystals in blends. Thus, the reduced degradation temperature of blends in TGA may be due to the fusion of smaller lactose crystal and degradation of noncrystalline lactose in the blends.

For further understanding the crystalline structure of PVA, lactose, and PVA–lactose blends, the X-ray diffraction measurements are

shown in Figure 3. Evidently, pure PVA exhibits only one marked and relatively broad diffraction peak at $2\theta = 19.17°$. With addition of 20% lactose, the peak of PVA becomes less intense and relatively broader, indicating its reduced crystallinity. When the lactose content increases, the diffraction peak does not show further declination; in contrast, it appears relatively sharp and narrow again. This result is especially evident in the 57/43 blending sample. Theoretically, hydrogen bonding interaction, if it exists, may decrease the crystal structure of PVA due to lactose incorporation into the PVA matrix. However, a relatively sharp WAXD peak indicated the existence of more crystal structures, which could be from lactose only. The results further confirm the DSC measurements; that is, in addition to hydrogen bonding interactions with PVA, lactose could still recrystallize in the PVA matrix. However, the crystal structure may be less perfect compared with the pure lactose sample.

Effect of PVA–Lactose Hydrogen Bonding Interaction on their Glass Transition Temperatures

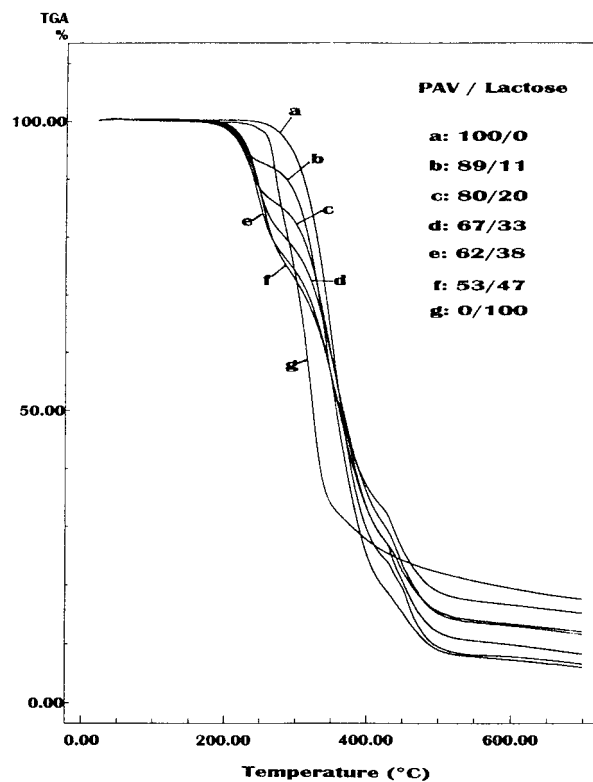The Tgs of PVA and its blends were plotted as a function of weight fraction of lactose in Figure 4.

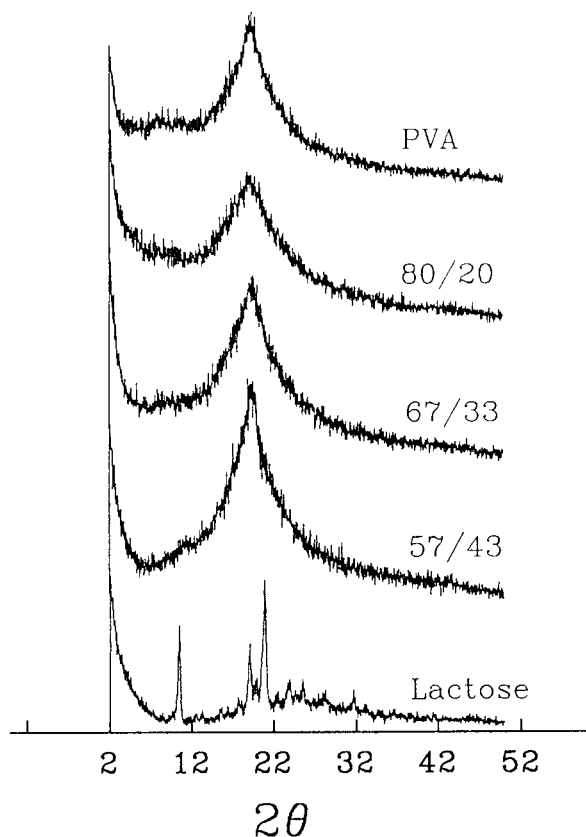**Figure 2** TGA thermograms of pure lactose and PVA–lactose blends.

Figure 3 Wide-angle X-ray diffraction curves for pure PVA, lactose, as well as PVA–lactose blends.

Evidently, Tg of both untreated and annealed samples increases with increasing lactose contents. Because lactose is highly crystalline, its Tgs can rarely be observed except for in a continuous amorphous state.[19] Therefore, the Tgs detected in the PVA–lactose blends represent only the PVA chain motion in response to adding a lactose component. The increase of Tgs may suggest that hydrogen bonding between the hydroxyl groups of PVA and lactose should be formed. These hydrogen bonds, acting as physical crosslinks, can effectively reduce the segmental motion and, in turn, increase the Tgs of PVA.

Annealing also increases the T_gs of the PVA–lactose blends. This result may be partially attributed to removal of residual moisture, which is known to act as a plasticizer to interrupt the intermolecular chain interaction, and lowering the T_g. However, this effect is considered small because of the low moisture contents in all PVA–lactose blends (0.1–0.3%, TGA). Another more significant aspect of annealing is the thermal relaxation effect, which could promote chain mobility and eliminate steric and spatial con-

straints.[20,21] Such thermal effects may also promote new hydrogen bonds. For instance, the T_g of the annealed PVA with 38% lactose is 12 °C higher than that of pure PVA, whereas the T_g of the same blending, which is not annealed, is only 6.7°C higher. The marked increase in T_g suggests that annealing may cause the formation of additional intermolecular hydrogen bonds in PVA matrix.

Correlation between Mechanical Behavior and Morphology

The stress–strain curves for PVA–lactose blends are shown in Figure 5. As expected, the mechanical properties of blends are different from those of pure PVA. Young's modulus is enhanced in compositions up to a 0.17 volume fraction of lactose (20% w/w) and is then reduced with lactose content up to 33% (Figure 6). The enhanced modulus of blends is consistent with the filler and hydrogen bonding effects. Lactose in PVA matrix could act as filler to enforce the modulus of blends. With lactose contents >33%, the self-association of lactose may become predominant, thereby reducing hydrogen bonding between lactose and PVA molecules and lowering the modulus of blends.

The tensile strength of blends increases with the volume fraction of lactose up to 33% (w/w),
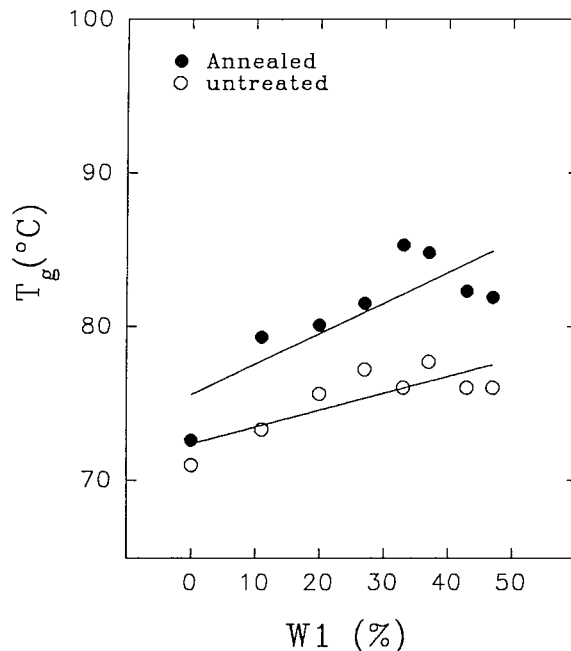

Figure 4 Glass transition temperature as a function of weight fraction of lactose for PVA–lactose blends.
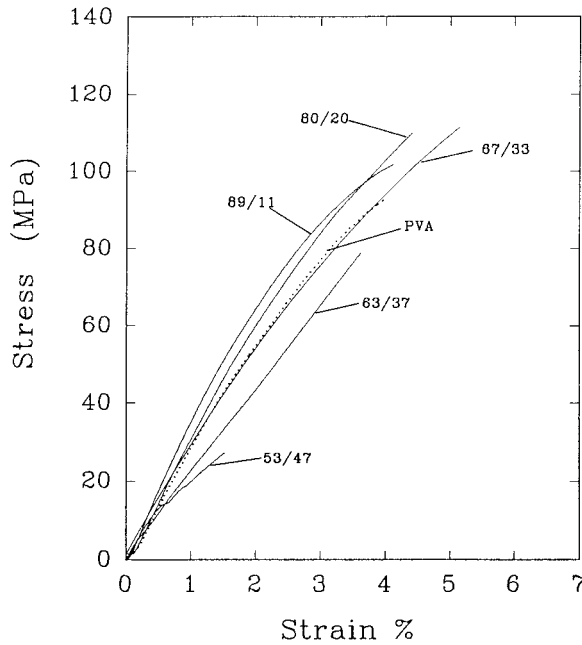
Figure 5 Stress–strain curves for pure PVA and PVA–lactose blends.

then decreases, as can be seen in Figure 7. The tensile test was conducted below the T_gs of blends; therefore, brittle fractures are expected.
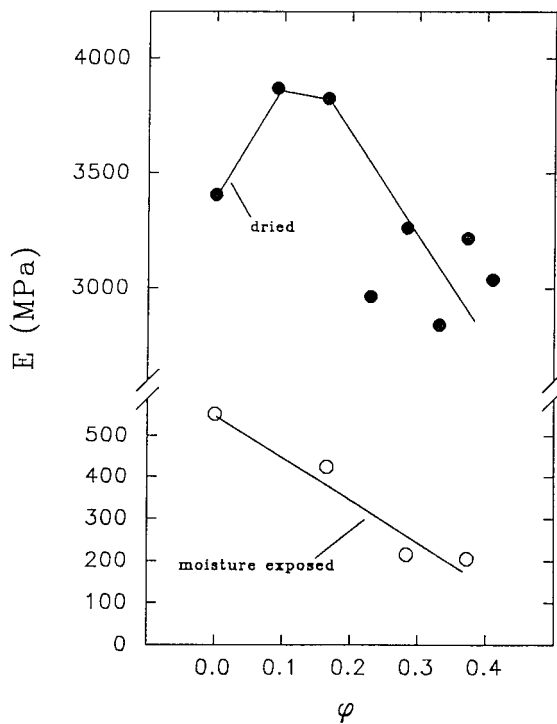

Figure 6 Young's modulus versus volume fraction of lactose in blends.
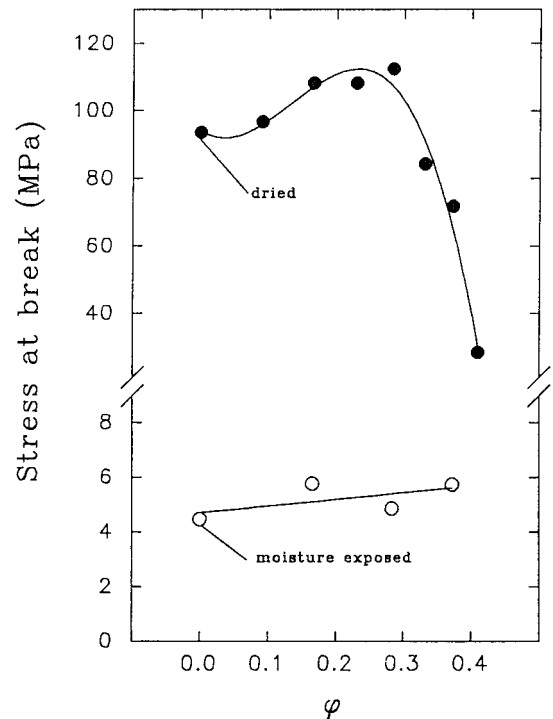

Figure 7 Stress at break versus volume fraction of lactose in blends.

This expectation is confirmed in Figure 5, where there is no obvious yield point and a linear relationship between stress and stain is observed. It is well known that brittle fracture in semi-crystalline polymers generally occurs in their amorphous regions involving the formation of stress-induced microcracks or crazes. Because heterogeneity, such as chain ends and ruptured bond, most likely concentrate in the amorphous region, these could lead to "disruption points" and stress concentrations.[22,23] The increase in stress clearly indicates that intermolecular hydrogen bonding between lactose and PVA could counteract these defects in PVA matrix. The multifunctional hydrogen bonding capacity of lactose may be physically cross-linked to reinforce PVA chains as well as its intercrystalline linkages.

The tension strengths of the PVA–lactose blends, however, are reduced as the lactose content exceeds a certain level. Similar effects are also observed in their strain behavior, as shown in Figure 8. The strain value rises to a maximum value at 0.25 volume fraction of lactose (27% w/w) and then decreases. Hydrogen bonding between PVA and lactose enforces the polymer matrix and resists elongation. However, in comparison with stress at break, the effects of lactose on elongation

is relatively small (only 1% increase), indicating a dominate brittle fracture. The most worthy finding is the optimum blending volume fraction of 33% (w/w) lactose for PVA. At this ratio, both stress and strain behaviors are enhanced.

Moisture Effects on Thermal and Mechanical Behavior

The formation of hydrogen-bonding complexes in blends is also evident from examining their thermal and mechanical behavior following exposure to 65% relative humidity (at 25°C) for 20 days. Dried lactose as well as PVA and PVA–lactose blends contain little moisture (0.1–0.3%, TGA). Following the extended exposure into the air, the moisture contents of PVA and PVA–lactose blends increase to >6% (Table II). The high moisture contents may be attributed to the lactose component. Although there is a little moisture absorbed by pure lactose, in blends, the hydrogen-bonding interaction of lactose with PVA may remarkably disrupt its crystal structure, as shown in both DSC and WAXD data. As a result, more amorphous regions and more abundant hydrophilic groups in blends could easily access and trap more moisture.
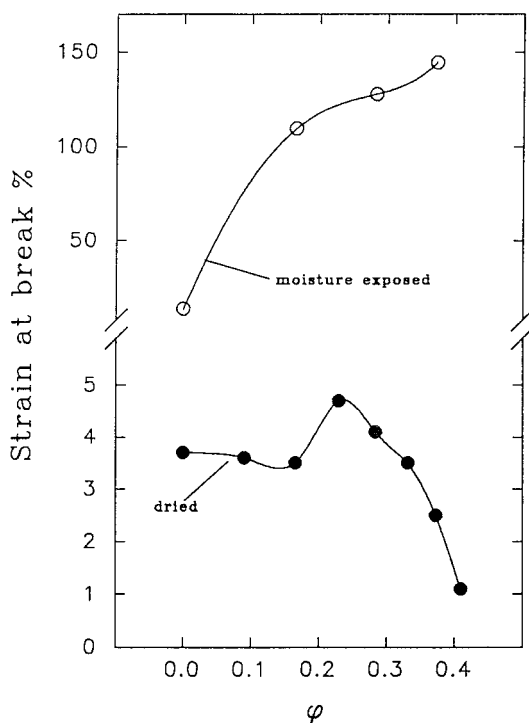
Table II   Properties of PVA–Lactose Films Exposed to Moisture at 25°C and 65% Relative Humidity for 20 Days[a]

PVA–Lactose (w/w)	M (%)	T_g (°C)	T_r (°C)	T_m (°C)	T_d (°C)
100/0	6.0	33	100	189	305
80/20	6.5	26	140	—	210
67/33	7.5	26	140	—	219
57/43	7.4	20	137	—	220
0/100	0.3	—	—	237	258

[a] M, moisture content measured by TGA; T_g, glass transition temperature; T_r, the temperature of release hydration water measured by DSC; T_m, melting point; T_d, decomposition temperature measured by TGA.

The moisture exposure also lowers the T_g value tremendously (~45°C), because the water molecules can act as a plasticizer to reduce chain interactions among PVA. The higher the moisture content, the larger the decrease of T_g in blends. On the other hand, as shown by DSC (Figure 9), there exists a very broad endothermic peak between 100 and 140°C. This peak is thought to relate to the endothermic process of releasing the hydrated water. These temperatures for blends are ~40°C higher than that of pure PVA. The discrepancy may indicate that water molecules in pure PVA matrix are free or weakly bonded. However, hydration water in blends might be bonded strongly into complexes with either PVA or lactose molecules.

The T_m peak of pure PVA almost diminishes in the blend containing 20% lactose. The PVA melting endotherm disappears completely in the 33 and 43% blends. As analyzed previously, addition
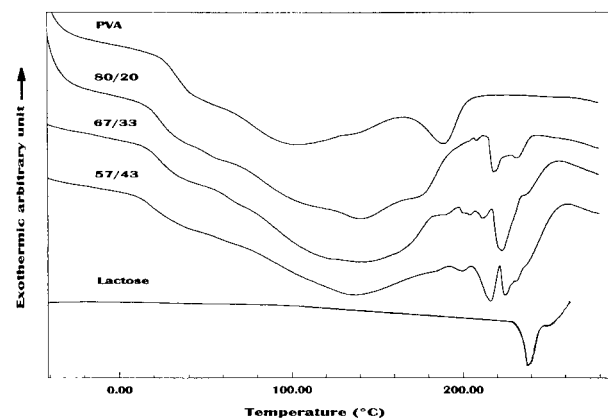

Figure 8   Strain at break versus volume fraction of lactose in blends.

Figure 9   DSC thermograms of moisture-exposed pure PVA, lactose, and PVA–lactose blends at 25°C and 65% relative humidity for 20 days.
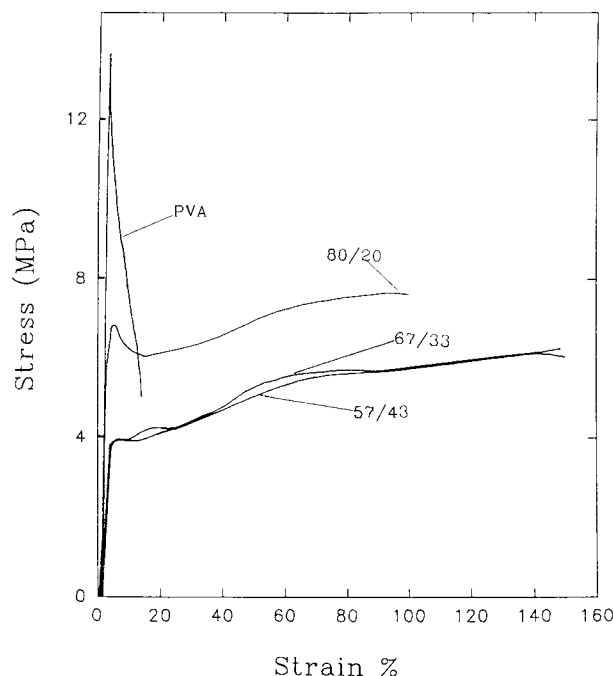
Figure 10 Stress–strain curves of moisture-exposed pure PVA and PVA–lactose blends at 25°C and 65% relative humidity for 20 days.

of lactose may reduce the perfection of PVA crystals in the blends. The vanishing melting endotherm may suggest that crystals of PVA are further destroyed by moisture permeated into PVA.[24] As for crystals of lactose in blends, there is no evidence that moisture uptake affects its structure. Neither melting peak temperature nor shape is altered.

Moisture exposure also significantly changes the stress–strain behavior of the PVA–lactose blends (Figure 10). Generally, the fractures of the moisture-exposed samples become ductile. All films display a yield point and neck formation. Moisture-exposed samples reduce both strength and modulus. The modulus decrease linearly (Figure 6), and the stress at break increase slightly (Figure 7) with increasing lactose contents. The most distinctive changes are the increases in elongation (Figure 8), where a 150% increase is obtained on the blend containing 43% lactose.

CONCLUSION

It is demonstrated that hydrogen-bonding interactions exist in PVA–lactose blends. The glass transition temperature of PVA increases with lactose content, suggesting the increasing formation of hydrogen-bonded PVA–lactose complex. DSC and WAXD data support that both PVA and lactose in the blends are recrystallizable through self- association. The hydrogen-bonding interactions in the PVA–lactose blends have also been shown to improve the thermal and mechanical properties of the blends. The study results suggest that lactose can be used directly in a substantial quantity as a modifier to improve the physical properties of PVA. The optimum content of lactose in blends is ~33%(w/w).

REFERENCES

1. Swift, G. Polym Degrad Stab 1994, 45, 215.
2. Osada, Y.: Koike, M. Chem Lett 1994, 209.
3. Philippova, O.E.; Karibyants, N.S.; Staodubtzev, S.G. Macromolecules 1994, 27, 2398.
4. Kondo, T.; Sawatart, C. Polymer 1994, 25(20), 4423.
5. Osada, Y. Adv Polym Sci 1987, 82, 1.
6. Aoki, T.; Kawashima, M.; Katono, H.; Sanui, K.; Ogata, N.; Okano, T.; Sakurai, Y. Macromolecules 1994, 82, 1.
7. Hu, C.M.; Chiang W.Y, Die Angewondte Makromoleculare Chemie 1990, 179, 157.
8. Zhang, X.; Takegoshi, K.; Hikichi, K. Polym J 1991, 23(2), 79.
9. Vazquez-Torres, H.; Cauich-Rodriquez, J.V.; Cruz-Ramos, C.A. J Appl Polym Sci 1993, 50, 777.
10. Zhang, X.; Takegoshi, K.; Hikichi, K. Polymer 1992, 33(22), 713.
11. Nagura, M.; Takagi, N.; Koyano, T.; Ohkoshi, Y.; Minoura, N. Polym J 1994, 26(6), 675.
12. Zhang, X.; Takegoshi, K.; Hikichi, K. Polymer 1992, 33(2), 713.
13. Bergfeldt, K.; Piculell, L.; Tjerneld, F. Macromolecules 1995, 28, 3360.
14. Lu, X.; Weiss, R. A.; Macromolecules 1995, 28, 3022.
15. Smith, P.; Eisenberg, A. J Polym Sci, Part B: Polym Phys 1988, 26, 569.
16. Tong, X.; Bazuin, C.G. Chem Mater 1992, 4, 370.
17. Fan, Xiao-Dong; Bazuin, C.G. Macromolecules 1995, 28, 8209.
18. Fan, Xiao-Dong; Bazuin, C.G. Macromolecules 1995, 28, 8217.
19. Sebhatu, T.; Elamin, A.A.;Ahineck, C. Pharm Res 1994, 11(9), 1233.
20. Pennacchia, J.R.; Dearce, E.M.; Kwei, T.K.; Bulkin, B.J.; Chen, J.P. Macromolecules 1986, 19, 973.
21. Wang, L.F.; Pearce, E.M.; Kwei, T.K. J Polym Sci, Part B: Polym Phys. 1991, 29, 619.
22. Elias, H.G. An Introduction to Plastics; VCH Publishers; New York, 1993.
23. Kinloch, A. J.; Young, R. J. Fracture Behavior of Polymers; Applied Science Publishers: London, 1983.
24. Elas, H.G. Macromolecules 1. Structure and Properties; Plenum Press: New York, 1984.