

Tensile Properties of Thermoplastic Starch-PVB Blends

C. Sita,¹ M. Burns,¹ R. Häßler,² W. W. Focke¹

¹*Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria, Lynwood Road, Pretoria 0001, South Africa*

²*Leibniz-Institute of Polymer Research, Hohe Str. 6, Dresden D-01069, Germany*

Received 5 April 2005; accepted 15 October 2005

DOI 10.1002/app.23512

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Blends of thermoplastic starch and recycled polyvinylbutyral from automotive windscreens were investigated. Mechanically compatible blends are formed at low to intermediate starch content. However, scanning electron microscopy and dynamic-mechanical analysis revealed a phase-separated nature for all blend compositions investigated. Tensile properties are negatively affected by aging in a high humidity environment and they deteriorate rapidly when the samples are soaked in water. Synergistic property

enhancement was observed for a compound containing 22% thermoplastic starch. It features a higher tensile strength, shows better water resistance, and is significantly less affected by aging. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1751–1755, 2006

Key words: starch; polyvinyl butyral; polymer blends; recycling; mechanical properties

INTRODUCTION

Thermoplastic starch (TPS) is a translucent amorphous material that looks and feels much like conventional plastics. It is obtained by “gelatinising” native starch in the presence of suitable plasticizers such as water or glycerol.^{1,2} A controlled extrusion-compounding process can achieve this: applying gentle heating and high shear causes the starch granules to absorb the plasticizers, allowing them to melt at a reduced temperature without decomposing.^{1–4} The TPS exiting the extruder is a viscous melt that can be shaped into pellets that can be injection molded into a variety of articles just like conventional plastics.

Plain TPS is inexpensive and biodegrades quickly. However, it has limited water resistance; properties and dimensional stability are influenced by moisture (humidity); it does not process as easily as conventional plastics; and the freshly molded material ages, i.e., its properties change over time.^{3–6} The latter is caused by retrogradation:^{4,7} the structural changes that include helix formation and crystallization that occur above the glass transition temperature.

The unacceptable physical and processing properties of TPS can be improved by blending with other polymers. To retain biodegradability, it is conven-

tional to use other biodegradable polyesters such as poly- ϵ -caprolactone, polyhydroxy butyrate, and polylactic acid.⁸ In this study, we considered the use of recycled polyvinyl butyral as a TPS-modifying agent.

Polyvinyl butyrate (PVB) is used primarily in the manufacture of safety glass, e.g., in vehicle windscreens and buildings. In the event of the glass shattering, the PVB interlayer acts as an energy absorber, holds broken glass fragments together, and prevents shard formation. The PVB used in safety glass comprises typically 55–70% PVB, with 30–45% plasticizer. The standard plasticizer for windscreen laminates is triethylene glycol di-2-ethyl hexanoate, but others, e.g., dibutyl sebacate, may also be used.

Large quantities of PVB are recovered from scrap windscreens through a mechanical delamination process. There is, however, very little interest in recycling this postconsumer waste stream because of a lack of suitable markets and the contamination with residual glass fragments.^{9,10} Consequently, it is disposed off in landfill or incinerated. Nevertheless, some PVB is recycled but this is, in the main, limited to recovered factory off-cuts.

The compatibility of PVB with other polymers is important, as it is likely that the end use for the recovered PVB will be in a PVB-polymer mixture, especially where the PVB imparts a useful effect on the blend properties. The objective of this work was to investigate the properties of TPS blends with recycled PVB.

EXPERIMENTAL

Vest Designs supplied the recycled PVB. It consisted of shredded off-cuts from the manufacture of automo-

Correspondence to: W. W. Focke (e-mail: walter.focke@up.ac.za).

Contract grant sponsors: THRIP program of the Department of Trade and Industry and the National Research Foundation of South Africa; African Products (Pty) Ltd.

tive windscreens. Metadynamics supplied anhydride (gypsum) powder with a mean particle size of 2 μm . Two PVB compounds, containing this filler, were prepared on a Berstorff 40 mm twin screw, corotating compounding extruder with an L/D of 42. First, a 66.6% compound was made and this was then diluted by re-extrusion with an equal mass of neat PVB.

Samples of HiMaizeTM were supplied by African Products. It is a commercial starch with an amylose content of 70%. The TPS compound was based on the following formulation: 66% HiMaizeTM, 15% glycerol, 15% water, 1.5% stearyl alcohol, and 2.5% precipitated silica. The native starch powder was preblended with the plasticizers and processing additives in a high-speed mixer. Thereafter, the mix was gelled using a 25 mm single screw laboratory extruder with an L/D ratio of 25. The conditioned TPS granules were used to prepare blends with PVB using the same laboratory extruder. The temperature profile along the barrel was 105–120°C at the feed section, 110–145°C at the compression and metering zones, and ~100°C at the die zone. The higher temperatures were required for blends containing higher amounts of starch.

Tensile test specimens, conforming to ASTM D638m, were injection molded using an Engel 3040 machine with an 800 kN clamping force. It was necessary to optimize the injection molder settings for each formulation to ensure flash-free mold filling without causing part warpage. Typical barrel temperatures, from the feeding zone to the nozzle, were as follows: 100–120°C/120–150°C/120–150°C/100–120°C.

The molded test specimens were conditioned at 30°C and 60% RH or were soaked in water at ambient to determine water resistance. Tensile tests were performed at 50 mm/min on a Model 4303 Instron machine.

The dynamic mechanical analysis (DMA 2980 from TA Instruments) was done on cut-offs from the tensile specimens that were conditioned for at least 30 days at 30°C and 60% RH. The DMA data were determined in bending mode (single cantilever clamp) at a frequency of 10 Hz and a heating rate of 1 K/min in a temperature range from –20 to 100°C.

X-ray diffraction (XRD) analysis was performed on a Siemens D-501 automated diffractometer. Low magnification scanning electron microscopy (SEM) images of fracture surfaces on gold-coated samples were obtained on a JEOL 840 SEM. SEM samples were prepared as follows: tensile dog bone specimens were fractured after immersion in liquid nitrogen. Small broken pieces were exposed for 2 days at 70°C to a 0.5% amylase suspension. The enzyme was Termamyl[®] 120L supplied by Novozymes. After exposure, the samples were recovered, repeatedly washed with distilled water, and dried at 35°C.

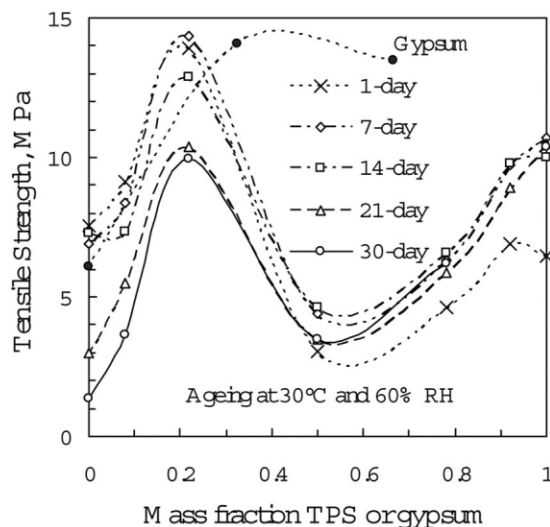


Figure 1 The effect of aging at 30°C and 60% RH on the tensile strength of TPS–PVB blends. Also shown are properties for the anhydride-filled PVB compounds tested after 14 days aging.

RESULTS AND DISCUSSION

The moisture content of the neat polymers and the blends increased during equilibration at 30°C and 60% RH. For the TPS, it was 2.4% and 3.6% after 14 and 30 days, respectively. By comparison, the moisture content of the recycled PVB after 30 days was 1.3% whereas for the blends with 22, 50, and 78% TPS, it was ~1.8%.

Figures 1 to 3 show the effect of aging at 30°C and a humidity of 60% RH on the tensile properties of the TPS–PVB blends and the gypsum (anhydride)-filled PVB. The tensile strength and Young's modulus of the neat TPS sample increase with aging because of retrogradation.^{4,7} For the neat PVB, the opposite is true and this is attributed to an increase in moisture content. Water apparently also plasticizes the PVB and thereby lowers its glass transition temperature and its tensile properties. The modulus of the plasticized PVB is rubber-like and decreases from ~5 MPa to 1 MPa on aging (Fig. 2). The modulus increases by two orders of magnitude, in a nearly log-linear manner, as the TPS content is increased to 100%. The moduli of the gypsum-filled PVB show a similar trend, also falling on a straight line. The modulus of the 33.3% gypsum-filled PVB compound is similar to those measured for TPS–PVB blends but the value at 66.6% gypsum is lower.

The elongation-to-break (ϵ_B) of neat the TPS compound shows a strong decrease in ϵ_B with time. This correlates with an increasing brittleness of these samples and is attributed to the retrogradation of the starch compound.⁷ The PVB and the blends rich in PVB are not much affected by aging (Fig. 3). The blends with 22% or less of PVB have elongation-to-break (ϵ_B) of less than 40%, i.e., similar to that of the

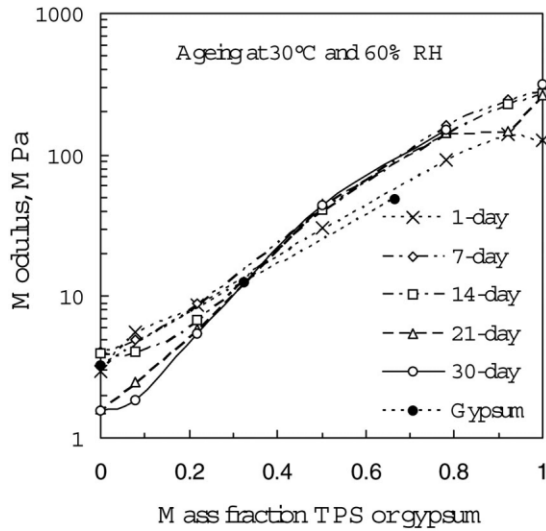


Figure 2 The effect of aging at 30°C and 60% RH on the tensile modulus of TPS–PVB blends. Also shown are properties for the anhydride-filled PVB compounds tested after 14 days aging.

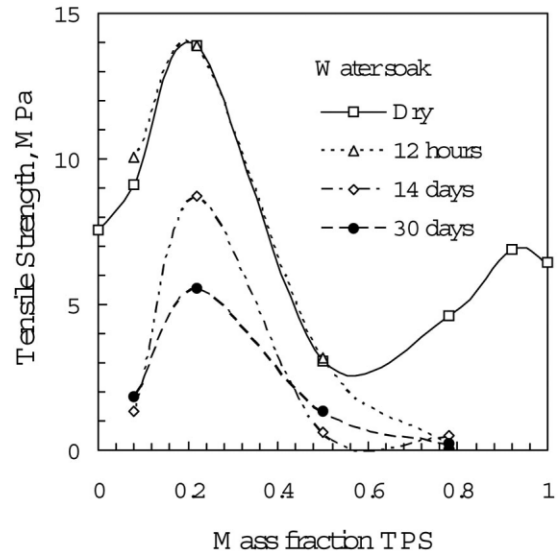


Figure 4 The effect of water soak on the tensile strength of TPS–PVB blends.

starch-based TPS. The ϵ_B exceeds 200% for blends containing 50% or more of PVB. This suggests that the continuous phase properties approach PVB behavior down to 50% PVB. The ϵ_B of the gypsum-filled PVB compound fall below the values obtained for the blends.

In general, the tensile strength of the blends that contain 50% or more TPS is lower than expected from the linear blending rule. However, the 22% TPS compound shows significantly higher values that are comparable with those achieved with gypsum as reinforc-

ing filler in PVB. In the latter case, the tensile strength at the higher filler loading is slightly reduced. However, it is still much higher than the values for the TPS–PVB blends containing 50% or more TPS.

While the 22% TPS compound also showed property losses on aging, it offered the best water resistance: Figure 4 shows that it was the only composition tested that retained a significant portion of its tensile strength in the water soak tests. Noteworthy is the complete loss of mechanical properties for the high starch content blends where the starch forms the continuous phase.

Figure 5 shows the DMA determined $\tan \delta$ results obtained in the -20 to 80°C temperature window. The

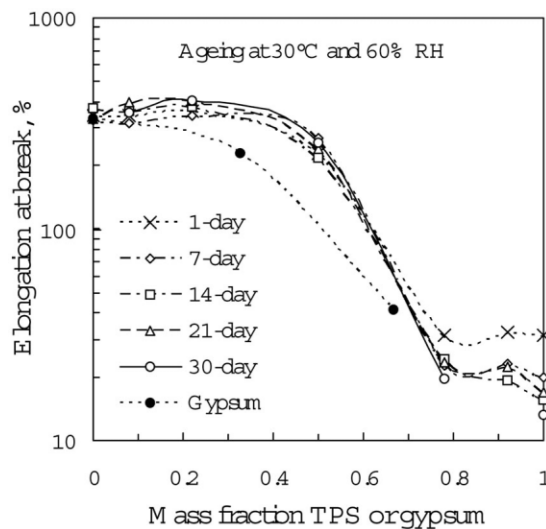


Figure 3 The effect of aging at 30°C and 60% RH on the elongation-at-break of TPS–PVB blends. Also shown are properties for the anhydride-filled PVB compounds tested after 14 days aging.

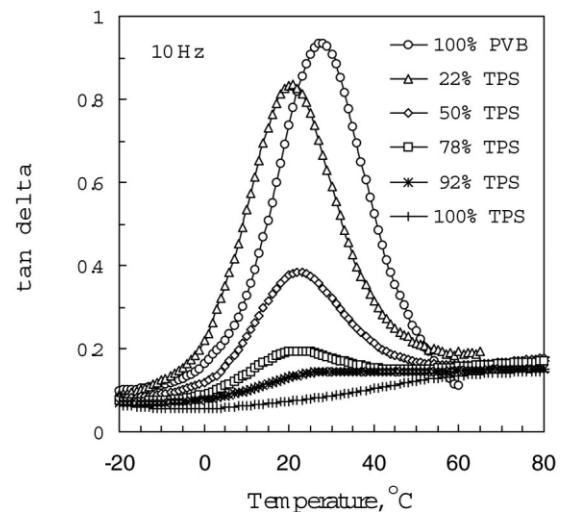


Figure 5 $\tan \delta$ at 10 Hz for TPS–PVB blends aged at 30°C and 60% RH for at least 30 days.

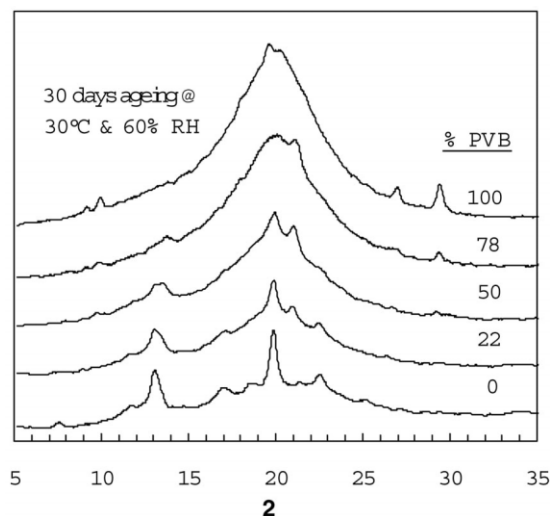


Figure 6 XRD spectra of TPS–PVB blends aged for 30 days at 30°C and 60% RH.

neat PVB shows a strong loss peak at 28°C. The neat TPS showed a weak loss peak below -45°C and a broad, but weak loss feature with two peaks at higher temperatures in the DMA (not shown in Fig. 5). The two high temperature peaks are located at 94°C and 126°C, respectively. Forssell et al.¹¹ also observed low and high temperature loss peaks using DSC and dynamic thermal analysis of barley starch–glycerol–water mixtures. They attributed this to phase-separation in the TPS: the system is composed of starch-rich and starch-poor regions with different glass transition temperatures (T_g s) corresponding to these two phases.

Figure 5 reveals that addition of TPS shifts the $\tan \delta$ peak temperature to a location that is about 5–7°C lower than that for the neat PVB. This could indicate a degree of compatibility between the starch and PVB. However, it is more likely that the observed lowering of the T_g is the result of the PVB phase scavenging the glycerol plasticizer from the TPS. This loss peak does not shift with changing blend composition and decreases in intensity as the TPS content is increased. These observations are consistent with a two-phase nature for the TPS–PVB blends.

XRD spectra for aged samples are presented in Figure 6. The spectrum for PVB showed a broad amorphous peak located at $\sim 2\theta = 20^{\circ}$. The TPS spectrum of TPS features two strong, sharp peaks at $2\theta = 13^{\circ}$ and 20° and also some other minor peaks. These peaks do not change much in intensity during aging. The blend with 78% TPS shows three peaks at $2\theta = 13^{\circ}$, 20° , and 21° , respectively. With aging, the first two peaks increase, whereas the third decreases in relative intensity up to the 21 day point. This indicates that the presence of PVB inhibits the crystallization of the starch. The blend with 22% TPS still shows the lower angle starch peak but it is now located at $2\theta \approx 13.5^{\circ}$.

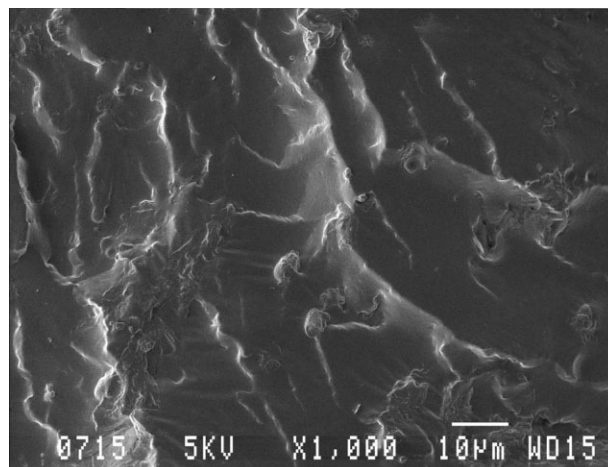


Figure 7 Scanning electron micrograph of a fracture surface of the 22% TPS containing blend.

SEM studies confirmed the two-phase structure of the TPS–PVB blends. Figures 7 and 8 show fracture surfaces for the 22% TPS blend, before and after enzyme erosion. On exposure to the enzyme, the rough fracture surface develops a wide distribution of cavities sizes ranging from ~ 1 to $50 \mu\text{m}$. This suggests that the cavities result from a loss of the starch phase. The image for the 50% TPS blend appears similar except that the cavities are more irregular in shape. As the starch content decreases, the number of cavities observed on the enzyme-eroded fracture surfaces decreases as well.

The SEM, TMA, and water resistance data all confirm the two-phase nature of the TPS–PVB blends. This is not surprising as most polymer pairs are thermodynamically immiscible.¹² Phase separation leads to the creation of internal interfaces. If these have a high interfacial tension, the adhesion between two

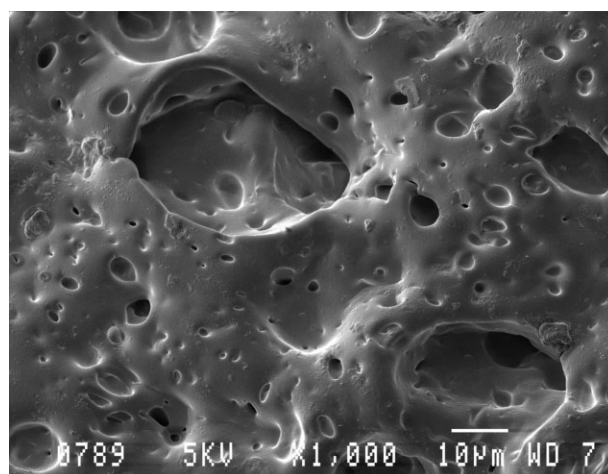


Figure 8 Scanning electron micrograph of an enzyme-eroded fracture surface of the 22% TPS containing blend.

phases will be poor. The end result will be poor stress transfer between phases and a loss in mechanical properties.¹² The blends rich in PVB show improved mechanical properties especially the compound with 22% TPS. This indicates a measure of mechanical compatibility in the blends. However, similar mechanical property improvement was obtained by merely using gypsum as filler. Thus, it is likely that, at low starch loadings, the high-stiffness starch domains simply act as dispersed reinforcing filler particles. The high elongation-to-break values are consistent with the PVB forming the continuous phase up to 50% TPS. The lower than expected tensile strength of this blend can be attributed to its coarse phase domain structure.

CONCLUSIONS

High amylose maize starch was used to prepare a TPS containing 15% glycerol as plasticizer. Blends with recycled PVB containing 8, 22, 50, 78, and 92% TPS were investigated. The effect of aging at 30°C and 60% RH on the tensile properties was determined. On aging, the Young's modulus and tensile strength of the TPS-rich blends increase while those of the PVB-rich blends decrease. The properties of the former are lower and those of the latter better than expected from the linear blending rule.

SEM, XRD, TMA analysis, and water soak tests confirm a phase separated blend morphology. The tensile strengths of the 8 and 22% TPS blends are of similar magnitude as gypsum-filled PVB. It is concluded that, at low TPS loadings, starch-rich domains act as physical reinforcements for the PVB matrix. The loss in mechanical properties above the 50% TPS content is ascribed to the starch phase becoming the continuous phase.

References

1. Shogren, R. L.; Swanson, C. L.; Thomson, A. R. *Starch/Stärke* 1992, 44, 335.
2. Lai L. S.; Kokini, J. L. *Biotechnol Prog* 1991, 7, 251.
3. Wiedmann, W.; Stuttgart, E. S. *Starch/Stärke* 1990, 43, 138.
4. Van Soest, J. J. G.; Vliegthart, J. F. G. *TIBTech* 1997, 15, 208.
5. Van Soest, J. J. G.; Knooren, N. *J Appl Pol Sci* 1997, 64, 1411.
6. Shogren, R. L.; Jusberg, B. K. *J Environ Polym Degrad* 1999, 2, 99.
7. Kim, J. O.; Kim, M. S.; Kwangju, M. S. *Starch/Stärke* 1997, 49, 71.
8. Bastioli, C. *Pol Degrad Stab* 1998, 59, 263.
9. Gorokhovskiy, A. V.; Escalante-Garcia, J. I., Gashnikova, G.Y., Nikulina, L. P., Artemenko, S. E. *Waste Manage* 2005, 25, 733.
10. Dhaliwal, A. K.; Hay, J. N. *Thermochim Acta* 2002, 391, 245.
11. Forssell, P. M.; Mikkila, M.; Moates, G. K.; Parker, R. *Carbohydr Polym* 1997, 34, 275.
12. Paul, D. R.; In *Polymer Blends*; Paul D. R., Newman S., Eds.; Academic Press: New York, 1978; Vol. 2, Chapter 12, p 35.