Study on Molecular Interaction Behavior, and Thermal and Mechanical Properties of Polyacrylic Acid and Lactose Blends

XIAO-DONG FAN,[1] YOU-LO HSIEH,[2] JOHN M. KROCHTA,[3] MARK J. KURTH[4]

[1] Department of Chemical Engineering, Northwestern Polytechnic University, Xi'an, China, 710072

[2] Department of Fiber and Polymer Science, University of California, Davis 95968, California, USA

[3] Department of Food Science and Technology, University of California, Davis 95968, California, USA

[4] Department of Chemistry, University of California, Davis 95968, California, USA

ABSTRACT: Polyacrylic acid (PAA) blending with lactose or polyol, a lactose derivative, is investigated by Fourier transform infrared, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and stress–strain tests. The IR spectra of PAA/lactose blends exist shifting around 1700 cm and 3400 cm^{-1}, implying intermolecular hydrogen-bonding interaction between two compounds. DSC data show that PAA and lactose are miscible below 17% lactose. At the higher content of lactose, phase separation occurs due to lactose self-association. Comparing to PAA/lactose blends, PAA/polyol systems show much weaker hydrogen-bonding interaction effect. All blending systems studied exhibit extensive reduction in their thermal and mechanical properties. The result suggests that both lactose and polyol cannot be used as effective additives to enhance the physical properties of PAA. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1921–1927, 2001

Key words: polacrylic acid; lactose; polyol; blends; hydrogen-bonding interaction

INTRODUCTION

In a previous paper,[1] we reported a novel blending system: polyvinyl alcohol (PVA) with lactose. Its morphology, thermal, and mechanical behaviors were studied based on hydrogen-bonding interaction in PVA/lactose blends. The result indicated that lactose can be used as a modifier, which can effectively enhance the thermal and mechanical properties of PVA. Specifically, in that study PVA selected is a semicrystalline polymer, upon blending, hydrogen bonding between

PVA, and lactose in their amorphous phase contributes largely to its physical properties.

Blending lactose with various water-soluble polymers, such as polyethylene oxide (PEO), polyacrylamide (PAAm), poly(N-isopropylacrylamide) (PNIPA), and polyvinyl pyrrolidone (PNVP) is continuously explored in our laboratory. One of the important reasons is that lactose, which is edible, biodegradable, and nontoxic, can also be used as a qualified additive to these polymers. The applications of these blends, especially in food, pharmaceutical, and household industries, possess potential valuations.

On the other hand, the hydrogen-bonding interaction in these systems show differently. For instance, there are oxygen or carbonyl groups in

---

Correspondence to: X.-D. Fan.

the segments of PEO and PNVP, when processing interaction with lactose; both of them could be a proton acceptor only. For PAA and PAAm, they have carboxyl or amide groups, which can play a role as both proton donor and acceptor, respectively. Different macromolecular structure could endow blends with different hydrogen bonding interaction, and in turn, give them different physical properties.

In this study, we focus our attention on the PAA/lactose blending system. For understanding the effect of small molecular structure on physical behavior of blends, we also choose polyol, a lactose derivative, to blend with PAA. It is well known that PAA is a strong self-associated polymer, where, at room temperature, the large majority of the carboxylic acid groups exist as intermolecular dimer.[2] Distinguished from PVA, PAA is also an amorphous polymer. Upon blending, we expect that the self-associated structure of intermolecular dimer in PAA can be affected due to intermolecular hydrogen bonding between lactose and PAA. Meanwhile, interfering polymer–polymer interactions in PAA can cause to influence its physical properties including their glass transition temperature, Young's modulus, and stress at break. We analyze and discuss the results based on molecular interaction behavior of PAA with lactose and its derivative.

EXPERIMENTAL

Materials

Both PAA and lactose were used as received without any further purification (Aldrich). Polyol was synthesized in this laboratory based on another project.[3] The characteristics of PAA, lactose, and polyol are listed in Table I.

Blend Preparation

The blends of PAA, containing up to 38 and 43% (w/w) lactose and polyol, respectively, were prepared at room temperature. PAA was first dissolved in deionized water by stirring overnight, following which lactose or polyol (5% solution) was added dropwise to the vigorously stirred PAA solution. After stirring for 2 h, the clear and homogeneous solution was cast onto a plate. The films obtained were 200 μm in thickness. The samples were dried under vacuum at room temperature for one day and 70°C for 12 h.
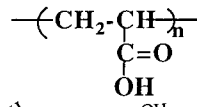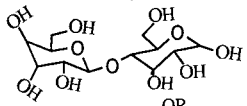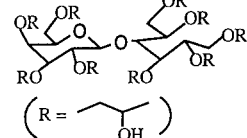
Infrared Measurements

Infrared spectra were recorded by using Mattson Calaxy Series FTIR 3000 spectrometer. The number of scans is 100 at a resolution of 4 cm^{-1}. The samples used for measurements were cast from methanol solution onto NaCl plates and dried at room temperature for one day and 70°C for 12 h.

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 20°C/min.heating rate. The DSC analyses were triplicated and the TGA measurements were duplicated for each sample. In order to completely eliminate the influence of moisture

Table I   Characteristics of Blend Precursors

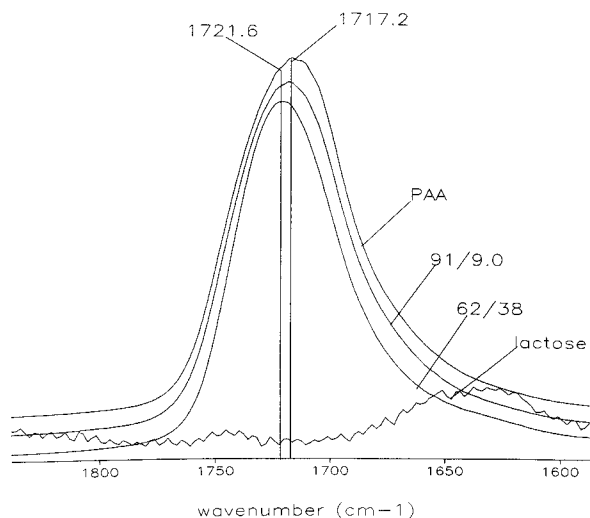| Name	Structure	Density (g/cm^3)	Molecular Weight	$T_{g\mathrm{DSC}}$ (°C)	$T_{m\mathrm{DSC}}$ (°C)
Polyacrylic acid (PAA)		—	450,000(M_w)	127	—
Lactose		1.59	324	—	238
Polyol[a]		—	1100	−26	—

[a] Reference 3.

Figure 1 Infrared spectra in the 1600–1800 cm^{-1} region of PAA, lactose, and their blends. The PAA/lactose weight percentage ratio used is as indicated on IR curves.

on thermal properties, the samples for PAA/lactose blends were first heated to 130°C, then quickly cooled to room temperature. The glass transition temperature was taken from the second heating data. For PAA/polyol blends, the samples were first heated to 100°C, then following cooling to −80°C, the glass transition temperatures were also taken from the second heating data.

Stress–Strain Test

Uniaxial stress–strain tests of PAA/lactose and PAA/polyol films were undertaken according to ASTM 882-91 using an Instron Model 1122 at 25°C and 65% relative humidity. All films were10mm in width and 200 μm in thickness. A 50-mm gauge length and a 10 mm/min. crosshead speed were employed.

RESULTS AND DISCUSSION

Intermolecular Hydrogen-Bonding Interaction

The infrared spectra of PAA, lactose and their blends in the 1600–1800 cm^{-1} region, are shown in Figure 1. This band is assigned as carbonyl stretching vibration. It is reported that two IR absorption[4] can be observed for carbonyl stretching around 1700 cm^{-1}. One at 1706 cm^{-1} corresponds to hydrogen bonded carbonyl in intermo-

lecular dimer, and the other at 1732 cm^{-1} is from nonhydrogen bonded including both isolated and terminal carbonyl groups.[5] In fact, the peak for PAA in our data can hardly be resolved into two bands. Only one prominent band at 1717 cm^{-1} can be observed. This may reflect a combination of bonded and free carbonyl vibration. In PAA/lactose blends, C=O absorption at 1717 cm^{-1} shifts slightly to higher frequency with increasing lactose contents (Fig. 1). This indicates the decrease in intermolecular cyclic dimer, and the increase in other types of hydrogen bonded C=O groups in blends. As there is no IR absorption band for lactose in this region, the intermolecular hydrogen-bonding interaction between hydroxyl groups in lactose and PAA is considered to being a main reason for band shifting.

The direct evidence of hydrogen-bonding interaction between lactose and PAA can be demonstrated by spectra changes of hydroxyl stretching vibration in 2400–3800 cm^{-1} region, as shown in Figure 2. In general, for aliphatic acid, the O—H stretching vibrations occur at 3490–3570 cm^{-1} for free hydroxyl groups and at 3000 cm^{-1} for acid cyclic dimer.[5] Here, we observed a broad band at 3100 cm^{-1} and a shoulder peak at 2950 cm^{-1} that can be assigned as —CH$_2$— symmetric stretching vibration for PAA. This band feature may reflect again a combination of IR absorption of free and associated hydroxyl groups. For lactose, a very broad peak around 3000–3800 cm^{-1} can be observed. Carefully examine this band, three peaks which exist at 3283, 3370, and 3464 cm^{-1} can be identified. This may reflect different hydrogen-bonded and free hydroxyl groups in both crystalline and amorphous phases of lactose.[6] When lactose in a lower content (91/9) in PAA matrix (Fig. 2), this band at 3464 cm^{-1} changes into a small
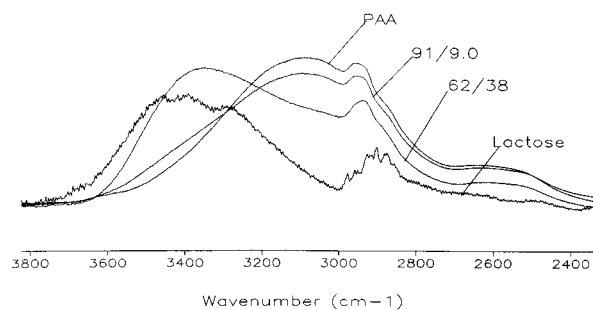

Figure 2 Infrared spectra in the 2400–3800 cm^{-1} region of PAA, lactose, and their blends. The PAA/lactose weight percentage ratio used is as indicated on IR curves.
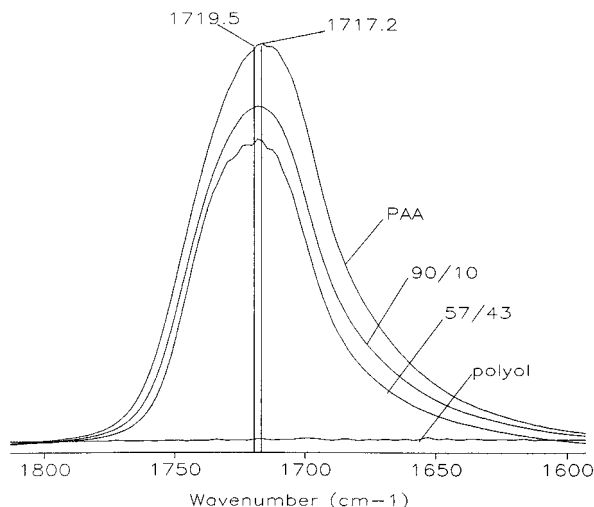
Figure 3 Infrared spectra in the 1600–1800 cm^{-1} region of PAA, polyol, and their blends. The PAA/polyol weight percentage ratio used is as indicated on IR curves.

shoulder at around 3400 cm^{-1}. This may indicate a miscible blending between lactose and PAA, and possible hydrogen-bonding interactions between hydroxyls in both products.

Interestingly, in the blending of high lactose content (62/38), the O—H stretching around 3100 cm^{-1} transforms into a much broader peak. This peak may overlap at least two peaks; one is at 3400 cm^{-1} and another is at 3100 cm^{-1}. According to previous analysis, both are related to free and hydrogen bonded O—H vibrations. Comparing with the absorption of pure lactose, the large and broad peak around 3400 cm^{-1} may be mainly from lactose component. The stretching vibration of free hydroxyl groups of lactose also shifts to lower frequency, indicating that some of them may be involved in hydrogen-bonding interactions with PAA. Actually, in this recipe, the mole ratio of hydroxyl groups is 1/1 stoichiometrically. Increasing intensity at 3400 cm^{-1}, compared with 3100 cm^{-1}, may suggest that this band also include some free hydroxyl groups from PAA component. The strong and large absorption band of hydroxyls at 3400 cm^{-1} may indicate the existence of strong intramolecular associations in lactose. As a result, some components of lactose may be phase separated from the PAA matrix. The result can be further confirmed by DSC measurements subsequently.

Figure 3 shows the IR spectra of polyol blended with PAA in the C=O stretching region. Evidently, even at higher polyol content (57/43),
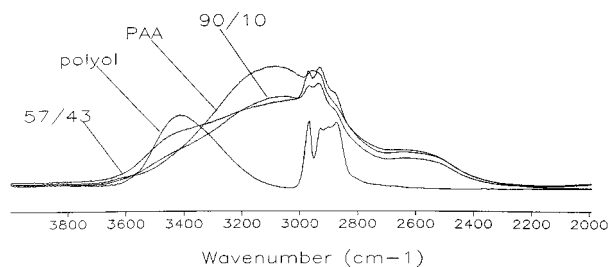
there exists little band shifting. No change of the C=O absorption suggests that intermolecular hydrogen-bonding interactions between polyol and PAA may be much weaker than that of PAA/lactose system. The result can be further observed in Figure 4, where IR spectra of O-H stretching for PAA, polyol and their blends from 2000 to 3800 cm^{-1} region are presented. As is shown in Figure 4, there is an absorption band at 3400 cm^{-1} for pure polyol, its broad feature indicates the existence of free and bonded hydroxyl groups. Upon blending with PAA, a small shoulder peak shows at the original place of 3400 cm^{-1} in both 90/10 and 57/43 blends. Besides, there is no obvious band shifting of O—H stretching for hydroxyl groups in PAA component.

Thermal Behavior

Figure 5 shows DSC thermograms of PAA, pure lactose, and PAA/lactose blends. There are two

Figure 4 Infrared spectra in the 2000–3800 cm^{-1} region of PAA, polyol, and their blends. The PAA/polyol weight percentage ratio used is as indicated on IR curves.
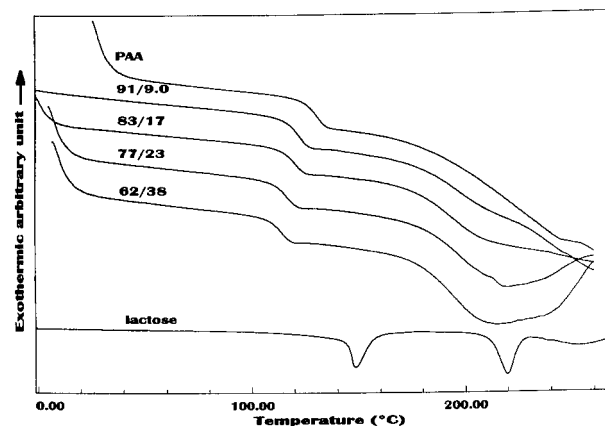

Figure 5 DSC thermograms of films for PAA, pure lactose, and PAA/lactose blends. The PAA/lactose weight percentage in blends is as indicated on curves.
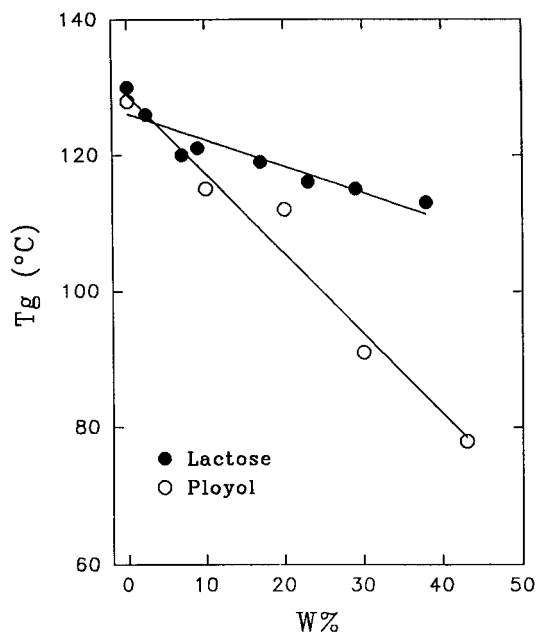
Figure 6 Glass transition temperature vs weight percentage of lactose, polyol in PAA/lactose, and PAA/polyol blends.

endothermal peaks for solution cast lactose. One is at 150 and another is at 216°C. They are referred to the release of bound water and melting of crystal.[7] For pure PAA, only one single glass transition temperature can be observed at 127°C, indicating its amorphous structure character.[8,9] Upon blending, the glass transition temperature (T_g) of PAA/lactose decreases gradually with increasing lactose content. Figure 6 presents the T_g of PAA/lactose blends versus weight percentage of lactose. Evidently, the T_g of blends declines with increasing lactose content. The decrease of T_g in PAA/lactose blends may suggest that hydrogen-bonding interactions between lactose and PAA may not be functionally as crosslinkers to enhance the physical properties of PAA. It also indicates that original carboxylic acid association could be a main factor to keep a relatively higher T_g in pure PAA. Although IR data support existing hydrogen-bonding interactions between lactose and PAA, they must be so weak that they can even be broken down at the elevated temperature during DSC measurement. As factors to cause the formation of hydrogen bonds in PAA/lactose system, the smaller molecular size of lactose should be a favorable factor to replace partially the interaction between carboxylic acid dimer in PAA.

Besides from Figure 5, when lactose content in blends reaches to over 17%, there is a relatively

broad endotherm peak at around 220°C. The width of this peak becomes broader following increasing lactose content. This endotherm is clearly related to the lactose component in blends. Comparing to pure lactose thermogram, this peak can be attributed to the melting of crystals of lactose in blends.

The onset temperatures of decomposition are 220°C for lactose and 210°C for PAA as shown in Figure 7. All blends show a gradual decrease in decomposition temperature with the increase in lactose content. The data obtained further support the data of IR and DSC that there exist some relatively weaker hydrogen-bonding interactions between lactose and PAA. These interactions can distort the original crystal structure of lactose, and polymer–polymer interaction in PAA. As a result, the decomposition temperature for blends decreases with the increase in lactose content.

Similar DSC result can be observed in PAA/polyol blends, as shown in Figure 8. The T_g of polyol is at −26°C. After blending with PAA, there is no T_g observed for blends around polyol's T_g region. Although there exists much weaker interactions in PAA/polyol system, as confirmed
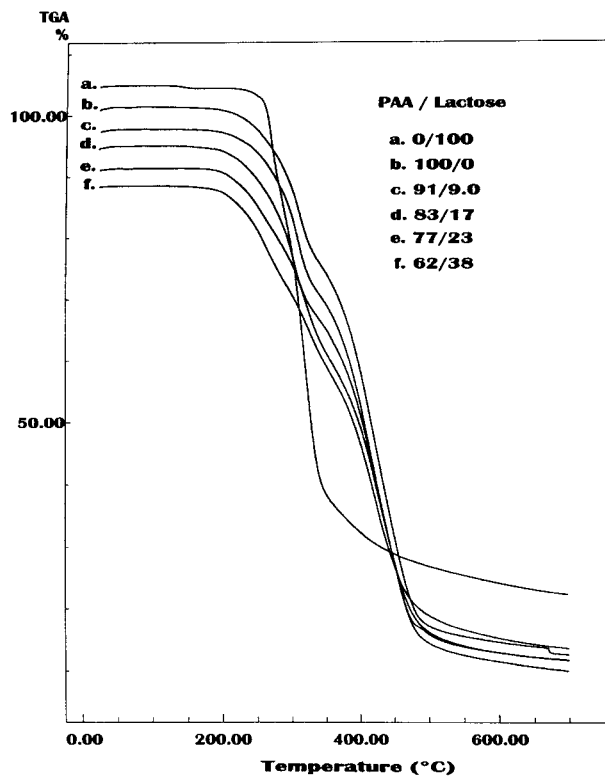

Figure 7 TGA thermograms for PAA, pure lactose, and PAA/lactose blends.
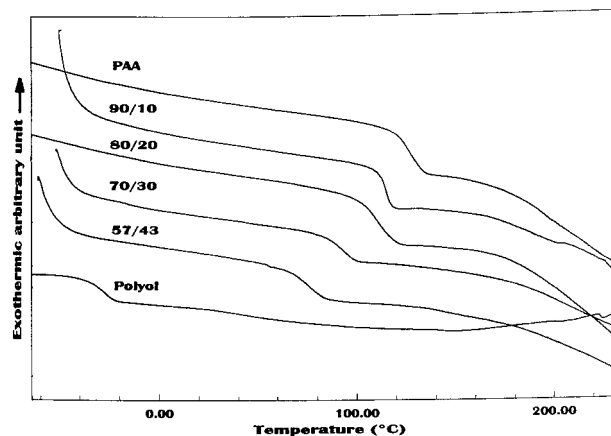
Figure 8 DSC thermograms of films for PAA, PAA/polyol blends, and pure polyol. The PAA/polyol weight percentage in blends is as indicated on curves.

by IR spectra, the blends demonstrates a good miscible feature in a relatively wide range polyol concentration. The T_g of blends also shows a gradual decrease with the increase in polyol content. Using T_g of blends plotted as a function of weight percentage of polyol (Fig. 6), a liner relationship is
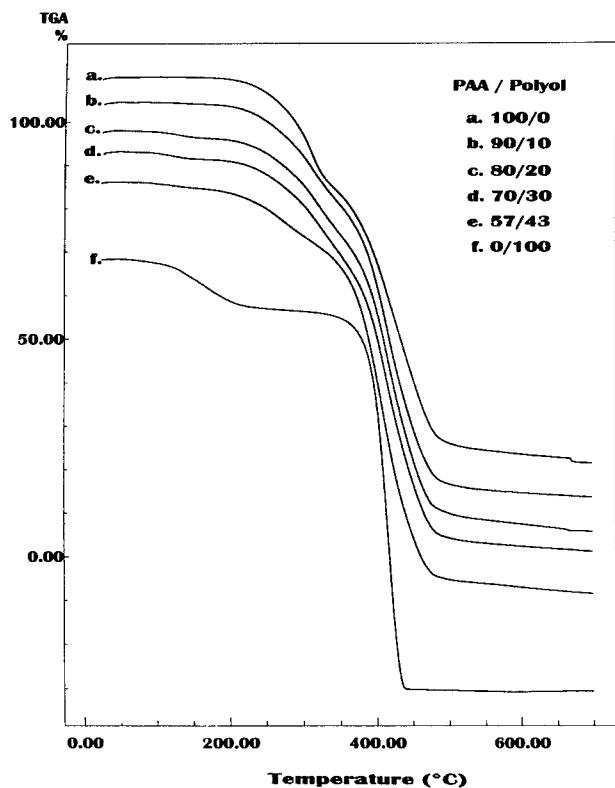

Figure 9 TGA thermograms for PAA, PAA/polyol blends, and pure polyol.

obtained. Compared with PAA/lactose system, the T_g declines more quickly for this system. The TGA data of PAA, polyol, and their blends are shown in Figure 9. As can be seen, for pure polyol, a weight loss plateau appears at 120°C, indicating that pure polyol contains an amount of water. Opposite to PAA/lactose blends, the onset temperatures of degradation present no obvious declination with the increase in polyol content.

Mechanical Properties of Blends

Young's modulus of blends vs weight fraction of lactose and polyol are plotted in Figure 10. Evidently, Young's moduli in PAA/lactose and PAA/polyol blends decrease with the increase in both small molecules. Besides, the modulus of PAA/polyol blends declines much faster than that of lactose/PAA system. The results can be referred to their different molecular structures and molecular interaction behavior with PAA. As is known, the molecular structure of lactose is rigid, and lactose is a solid product. While the molecular structure of polyol is flexible, it is also a liquid at room temperature. As is analyzed previously, there are relatively weaker hydrogen-bonding interactions in PAA/lactose, and much weaker interactions in PAA/polyol system, compared to strong self-associated carboxylic acid dimer in
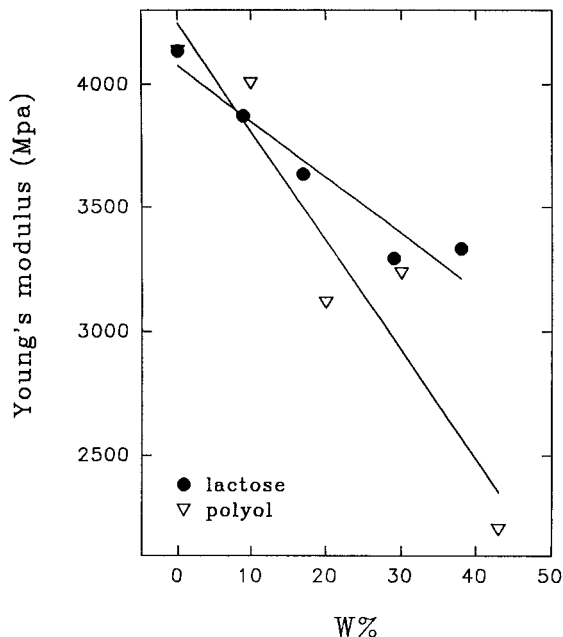

Figure 10 Young's modulus of PAA/lactose and PAA/polyol blends vs weight percentage of lactose and polyol.
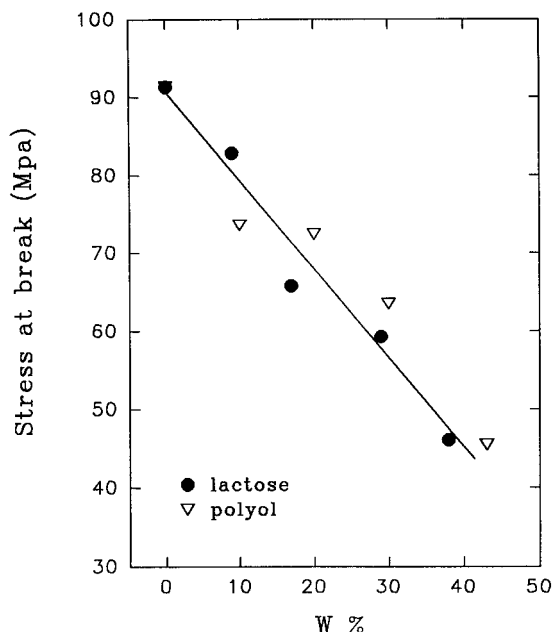
Figure 11 Stress at break for PAA/lactose and PAA/polyol blends vs of weight percentage of lactose and polyol.

pure PAA. This may be a main reason to cause the reduction of modulus of both systems. On the other hand, as polyol is much more flexible than lactose, its blending system should possess relatively lower modulus, compared to the lactose/PAA system. Figure 11 presents the stress at break vs weight percentage of lactose and polyol. Clearly, both systems not only have lower mechanical strength, but also the stress at break decreases with the increase in small molecules content. Because pure PAA is a strong associated polymer, at a completely dried state, the tensile property of PAA samples usually presents a brittle fracture at room temperature. The mechanical test shows that both blending systems exhibit typically brittle fracture behavior; therefore, the mechanism for fracture should be involved in the formation of stress-induced microcracks.[10] Actually, lactose and polyol my act as foreign additives in PAA matrix; as a result, decrease their stress

at break following the increase in component of small molecules.

CONCLUSIONS

Infrared spectroscopic analysis, DSC, TGA, and stress–strain tests can be used to study the blending systems of PAA/lactose and PAA/polyol. The IR bands of carbonyl and hydroxyl stretching vibration in PAA/lactose blends exhibit shifting around 1700 and 3400 cm^{-1}, respectively. This may imply the existence of hydrogen-bonding interactions between two compounds. DSC data show that, below 17% lactose, PAA/lactose is miscible. At the higher content, phase separation happens for PAA/lactose blends. The glass transition temperature, Young's modulus, and stress at break decrease with increasing lactose and polyol contents for both blending systems. The results indicate that hydrogen-bonding interaction between PAA and lactose may be weaker than carboxylic acid association in pure PAA.

REFERENCES

1. Fan, X.-D.; Hsieh, Y.-L.; Krochta, L. M. J Appl Polym Sci, in press.
2. Lu, X.-Y.; Weiss, R. A. Macromolecules 1995, **28**, 3022.
3. Wison, M. E.; Hu, M.-H.; Kurth, M. J.; Hsieh, Y.-L.; Krochta, J. M. J Appl Polym Sci 1996 59,1759.
4. Lee, Y. J.; Painter, P. C.; Coleman, M. M. Macromolecules 1988, 21, 954.
5. Coleman, M. M.; Yang; X.-M.; Painter, P. C. Macromolecules 1992, **25**, 4414.
6. Zadow, J. G. Whey and Lactose Processing; Elsevier Applied Science: New York, 1993.
7. Sebhatu, T.; Elamin, A. A.; Ahineck, C. Pharmaceut Res 1994, 11(9),1233.
8. Maurer, J. J.; Eustace, D. J.; Ratcliffe, C. T. Macromolecules 1987, 20, 196.
9. Vazquez-Torres, H.; Cauich-Rodriguez, J. V.; Cruz-Ramos, C. A. J Appl Polym Sci 1993, 50, 777.
10. Kinloch, A. J.; Young, R. J. Fracture Behaviour of Polymers; Applied Science Publishers: London, 1983.