

# Thermomechanical Behavior of Poly(vinyl alcohol) and Sugar Cane Bagasse Composites

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**ABSTRACT:** Fibers from renewable resources are gaining interest for use as fillers in hybrid composite materials. Particularly waste material such as sugar cane bagasse offer large availability, biodegradability, and low cost. Influence of single components on composite material properties is an important parameter to be evaluated. Composites of poly(vinyl alcohol) (PVA) at 88 and 98% saponification degrees and sugar cane bagasse (B) were prepared by casting water suspensions of the components and characterized for their dynamic mechanical behavior. The storage modulus below and above the glass transition and the shape of the relax-

ation process are strongly influenced by the amount of B. Good adhesion was observed at the lignocellulosic fiber-synthetic polymer interface. Urea and glycerol are able to plastify the PVA/B composites thus giving rise to a decrease of the glass transition temperature and to a widening of the glass transition temperature gap. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 426–432, 2004

**Key words:** poly(vinyl alcohol); sugar cane bagasse; lignocellulosic fillers; composite films; dynamic mechanical analysis

## INTRODUCTION

Thermoplastic composites based on synthetic polymers and various amounts of organic fillers from renewable resources are very interesting as low environmental impact materials.<sup>1</sup> The need for economically feasible degradable products, which do not adversely affect the environment upon disposal, has intensified the attention for alternate sources of raw material plastic items. Raw material availability and production cost are a limiting factor for the introduction into the market of new plastic items, which have to compete with low cost commodity items based on relatively cheap polymeric materials such as poly(ethylene) or poly(vinyl chloride); the research interest has moved toward inexpensive materials, such as agriculture by-products with non-food industry competition.<sup>2–5</sup> Not only does production of such composites allow for the use of natural, eco-compatible, and eventually biodegradable materials, but it also revalues by-products bound to become waste. In Brazil 50% of sugar cane production (311 Mt/y) is used for ethanol production, and these volumes are expected to increase further in the future.<sup>3</sup> Successful blending of synthetic polymers with starch or lignocellulosic materials depends on matching the structural properties

and interaction characteristics of the polymeric components. Breaking the inter- and intrachain hydrogen bonds of natural polymers to establish new interactions between the natural polymer and the added synthetic polymer is one possible approach. Indeed, the hydrophilic character of the fillers makes difficult their blending with hydrophobic polymers unless compatibilizing agents are added.<sup>6,7</sup> However, this approach often is too expensive and production procedures become rather complicated. In this respect, poly(vinyl alcohol) (PVA) can be selected as the synthetic component because hydroxyl and carboxyl groups are suitable for hydrogen bonding, thus resulting in a good compatibility with natural heterofunctional fillers. In addition, PVA is water soluble, thus allowing for film productions by casting of water suspensions of the components. In the past, PVA and starch films were prepared by casting and melt blow extrusion<sup>8–11</sup> and the resulting products were suitable for use as agricultural mulch films and water-soluble laundry bags.<sup>12</sup> In addition, PVA and cellulosic materials presented good miscibility in casting films probably because of their mutual capability to form strong intra- and intermolecular hydrogen bonds.<sup>13</sup> Intermolecular interactions were also observed in PVA and  $\beta$ -chitin composites<sup>14</sup> as well as in PVA and chitosan or pectin composites.<sup>15</sup>

As a part of our continuing research program aimed at the preparation and evaluation of environmentally degradable polymers for various applications in agri-

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cultural practices, with specific reference to the *in situ* formulation of self-fertilizing mulching films, we considered the possibility of producing degradable films based on PVA and lignocellulosic fillers by casting or spraying water suspensions of the polymeric components.<sup>16</sup> Sugar cane bagasse (B) presence in PVA-based water suspensions showed enhanced PVA soil structuring effect and time of duration of the treatment applied on the soil.<sup>17</sup> Moreover the presence of lignocellulosic fillers in composites bound to degrade directly in the field provide the added value effect of releasing the lignocellulosic in the soil, which will convert to humic substances, with positive agronomic effects. Mechanical properties of the PVA/lignocellulosics composites are related to the polymer/fiber ratio and to the type and amount of plasticizers introduced in the formulation.<sup>18</sup>

Thus studying the effect of a single component of the hybrid composites on thermomechanical properties is an important tool to select formulations and to understand component interactions.

In this paper, we report the thermomechanical behavior of composite based on PVA and B composites as a function of the polymer/filler ratio and of the type and amount of selected plasticizer. B is the exhausted fiber left from crushing sugar cane to facilitate extraction of sugar juice. B is not a homogeneous material, it is indeed constituted by fibers with a small fraction characterized by a spherical shape.<sup>19</sup> PVA is produced by hydrolysis of poly(vinyl acetate) and commercially different grades at different amounts of residual acetate groups are available, which result in significant property variations. In particular, the Young's modulus, the ultimate strength, and the glass transition temperature depend on the hydrolysis degree. The water solubility of PVA reaches its maximum at 87–89% saponification degree.<sup>20</sup> Further increase in the hydrolysis degree results in an increased water resistance because of the occurrence of higher levels of intramolecular hydrogen bonding. Accordingly, in the present study two different grades of PVA (hydrolysis degree of 88 and 98%) were employed.

Since these composites should be employed as mulching films for agriculture or horticulture applications, urea was introduced in the compositions as a plasticizer and fertilizing agent. Consequently, the effect of urea and urea-glycerol content on the thermomechanical properties of the composites was also evaluated.

## METHODS

### Materials

PVA Mowiol 08/88 (PVA88), having  $M_w$  67 kDa and 88% degree of saponification, and Mowiol 10/98 (PVA98), having  $M_w$  61 kDa and 98% degree of sa-

**TABLE I**  
Compositions of the Tested PVA/B Composite Films

Sample	PVA <sup>a</sup> (wt-p)	B (wt-p)	Urea (wt-p)	Glycerol (wt-p)
PVA	100	0	—	—
PB10	90	10	—	—
PB30	70	30	—	—
PB50	50	50	—	—
PBU10	100	100	10	—
PBU30	100	100	30	—
PBU50	100	100	50	—
PBGU10	100	100	10	10
PBGU30	100	100	30	30
PBGU50	100	100	50	50

<sup>a</sup> PVA was, respectively, Mowiol 08/88 and Mowiol 10/98; wt-p, weight parts.

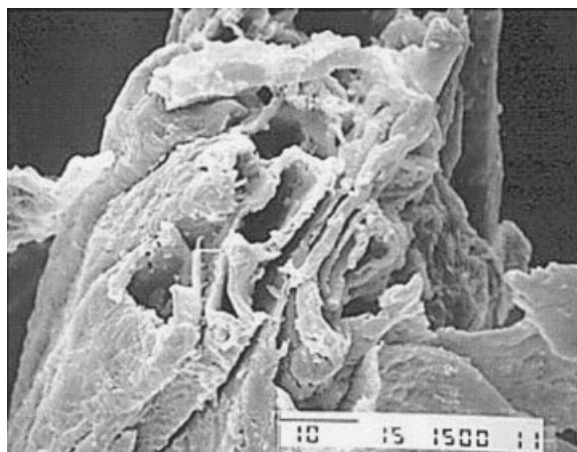
ponification, were purchased from Hoechst and used as received. B was kindly supplied by Copersucar (Brazil). Before use, fibers were thermally conditioned in an oven at 50°C for 24 h and grinded with a blade grinder. The resulting powder was sieved and the fraction passing through a 70-mesh sieve (0.212 mm) was collected and used in the preparations. B was analyzed at the Faculty of Agriculture, University of Pisa, and its composition was crude fibers 42.6%, cellulose 29.2%, lignin 10.5%, crude protein 9.1%, fat 2.6%, and ash 6.0%. Reagent grade glycerol and urea were purchased, respectively, from Baker and Carlo Erba. They were used as received.

### Preparation of the composites

Stock solutions of PVA with a concentration of 10.0% by weight were prepared by dispersion of the polymer in cold water and then by heating the dispersion under vigorous stirring for 60 min at a temperature that depends on the degree of saponification: 80°C for 88% degree of saponification and 90°C for 98% degree of saponification. The resulting PVA solutions remained clear once cooled down at room temperature. The PVA solutions were stored at 4°C before their use to avoid bacterial attack. The composites were prepared by sequential addition under stirring of PVA solution, urea and/or glycerol, and B. Water was added to obtain a 10% by weight of the overall concentration. The resulting viscous brown suspension was stirred for 1 h at 80°C. Water was added to compensate for evaporation during the heating process. Compositions of the prepared composites are reported in Table I.

### Film preparation

Twenty grams of the water suspension prepared as above was poured in an 8-cm-diam Teflonated plate. The plate was left for 24 h at room temperature and then heated in an oven at 50°C for 2 h and finally



**Figure 1** SEM micrograph (1500 $\times$ ) of sugar cane bagasse (B) fibers.

cooled down to room temperature before removing the formed films. Prior to testing, the samples were stored for 7 days in a desiccator under 50% relative humidity as generated by 45%  $\text{H}_2\text{SO}_4$  (ASTM E 104–85).

#### Dynamic mechanical analysis (DMA)

Rectangular 5  $\times$  10 mm strips of cast films were analyzed by a Perkin–Elmer DMA-7 dynamic-mechanical analyzer, employing extension geometry. In each set of dynamic mechanical measurements, a 150% static-to-dynamic stress ratio was chosen. Time–temperature scans were recorded at 4 $^\circ\text{C}/\text{min}$  heating rate and at 1 Hz frequency. Film thickness was determined by averaging three measurements along the test length using a pocket thickness gauge from RS.

#### Scanning electron microscopy (SEM)

SEM inspections of PVA and B composites were carried out by a Jeol T300 scanning electron microscope. The film samples were prepared by critical point drying, sputtered with gold, and observed at 10 KeV.

## RESULTS AND DISCUSSION

A SEM micrograph of sieved B fibers is shown in Figure 1. Fiber diameter and length ranged from about 10–50 to 100–400  $\mu\text{m}$ , respectively. Low density and high volume-to-weight ratio of B strongly influenced the mechanical properties of the prepared composites. B was not able to form films by casting from water and only a fibers aggregate was obtained.

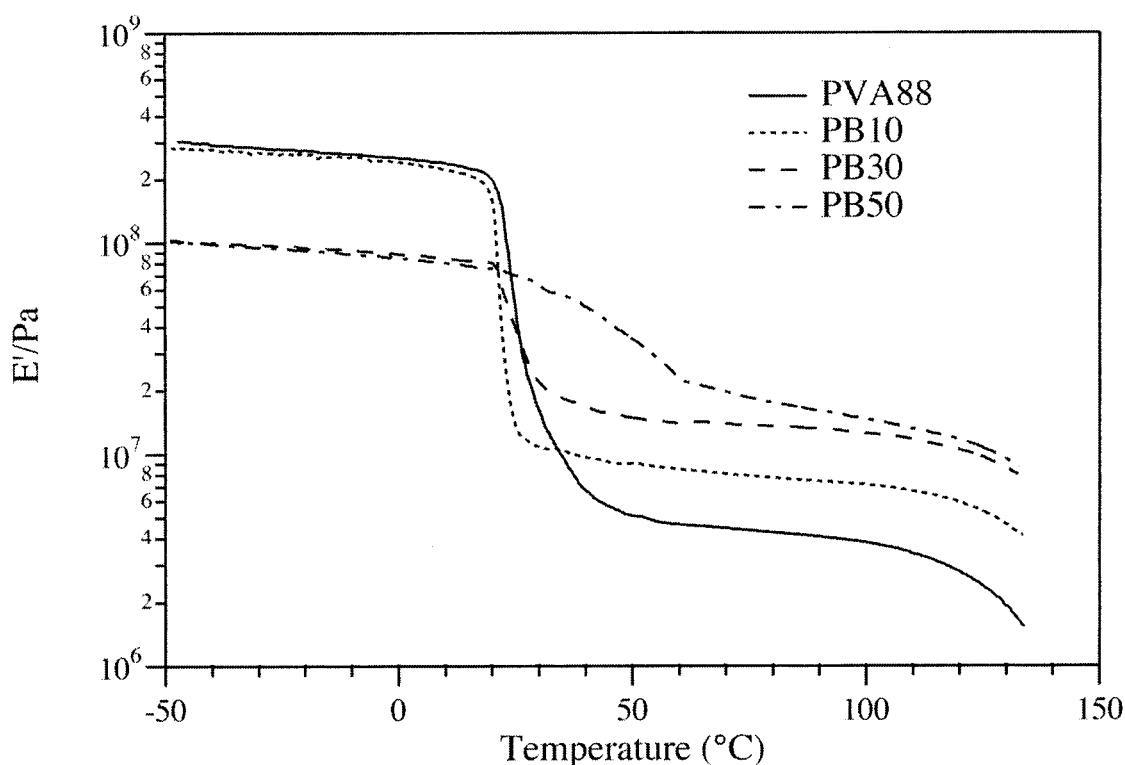
By contrast, self-sustaining cast films were prepared at different PVA/B weight ratios. In particular, three compositions were employed: PVA/B = 90/10, 70/30, and 50/50. The various composites were marked PB*n*

where *n* is the % wt of B. Thickness of the cast films increased progressively from 0.3 to 0.6 mm, with the fibers content increasing from 10 (PB10) to 50% (PB50). With a filler content of 10%, films were translucent but became opaque above 30% of B. As the amount of B increased, a substantial increase in brittleness and a decrease of flexibility was observed. No appreciable difference was detected between films prepared with PVA at 88% (marked PVA88) or 98% (marked PVA98) degree of saponification whereas the films also containing glycerol or urea appeared more flexible and soft.

The trend of the storage modulus  $E'$  of PVA88 and PB*n*, as a function of the temperature, is shown in Figure 2. A relaxation, centered at about 25 $^\circ\text{C}$  and corresponding to the glass transition of either PVA or the PVA component of the blend, was observed for all the samples. The glass transition temperature ( $T_g$ ) of the PVA was not substantially influenced by the amount of B, although an increase of the  $T_g$  was observed at compositions above 30% of B. Both the values of the modulus below and above the transition and the shape of the relaxation process were strongly influenced by the amount of B. In particular, the storage modulus increased above  $T_g$  and decreased below  $T_g$  as the amount of B increased. A concomitant spreading of the glass transition process was observed. The modulus increase above the  $T_g$  with the increasing content of B is probably due to the reinforcing effect of B on PVA. This suggests a good compatibility of PVA with B, in agreement with the SEM picture of a fracture of PVA/B composites (Fig. 3) that indicates a good adhesion at the lignocellulosic fiber–synthetic polymer interface. Figure 4 illustrates the temperature dependence of  $\tan\delta$  for PVA88 and PB*n* films. Indeed, for sample PB30 the relaxation process appears structured into two components that can be tentatively attributed to the glass transition of the pure PVA and to the transition of PVA interacting with fibers. This second transition becomes the prevailing one for sample PB50. A similar behavior was reported for systems consisting of pectin and PVA.<sup>21,22</sup>

The effect of urea was studied starting from a composition of 100 weight parts of B in 100 weight parts of PVA (PB50) and progressively increasing the amount of urea from 0 to 10, to 30, and to 50 weight parts to give PBU10, PBU30, and PBU50 samples, respectively (Table I). Figures 5 and 6 show the temperature variation of  $E'$  and  $\tan\delta$  for the above samples.

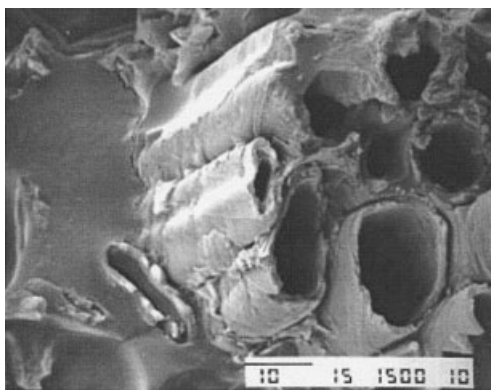
A significant widening of the glass transition process is observed for increasing amounts of urea. The storage modulus decreased after  $T_g$  as the amount of urea increased. This behavior is attributed to a plasticizing action of urea on PVA/B composites. Thus  $T_g$  is shifted by an increasing urea content from 53 $^\circ\text{C}$  of PB50 to 21 $^\circ\text{C}$  of PBU50.



**Figure 2** Temperature variation of storage modulus (1 Hz frequency) of PVA88/B composites containing 10 (PB10), 30 (PB30) and 50% by weight (PB50) of B.

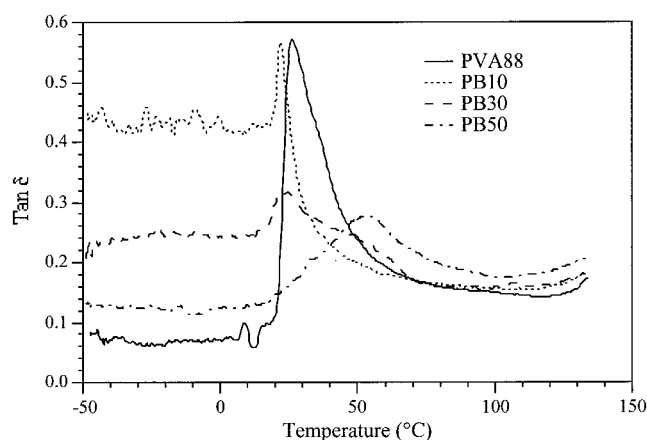
The trend of the  $\tan\delta$  curve presents a progressive widening with an increasing urea amount, particularly for PBU30 and PBU50. The  $\tan\delta$  curve of PBU50 presents a shoulder at about 10°C (Fig. 6). The observed structuring of the transition suggests a certain degree of heterogeneity in the urea distribution inside these composites. The reported trends indicated that urea was able to plastify the PVA/B blend, thus for amounts of urea over 30 weight parts, heterogeneity is observed.

Glycerol is a commonly used plasticizer for PVA and for PVA composites with natural polymers. The

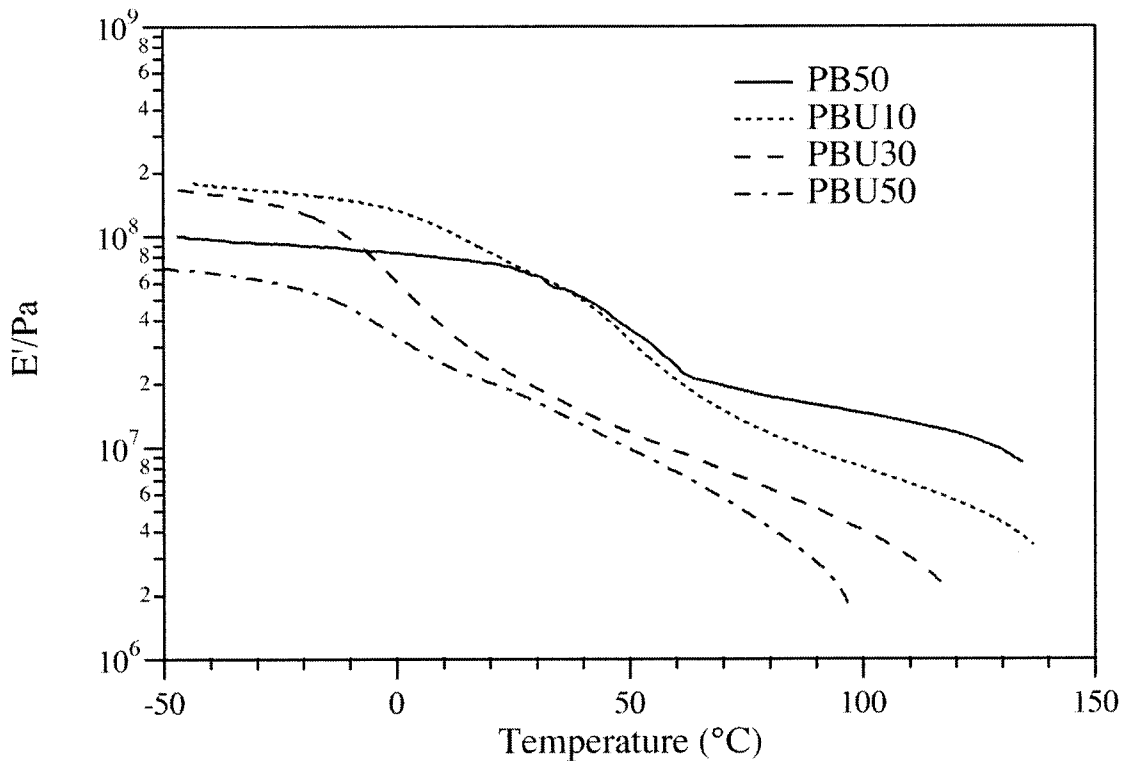


**Figure 3** SEM micrograph (1500 $\times$ ) of the cold fracture of PB50.

addition of equal amounts of urea and glycerol, leading to samples PBGU $n$ , where  $n$  indicates the amount of both urea and glycerol, produced a substantial decrease of the storage modulus, at temperatures above the glass transition (Fig. 7) and an additional widening of the transition process. Sample softening was also observed shortly after  $T_g$ .  $T_g$  is shifted by increasing urea/glycerol content from 53°C of PB50 to 16°C of PBUG50. The trend of the  $\tan\delta$  curve presents a pro-



**Figure 4** Temperature variation of  $\tan\delta$  (1 Hz frequency) of PVA88 and PB $n$  composites containing 10 (PB10), 30 (PB30) and 50% by weight (PB50) of B.

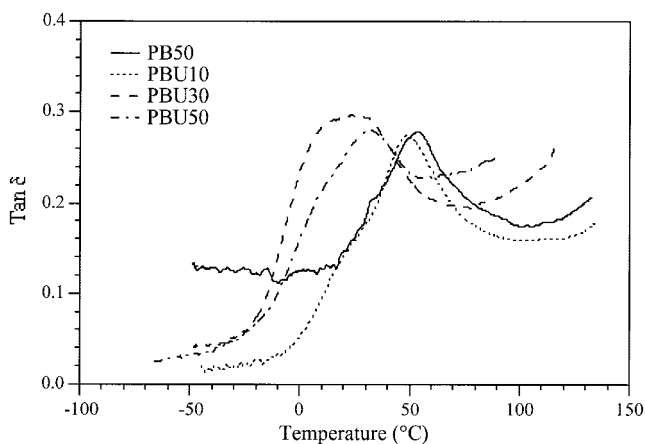


**Figure 5** Temperature variation of storage modulus (1 Hz frequency) of 100:100 PVA88/B composites, containing 0 (PB50), 10 (PBU10), 30 (PBU30), 50 (PBU50) parts by weight of urea.

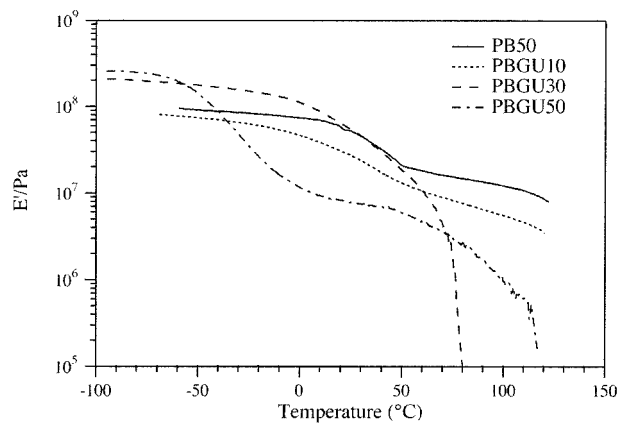
gressive widening with increasing of urea/glycerol amount (Fig. 8). This effect is particularly stressed in PBUG50, which presents several shoulders and suggests a certain degree of heterogeneity and loss of cohesiveness for this sample.

A similar comparison was made for samples in which PVA98 replaced PVA88. The addition of B at the PVA98 matrix produced an increase in the storage modulus at temperatures above the glass transition as

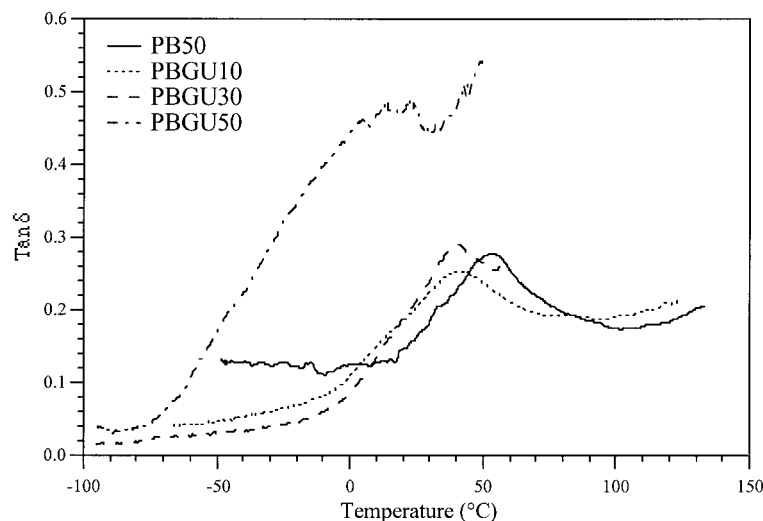
observed for PVA88-based samples. Interestingly, at temperatures below the glass transition, storage modulus increased for B content of 10 and 30%, from  $3 \times 10^8$  Pa (PVA98) to  $1 \times 10^9$  Pa (PB10, PB30), while for 50% of B (PB50), the storage modulus was similar to PVA98. A parallel spreading of the glass transition process with an increase of B percentage was observed. This indicates an efficient reinforcing effect on the PVA matrix by B, possibly due to the higher con-



**Figure 6** Temperature variation of  $\tan \delta$  (1 Hz frequency) of 100:100 PVA88/B composites, containing 0 (PB50), 10 (PBU10), 30 (PBU30), 50 (PBU50) parts by weight of urea.



**Figure 7** Temperature variation of storage modulus (1 Hz frequency) of 100:100 PVA88/B composites, containing 0 (PB50), 10 (PBGU10), 30 (PBGU30), 50 (PBGU50) parts by weight of both urea and glycerol.



**Figure 8** Temperature variation of  $\tan \delta$  (1 Hz frequency) of 100:100 PVA88/B composites, containing 0 (PB50), 10 (PBUG10), 30 (PBUG30), 50 (PBUG50) parts by weight of both urea and glycerol.

tent of hydroxyl groups in PVA98. Similar to what was observed for samples based on PVA88, the  $T_g$  increased significantly just for PB50 (Table II) in the absence of urea and glycerol.

The addition of urea in PVA/B composites produced a consistent decrease of the  $T_g$  (Table II) from 35°C of PB50 to 6°C of PBU50. Interestingly, for PVA98-based samples, the plasticizing effect of glycerol was more consistent and  $T_g$  was additionally lowered up to -40°C of PBUG50. With the addition of urea and urea/glycerol a widening of the relaxation process, qualitatively similar to that observed for PVA88 composites, was also observed.

## CONCLUSION

Several water suspensions of PVA at 88 and 98% degree of saponification and B were prepared to give,

**TABLE II**  
Glass Transition Temperature of Composite Films Based on PVA88 and PVA98

Sample <sup>a</sup>		Sample <sup>b</sup>	
Type	$T_g$ (°C)	Type	$T_g$ (°C)
PVA88	26	PVA98	27
PB10	22	PB10	22
PB30	23	PB30	23
PB50	53	PB50	35
PBU10	49	PBU10	33
PBU30	32	PBU30	10
PBU50	21	PBU50	6
PBGU10	41	PBGU10	6
PBGU30	39	PBGU30	-9
PBGU50	16	PBGU50	-40

<sup>a</sup> Sample based on PVA88.

<sup>b</sup> Sample based on PVA98.

by casting, composites whose dynamic mechanical behavior was investigated. The addition of glycerol and urea in the formulations produced a significant effect on the relaxation properties of the composites. The  $T_g$  of both PVA samples was not substantially influenced by the amount of B, although an increase in the  $T_g$  was observed at B contents above 30%. However, the values of the modulus below and above the glass transition and the shape of the relaxation process were strongly affected by the amount of B. In particular, the storage modulus decreased below the  $T_g$ , for PVA88 composites, but increased for PVA98 composites upon increase of the B content. In both cases, an increase of the storage modulus was observed at temperatures above the  $T_g$ . This indicates a good adhesion at the lignocellulosic fiber-synthetic polymer interface as confirmed also by SEM analysis of the composites. The addition of urea and glycerol resulted in plastification of the PVA/B composites, thus producing a decrease of the  $T_g$  in the relevant cast composite laminates and a widening of the relaxation process for both composites based on PVA88 and PVA98.

## References

- Vogl, O. J. *Macromol. Sci, Pure Appl Chem* 1996, A33, 363.
- De Graff, L. A.; Kolster, P. *Macromol Symp* 1998, 127, 51.
- Doane, W. M. *J Polym Mater* 1994, 11, 229.
- Feil, H. *Macromol Symp* 1998, 127, 7.
- Steinbüchel, A. *J Macromol Sci, Pure Appl Chem* 1995, A32, 635.
- Mucha, M.; Pieklielna, J.; Wieczorek, A. *Macromol Symp* 1999, 144, 391.
- Rowell, R. M.; Sanadi, A. R.; Caulfield, D. F.; Jacobson, R. E. In *First International Lignocellulosics-Plastics Composites*, March 13-15 1996, Sao Paolo, Brazil; Leao, A. L.; Carvalho, F. X.; Frollini, E., Eds.; 1997, p. 23.
- Otey, F. H.; Mark, A. M.; Mehlretter, C. L.; Russell, C. R. *Ind Eng Chem Res* 1974, 13, 90.

9. Otey, F. H.; Westhoff, R. P.; Doane, W. M. *Ind Eng Chem Res* 1987, 26, 1659.
10. Lahalih, S. M.; Akashah, S. A.; Al-hajjar, F. H. *Ind Eng Chem Res* 1987, 26, 2366.
11. Chen, L.; Imam, S. H.; Gordon, S. H.; Greene, R. V. *J Environ Polym Degrad* 1997, 5, 111.
12. Otey, F. H.; Doane, W. M. In *Starch Chemistry and Technology*; Whistler, R. L.; Bemiller, J. M.; Paschall, E. F., Eds.; Academic Press: New York, 1984; 2nd ed., p. 389.
13. Nishio, Y.; St J Manley, R. *Macromolecules* 1988, 21, 1270.
14. Lee, Y. M.; Kim, S. H.; Kim, S. J. *Polymer* 1996, 37, 5897.
15. Fishman, M. L.; Coffin, D. R.; Unruh, J. J.; Cooke, P. H. *Polym Mater Sci Eng* 1995, 72, 181.
16. Kenawy, E. R.; Cinelli, P.; Corti, A.; Miertus, S.; Chiellini, E. *Macromol Symp* 1999, 144, 351.
17. Bargiacchi, E.; Chiellini, E.; Cinelli, P.; Corti, A.; Magni, S.; Miele, S. U.S. Patent Application 09 450 016, 1999.
18. Chiellini, E.; Cinelli, P.; Imam, S. H. *Biomacromolecules* 2001, 2, 1029.
19. Nassar, M. M.; Ashour, E. A.; Swahid, S. *J Appl Polym Sci* 1996, 61, 885.
20. Okaya, T. In *Polyvinyl Alcohol Development*; Finch, C. A., Ed.; Wiley: Chichester, UK, 1992, p. 4.
21. Coffin, D. R.; Fishman, M. L.; Ly, T. V. *J Appl Polym Sci* 1996, 57, 71.
22. Coffin, D. R.; Fishman, M. L. *J Appl Polym Sci* 1994, 54, 1311.