

Thermoplastic Biopolyester Natural Fiber Composites

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ABSTRACT: Natural fiber–biopolymer composites have been prepared using flax and poly(3-hydroxybutyrate) biopolyesters (PHB). The biopolyesters consist of the homopolyester PHB and its copolymers with 5 and 12% 3-hydroxyvalerate (PHV). These biopolymer–natural fiber composites provide structures totally composed of biodegradable and renewable resources. The adhesion between the fibers and the polyesters was better than for analogous polypropylene composites. Wetting of the fibers by the polyesters was observed using scanning electron microscopy. The composites were limited by the properties of the polyesters. PHB is a brittle polymer though flexibility is improved in its copolymers with PHV, but at the expense of crystallization rate. Nucleation was increased by the fibers

and silane coupling agent used as adhesion promoter. The melting temperature was influenced by the promoted adhesion and copolymerization. The bending modulus was increased in the composites and dynamic mechanical analysis provided storage modulus of as much as 4 GPa at 25°C with a smaller component as the loss modulus. The maximum in the loss modulus curve was taken as the glass transition temperature, and this increased in the composites. The influence of silane coupling agent was found beneficial for the material properties of the biopolyester–flax composites. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2114–2121, 2004

Key words: natural fiber; flax; poly(hydroxybutyrate); biopolymer; polyester; composite

INTRODUCTION

Composites prepared from glass fibers are widespread high-performance materials.¹ However, glass fibers have a high density, are difficult to recycle, and do not biodegrade. Comparison with bast natural fibers such as flax shows that though glass has superior absolute properties, the specific mechanical properties of flax are comparable. Figure 1 shows a comparison of some natural fibers, including flax as used in this study, with glass fibers. The specific properties of flax are comparable with those of glass, though in absolute terms glass has much greater modulus and strength.

Poly(3-hydroxybutyrate) (PHB) has moderate, though brittle, mechanical properties. Its properties can be greatly enhanced in composites with glass fiber, but also with minerals such as talc and calcium carbonate. The modulus and tensile strength of glass fibers is far greater than PHB, so much so that the properties of the glass fibers are unnecessarily high. A natural fiber such as flax has modulus and tensile strength so much greater than PHB that significant enhancement of properties can be expected if interfacial bonding is suitably high. The combination of PHB and flax provides a system completely composed of renewable natural resources. The composites will also

be readily biodegradable, unlike any composites with glass fibers.

The cellulosic fibers tend to degrade at about 200°C and quickly become friable with loss of water. This embrittlement must be avoided if cellulosic fibers are to be used as a reinforcement in composites. PHB has a low enough processing temperature to allow molding without degradation of the fibers. The melting temperature of PHB is high enough to ensure that its heat distortion and softening temperatures will provide stable thermal properties to the composites.

A recent overview² of biodegradable polymers discussed potential use of biochemically synthesized PHB and its copolymers in industry. PHB, a biotechnologically produced polyester that constitutes a carbon reserve in a wide variety of bacteria,³ has attracted much attention as a biodegradable thermoplastic polyester,^{4–6} and has high potential as an environmentally degradable plastic⁷ as it can be degraded to water and carbon dioxide under environmental conditions. Brittleness and slow crystallization of PHB inconvenience its processability.⁸ In order to improve these properties, PHB and poly(3-hydroxyvalerate) (PHV) are biosynthesized into a copolymer (PHB–PHV*).⁹ PHB–PHV copolymers were first manufactured in 1983⁷ and were intended as biodegradable substitutes for various containers.¹⁰ The current and potential uses of PHB and its copolymers have been reviewed for motor oil containers, film formation, and paper-coating

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*The common abbreviation is also PHBV²³ or PHB/HV.²³

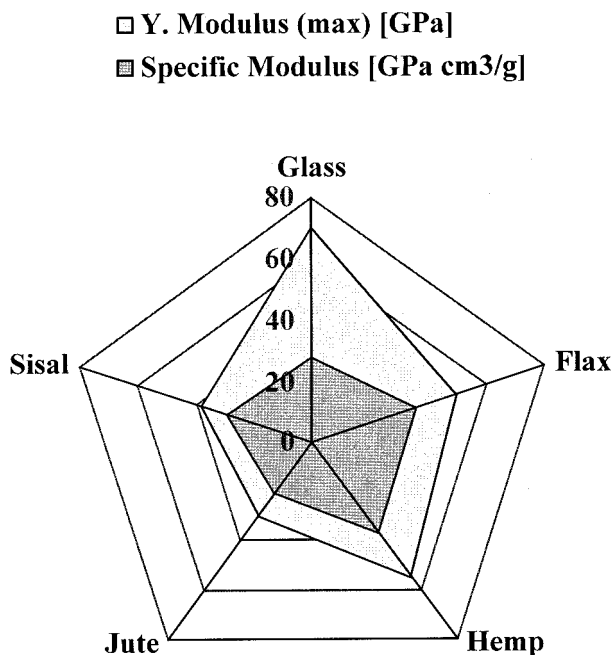


Figure 1 Properties of natural fibers compared with those of glass fibers, including flax as used in this study. (The specific modulus is the modulus divided by density.)

materials.¹¹ Due to its biodegradability through natural media and easy processability, PHB-PHV copolymers have been targeted for the replacement of non-degradable polymers in commodity application.¹²⁻¹⁴ The commercialization of PHB-PHV has been prevented due to high cost, the small difference between thermal degradation and melting temperature, and the low impact resistance due to high crystallinity. The melting temperature has been reported at 180°C¹⁵; however, it can be changed (decreased) with varying PHV content. Other polymers with similar melting temperatures are expected to be suitable for formation of composites with natural fibers, such as polypropylene.^{16,17}

Copolyesters of PHB with PHV show increased flexibility.¹⁸ The two monomers in the copolymer have been shown to cocrystallize. Such a cocrystallization is unusual for comonomers of differing structure in polymers. The cocrystals form slower than the crystals of homopolymer PHB, the crystallinity is decreased, and the melting temperature lowered, in the copolymers. The decreased crystallization rate could be a problem for production of composites in the times experienced with typical processing equipment. The copolymers are essential to reduce the brittleness of PHB and provide composites that should have the most useful properties. In addition, the glass transition temperatures of the copolymers are decreased relative to the amount of comonomer included. This is beneficial in increasing the flexibility of the biopolyesters.

Several bast fibers are suitable for preparation of composites.¹⁹ All have high specific modulus and strength. Fibers such as flax, hemp, kenaf, ramie, and sisal can be used. Flax is a good choice, for both properties and availability. The low density of flax relative to glass is an advantage when their specific modulus and strength are compared, they have comparable specific properties (Fig. 1). If the modulus of flax is compared with that of PHB and the copolyesters, then it is obvious that flax has properties well in excess of the polymer. There is no need for the higher values of glass to be required. They may be needed for high-performance polymers such as nylon and polyester, but not for polypropylene, PHB, and the copolyesters.

The aim of this research is to prepare composites from flax (untreated and treated with a silane coupling agent) and PHB and its copolyesters with PHV in order to study morphology and materials properties of the composites. The biopolyesters have melting temperatures of 170°C and less so that the upper limit of 200°C is not exceeded during processing. The initial decomposition is due the loss of water; this makes the flax fibers brittle, and so their suitability for reinforcement of composites is reduced. The polar biopolyesters are expected to show good adhesion to flax. In this respect they should be better than polypropylene, a nonpolar polymer. Polypropylene has been used in natural fiber composites but it performs best if surface modification is carried out to increase the polarity and hence the adhesion.^{20,21} Silane coupling agents²² have been successfully used as adhesion promoters in polymer-glass composites for the past three decades, and only recently have been employed in the natural fiber reinforced composites. To our knowledge, application of silanes has not yet been reported in biopolyester-natural fiber composites. A recent study by Reinsch et al.²³ reported increased crystallization in the presence of wood fiber in PHB-PHV copolymers. We assume that crystallization can be even further increased with the application of a silane coupling agent.

The morphology of the flax biopolyester composites will be studied using scanning electron microscopy (SEM), and the crystallization by differential scanning calorimetry (DSC). Mechanical properties will be studied using dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

PHB and its copolyesters with PHV were obtained from Sigma-Aldrich Co. (Castle Hill, NSW, Australia).

The properties of the polymers used in this study have been reported¹⁸ as follows: weight-average and number-average molecular weights (M_w and M_n) of PHB are 2.3×10^5 and 8.7×10^4 g mol⁻¹, respectively;

TABLE I
Designations and Thermal Properties of Biopolyester–Natural Fiber Composites Used in This Study

Composite material	Designation	T_c (°C)	T_m (°C)	T_g
PHB–flax	PHB-F	80.1	174	18.2
PHB–silane-treated flax	S-PHB-F	74.6	172.7	24.5
(PHB with 5% PHV)–flax	PHB-PHV5-F	80.3	165.2	24
(PHB with 5% PHV)–silane-treated flax	S-PHB-PHV5-F	75	170	23.3
(PHB with 12% PHV)–flax	PHB-PHV12-F	52.4	159	17.4
(PHB with 12% PHV)–silane-treated flax	S-PHB-PHV12-F	53	163.5	26

the M_w and M_n of PHB–PHV are 4.54×10^5 and 1.53×10^5 g mol⁻¹, respectively. The coupling agent was trimethoxymethylsilane, Ricafix EP 280, supplied by RCA International Pty. Ltd., Melbourne, Australia.

The flax was Durafiber grade 1 from Cargill (Saskatchewan, Canada). The fibers were dried in a vacuum oven for 5 h at 40°C to remove any moisture that may inhibit the polymers bonding to the fiber surface. These fibers were then cut into pieces no bigger than 0.5 cm in length.

A 0.1% solution of silane coupling agent and water was prepared. The fibers were immersed in the solution and stirred until dried at room temperature. The treated fibers were further dried in a vacuum oven for 3 h, before being used in the sheet preparation step.

Sheet preparation

The preparation of the composites involved dissolving the biopolyesters in chloroform then dispersing flax into the solution. A known mass of polymer was weighed and dissolved in minimal solvent (20–30 mL/g) under reflux. Once dissolved the required amount of treated or untreated flax fibers were introduced with stirring. The prepared polymer–natural fiber mixture was poured onto a glass plate. The natural fibers were manually separated from bunches in order to obtain a more even fiber distribution. The sheet was left to dry in the atmosphere and was then removed from the glass plate, and dried in a vacuum oven at 40°C for 4 h to remove any excess solvents.

The sheet was then cut into small pieces and pressed into a sheet in a heated press at 180°C. No pressure was applied for 5 min, then 2 tonnes pressure were applied for 5 min and finally 3.5 tonnes pressure were applied for 5 min. The sheet was further pressed into a bar, under the same conditions in the heated press, using a 1 mm teflon sheet as a spacer.

Compositions and designations of the prepared composites are presented in Table I.

Differential scanning calorimetry

Differential scanning calorimetry (DSC 7, Perkin–Elmer) was used for the thermal analysis of the pure

polymers and composites. The samples were placed in sealed 10 mg aluminum pans under constant nitrogen flow. DSC was performed by first heating a composite sample of about 2–5 mg to 200°C at 10°C/min for 2 min to erase prior thermal history and for measurement of the melting of the as formed sample, then cooled at 10°C/min to measure the crystallization. Cooling was continued to 10°C and then the sample was heated at 10°C/min to 200°C to study the glass transition and melting. The second thermal cycle provided accurate results on the melting temperature (T_m), measured from the peak value of the endotherm, and the T_c , measured from the lowest peak value of the exotherm.

Dynamic mechanical analysis

DMA is a thermal analysis technique used to measure changes in the viscoelastic response of a material as a function of temperature, time, or deformation frequency. DMA was performed in the three point bend mode using a Perkin–Elmer DMA 7e Dynamic Mechanical Analyzer with a TAC 7/DX Thermal Analysis Instrument Controller and an Intracooler 2. A dynamic force of 400 mN and a static force of 500 mN were used with a frequency of 10 Hz, and the temperature scan ranged from –50 to 120°C.

The samples were cut from the sheets, with dimensions 1 mm × 18 mm × 10 mm. The samples were kept as similar as possible in order to obtain a reliable comparison between the results from different materials. Storage modulus (G') and loss modulus (G'') were recorded as a function of temperature. The glass transition temperature (T_g) was obtained by determining the peak temperature of the loss modulus profile. The definition of the glass transition temperature as the temperature at which $\tan \delta$ (where $\tan \delta = G''/G'$ and δ is the phase angle) attains its maximum value is very common in the literature. In a recent study by Rieger²⁴ it was shown that the loss modulus curve provided a more reliable and accurate measure of T_g . Polymers are viscoelastic materials that contain both elastic and viscous phases; thus both storage and loss modulus are important for the analysis.



Figure 2 SEM image of PHB-flax composite surface morphology; good surface wetting is characteristic for these biopolyesters.

Scanning electron microscopy

SEM was used to observe the microstructure of the composites and the surface morphology. The instrument was a Phillips XL 30 Oxford 6650 SEM with an acceleration voltage of 142 eV. The samples were coated with gold to provide about 200 Å gold layer thickness using a vacuum sputter coater.

Optical microscopy

Optical microscopy (OM) was used to investigate the melting and crystallization processes in complex biopolyester–natural fiber composites. A hot stage (Mettler FP82) was mounted under an optical microscope (Nikon Labophot), which was fitted with a video camera (Sony) connected with a video monitor by a digital video camera. Small sections of composites, containing only a few natural fibers, were placed on a glass slide and inserted into the hot stage. The samples were heated to 190°C, held at that temperature for 4 min, and then cooled below the crystallization temperature. The interphase regions between treated and non-treated natural fibers and each polymer matrix were closely monitored.

RESULTS AND DISCUSSION

Composite microstructure

SEM images of PHB-F and PHB-PHV5-F are shown in Figure 2 and Figure 3, respectively. The former image shows very good wetting between PHB and the flax fiber, with a slightly rough polymer surface. For the copolymer with PHV (Fig. 3), wetting between the copolymer and the flax appears to be slightly improved due to the smoother polymer surface. Both composite morphologies show that wetting between the biopolyesters and the natural fibers is so good that

there is virtually not enough polymer to provide consolidation of the structure within 50:50 volume ratio of the constituents.

Melting and crystallization

DSC results are summarized as the melting and crystallizing temperatures of the materials used in this study (Table I). During the DSC heating scan, the biopolyesters show two separate endothermic peaks associated with the occurrence of melting, recrystallization, and remelting in the melting region.¹⁸ The low-temperature peak is associated with the as-formed crystals while the high-temperature peak is associated with the melting of crystals formed from the recrystallization process during the DSC heating scan. The second peak is the melting temperature, T_m .

Effect of copolymerization

Both T_c and T_m decreased with copolymers of PHB and 12% PHV. The result is improved processability, as the composites can be melted at lower temperature. In this way, the natural fibers are protected from thermal degradation during recycling. However, this can negatively affect the material properties, especially at higher temperatures.

Effect of silane coupling agent

T_m was both reduced (PHB-F) and increased (PHB-PHV-F) with silane coupling agents, obviously due to different chemical interactions with PHB and its copolymers. T_c was significantly reduced for silane treatment of PHB-F and PHB-PHV5-F.

Observation of crystallization

OM images showing fiber–matrix interphases of selected systems after crystallization from the melt are

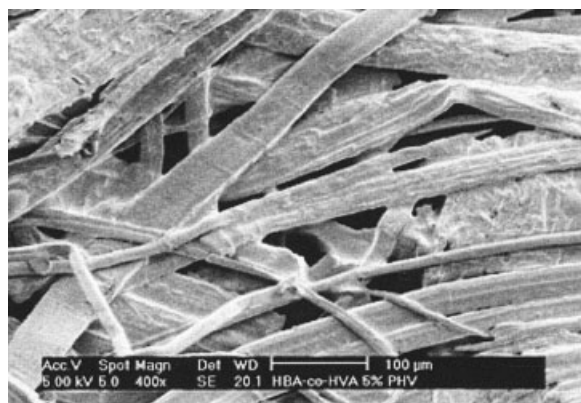


Figure 3 SEM image of PHB-co-PHV-flax composite with 5% of PHV; the surface morphology is similar to that of PHB-flax.

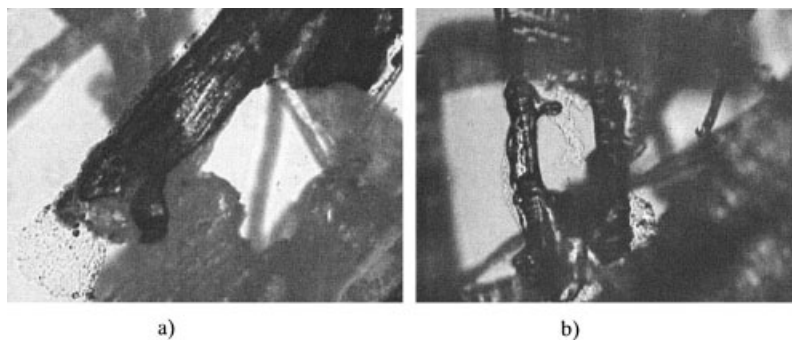


Figure 4 OM images of (a) S-PHB-F and (b) PHB-PHV12-F composites after crystallization.

presented in Figure 4 and Figure 5. The PHB-F interphase region did not show visible crystallization at 200 magnification, and the polymer was highly viscous in contact with the flax fibers. After the silane coupling agent was applied on the flax fibers, sporadic crystalline regions appeared at the edges of the flax fibers, as shown in Figure 4(a). A similar pattern was observed for nontreated flax fibers and the PHB-PHV copolymer, as shown in Figure 4(b). It has previously been reported that the strong effect of reinforcing (natural) fibers on crystallization is present in both PHB and its copolymers.²³ With addition of the silane coupling agent, nucleation is expected to increase. A good example of highly crystalline structure (S-PHB-PHV5), initiated and enhanced with nucleation from the silane treated flax fiber surface, is shown in Figure 5(a–d). The four OM images show the process of rapidly

growing spherulitic nucleation from the fiber edges towards the polymer, thus creating brittle borders and inconsistencies in the polymer structure. Since the silane coupling agent did not affect crystallization of PHB to such a high degree [Fig. 4(a)], we assume that this phenomenon can be attributed to the better flow of the copolyester, since it has a lower melting temperature.

S-PHB-PHV12-F appeared so highly viscous that the flax fibers were tightly bonded by the polymer and the interphase between the fibers and the polymer was hardly visible by OM.

Dynamic mechanical properties

The storage (G') and loss (G'') modulus vs temperature for the biopolyester–natural fiber composites with and

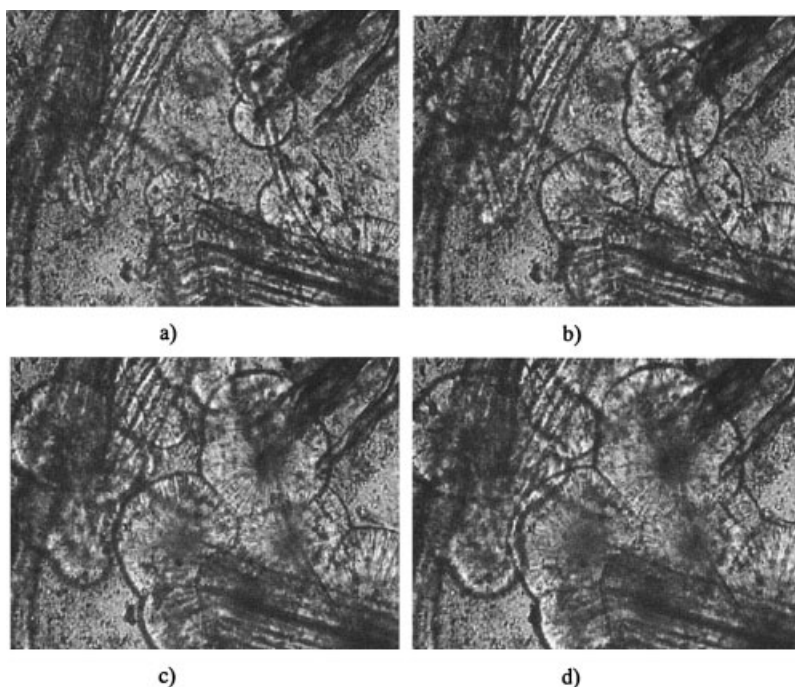


Figure 5 OM images showing the process of nucleation during crystallization after melt of S-PHB-PHV5-F.

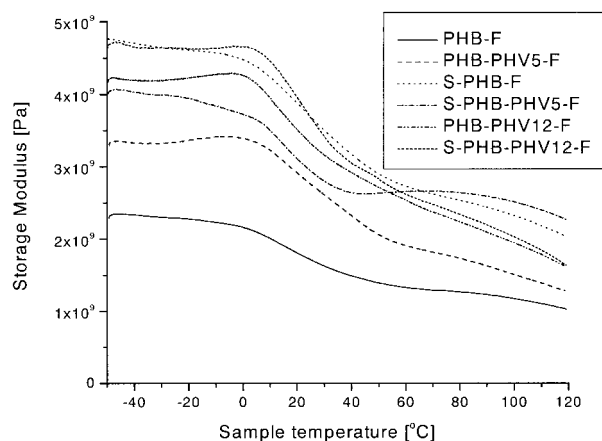


Figure 6 DMA results: storage moduli of the composite systems used in this study.

without silane treatment are presented in Figure 6 and Figure 7, respectively. Values of the storage and loss modulus at discrete temperatures (-50 , 0 , 10 , 50 , and 100 °C) are shown in Table II.

Storage modulus (G')

G' changed significantly between the various composite compositions. The decrease in G' in the region centered on 0 – 30 °C corresponds to the glass transition of PHB and PHB–PHV. The basis for the following discussion is relative comparison between PHB–F and the other five systems. The highest value of the modulus at -50 °C was for the composite of PHB with silane-treated fibers (4.76 GPa). This is greater than the modulus of isotactic polypropylene (~ 3 – 4 GPa), which is an alternative polymer for preparation of natural fiber composites. The modulus at -50 °C of the PHB fiber composites without silane treatment was 2.31 GPa, so that silane treatment is shown to provide a significant improvement to the composites. Though the values quoted are at -50 °C, the comparison between the treated and untreated fiber composites is similar at any other temperature over the range of temperatures studied. The improved modulus when the fibers were silane treated is through better interfacial bonding between PHB and the fibers, and an increase in transcrystallinity near the fiber interfaces as observed by polarized optical microscopy. It has previously been reported¹⁷ that a transcrystalline region in fiber-reinforced thermoplastics can improve the overall mechanical properties.

S-PHB–PHV12-F also showed a high G' of 4.67 GPa at -50 °C. This G' curve follows that of S-PHB-F, having higher values after the glass transition temperature. It is evident from the G' curves of the other systems that PHV increased storage modulus of the composite. The PHB–PHV copolyesters are slower to

crystallize than the homopolymer, PHB, yet the PHV component is necessary to reduce the brittleness compared with PHB. The silane treated flax fiber composite with PHB–PHV5 was observed to show an increase in nucleation density compared with the composite with the untreated fibers under the same conditions. The increased nucleation has provided smaller crystals that result in a transcrystalline interphase region, with improved bonding between the fiber and the matrix. The composites with PHB–PHV12 copolyester showed higher increase in storage modulus than that of PHB–PHV5, achieving its maximum value with additional application of the silane coupling agent (S-PHB–PHV12-F).

Comparison of the composites with untreated fibers shows that the PHB–PHV12 is stiffer than PHB–PHV5, with PHB being lowest. Comparison of the silane-treated fiber composites shows that the copolyester composites have higher storage moduli as compared to untreated systems, approaching that of the silane-treated PHB composite by increasing PHV content. The storage modulus of the composites is overall determined by a combination of the effects of polymer modulus, nucleation, and interfacial bonding. Treatment of the fibers with a silane to improve interfacial bonding proved to be successful for all biopolyester–flax composite systems used in this study.

Loss modulus

Flax fiber reinforcement shifted the loss modulus peak, defined as the glass transition temperature (T_g), towards higher temperature. The loss modulus curves for all systems are shown in Figure 7. The silane-treated fiber composites had a slightly different T_g to the untreated in each case but the effect was different. PHB–PHV12 composites had the highest T_g with silane-treated fibers, while PHB–PHV5 had higher a T_g

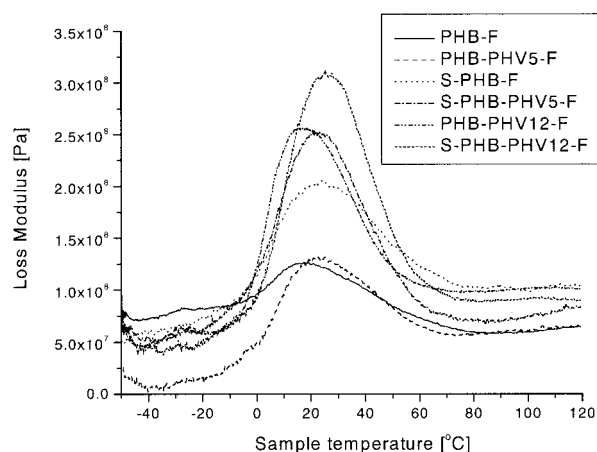


Figure 7 DMA results: loss moduli for the composites used in this study.

TABLE II
Values of Storage (G') and Loss (G'') Moduli (in GPa) for Biopolyester–Natural
Fiber Composites at Selective Temperatures

Material	–50°C		0°C		10°C		50°C		100°C	
	G'	G''	G'	G''	G'	G''	G'	G''	G'	G''
PHB-F	2.31	0.07	2.16	0.09	2.01	0.12	1.39	0.08	1.17	0.06
PHB–PHV5-F	3.34	0.02	3.39	0.05	3.23	0.09	2.06	0.08	1.51	0.06
S-PHB–PHV5-F	4.03	0.06	3.72	0.12	3.5	0.19	2.63	0.12	2.51	0.07
PHB–PHV12-F	4.18	0.06	4.26	0.12	3.96	0.23	2.71	0.12	1.94	0.1
S-PHB–PHV12-F	4.67	0.07	4.66	0.09	4.45	0.19	2.84	0.15	2.0	0.09
S-PHB-F	4.76	0.05	4.48	0.11	4.2	0.17	2.9	0.14	2.32	0.1

^a Designations of the materials are shown in Table I.

with untreated fibers. The T_g for each composite as measured by DMA is shown in Table I. The increased T_g in the presence of flax is due to the volume fraction of flax fibers providing a stiff framework within the composite and arresting the segmental motion of the polymer molecules. T_g is also sensitive to crystallinity and interfacial bonding with the fibers, so the reason for the change in T_g effect with and without silane coupling cannot be explained. The effect on the composites compared with the pure polymers is significant, so the fibers do have a considerable affect by modification of the bulk properties of the matrix polymer.

A large difference in the T_g with the treated and untreated fibers is observed. The range of the G'' peak was broad for PHB systems and the peak is not as distinct as that of the modified fiber composites with copolymers. Since the storage modulus of the treated fiber composite was the highest, and this fact corresponded with the highest values of T_g , means that the fiber–matrix bonding improved by the silane coupling agent plays a dominant role in stiffness of the composites. The slow rate of crystallization of the PHB polymers and particularly the copolymers with PHV means that in any of the systems studied crystallization will not be complete. It may be necessary to add separately an efficient nucleating agent to provide composites with well-defined properties. Another important variable is the water content of the flax fibers. Water content is generally about 8% by mass in cellulose fibers. If the water is removed, the fibers become too brittle to be suitable for composite formation. Thus, future work should involve replacement of water in natural fibers in order to protect and stabilize their mechanical properties.

CONCLUSIONS

- Biodegradable PHB–flax and PHB–PHV–flax biocomposites possess good mechanical properties,

comparable to or better than those of commercial thermoplastic polymers.

- Application of the silane coupling agent, the adhesion promoter successfully used for glass fiber reinforced composites, improved the storage modulus of PHB–flax biocomposites up to 106%.
- Biocomposites made of flax and PHB–PHV copolymer, with 5% mol PHV and 12% mol PHV content, had storage modulus increase up to 44.5 and 81%, respectively. Their respective loss moduli also increased proportionally.
- Application of the silane coupling agent significantly improved the storage modulus of PHB–PHV–flax biocomposites and increased their melting temperature, thus improving processability. The silane coupling agent in the PHB–PHV copolymer with 5% mol PHV content and flax fibers caused rapid nucleation and spherulitic crystallization, initiated at the interphase between the fibers and the biopolymer.

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