Dynamic Mechanical Thermal Analysis of Biocomposites Based on PLA and PHBV—A Comparative Study to PP Counterparts

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ABSTRACT: The primary objective of this study was the investigation of thermo-mechanical behavior of cellulosic fiber reinforced polylactid (PLA) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) biopolymers. Both PLA and PHBV were processed with 30 wt % of cellulosic fibers; moreover, to improve the processability and mechanical performance, PHBV was previously blended with 30% by weight poly(butylene adipate-*co*-butylene terephthalate) (PBAT). Secondary target was the comparison of the obtained results to natural fiber reinforced polypropylene (PP) composites reinforced with exact the same fibers and processed by using identical techniques. For validation the thermo-mechanical properties, a dynamic mechanical thermal analysis (DMTA) was applied. Storage modulus (E'), loss modulus (E''), and loss factor (tan δ) were determined. The DMTA results indicate decreased polymer chain motion with resulting improvement of stiffness expressed by the storage modulus. Finally, the effectiveness of fiber on the moduli was investigated. The C coefficient differs in dependence on fiber type, use of coupling agent, and the reference temperature in glassy state.
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INTRODUCTION

Growing environmental responsiveness and new regulations on the use of non-renewably resources for energy recovery and material applications are encouraging industry to research and develop more ecologically friendly bio-based composites. In long-established technical areas, the major engineering resin is still the polypropylene (PP) based composite, mainly reinforced with glass fibers or filled with minerals. Because of its high density and dubiousness recycling, composites reinforced with natural fibers are beginning to find market place and consumer acceptance in wide range of technical applications.[1–5] In addition, new bio-based polymeric matrices are being under consideration as a possible substitute for petrochemical plastics. Besides thermoplastic starches[6–9] and cellulosics,[1,5] polylactide (PLA) and polyhydroxyalkanoates (PHA) seem to be the most important representatives of the biopolymer group. Their major advantages are large-scale availability, thermoplastic nature, and the bio-based carbon content that is in the main of ∼100%. Moreover, PLA and PHBV can be biodegradable, however, under defined conditions only.[3–10]

Considering the application in technical areas, some basic properties, for instance thermo-mechanical parameters and an entire spectrum of material performance, must be widely characterized. Among others, processability, durability, aging, but first of all, materials mechanical performance is the basic material data that has to be well defined.

Quasi-static tests are mostly used for basic characterization of engineering parameters as stiffness (E-modulus), stress (strength), and yield- or strain at fracture. For description of composite dynamic properties, different impact tests (e.g., Charpy, Izod, falling dart, etc.) are being used. Unfortunately, neither static nor impact tests describe the composites mechanical behavior completely.

For investigating the composite response on cycling–loading under changing temperature, a dynamic mechanical thermal analysis (DMTA) is commonly in use.[11–20] Most polymers behave both like an elastic solid and a viscous fluid. It is very important to define the viscous component as the inelastic part is critical for many applications and for the long-time behavior under increased temperature (e.g., creep). DMTA enables the microstructural characterization of composites, their constituent phases, and interfaces in composites. It also allows a prediction of composite mechanical behavior under real-life conditions.

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Finally, biocomposites described in literature are very often reinforced with undefined natural fibers. In the present article, only tailor-made technical natural fibers are used. A comparison of fully bio-based biocomposite to natural fiber reinforced petrochemical equivalent on PP basis contributes to establishing fully "green composites" as engineering materials. Furthermore, the present study contributes to comprehension of the structural changes occurring under non-isothermal conditions in relation to composites processing on conventional production machine and resulting composition.

EXPERIMENTAL

Materials Used

Polymers used in the study are shown in Table I.

For composites reinforcement following cellulosic fibers were used:

Abaca: from Manila Cordage (Calamba City, Philippines); diameter 150 ± 50 μm, density 1.5 g cm^{-3}, elementary fiber diameter 10–30 μm, tensile strength ~800–900 MPa.[20] The fiber quality owing to FIDA (Fiber Industry Development Authority) is S3. Abaca was delivered by Rieter Automotive Systems. The advantage of abaca is the precise growth- and preparation control of the fibers (cooperation with the fiber manufacturer Manila Cordage) as well as improved mechanical properties compared to other natural fibers.[21]

Jute and Flax: from J. Schilgen GmbH & Co (Emsdetten, Germany); twisting 3.6/1, elementary fiber diameter 60–110 μm.

Man-made cellulose: from Cordenka GmbH (Obernburg, Germany), Fibre type Cordenka® 700 Super3, $d$tex = 2440, number of mono-filaments 1350, tensile strength 900 MPa, elementary fiber diameter 12 μm. Man-made cellulose is a chemical fiber of natural origin, whose source is the cellulose pulp from different wood species.[22,23]

For all composites, a matrix-to-fiber weight ratio of 70/30 was used. In biopolymers no coupling agent was added. For PP-based composites 5% by weight maleic acid anhydride grafted PP (MAH-g-PP) from Clariant (TP Licocene PP MA 6452) was applied, the content of which is related to the fiber load.

Composite Processing

Due to their polyester nature, PLA and PHBV were pre-dried in a convection oven (at least 16 h at 80°C, moisture content < 0.02%) then processed on a single- (Schwabenthan, Polytest 30P, L/D = 25, D = 30 mm for PHBV) and twin-screw extruder (Haake, Rheomex PTW 25/32, L/D = 32, D = 25 mm for PLA). PP was not dried prior to processing. To improve the melt stability and ductility, the PHBV was blended with Ecoflex (27.6% by weight) and processing aids (2.4% by weight).

The addition of continuous filament took place in an extruder via a coating die. Afterwards, the pellets were dried at 80°C in a convection oven (moisture content <0.3%) and finally compounded on the single-screw extruder to enhance the fiber distribution. The pellets were then injection molded into "dog-bone" test specimen (Kloeckner Ferromatik FM 85, nominal clamping force 850 kN, screw diameter 40 mm, L/D = 21,

Table I. Characterization of Polymers Used

| Polymer	Manufacturer	Composition[a]	T_m [°C] (DSC)	MVR [cm³/10 min]	M_w [g mol^{-1}]
Poly-(3-hydroxybutyrat-co-3-hydroxyvalerat) (PHBV)	Tianan Biological Material Co., Ltd., (Ningbo, China)	97% 3HB/3% 3HV	162	61.3 (170°C/2.16 kg)	520,000[a]
Polylactid 4042D (PLA)	NatureWorks LLC (Blair, Nebraska)	D-lactid content 3.7–4.6%	150	3–5 (190°C/2.16 kg)	171,000
Polypropylen 575P (PP)	Sabic Deutschland (Düsseldorf, Germany)	homopolymer PP	167	4–6 (190°C/2.16 kg)	509,000[a]
poly(butylene adipate-co-butylene terephthalate) (PBAT/Ecoflex F)	BASF SE (Ludwigshafen, Germany)	based on the monomers butanediol, adipic acid and terephthalic acid	120	4–8 (190°C/2.16 kg)	n/a

[a] As reported by the manufacturer.
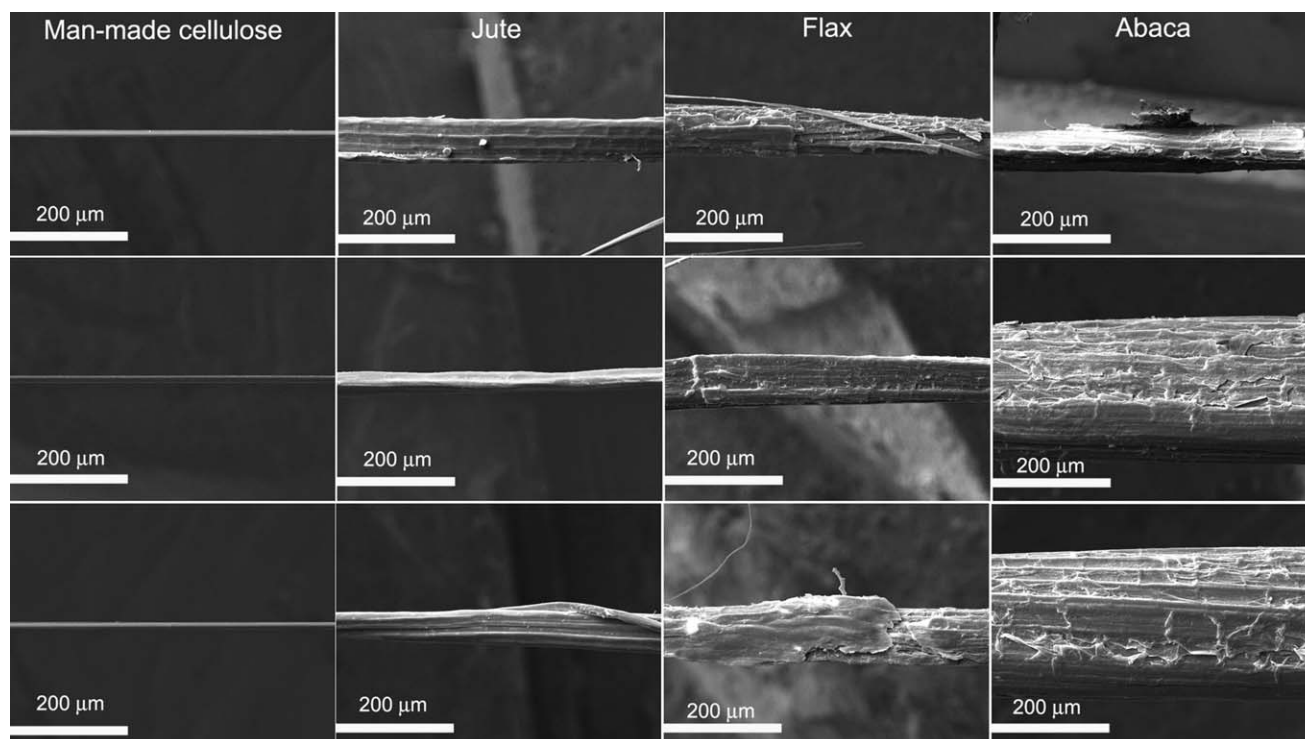
Figure 1. Diversity of longitudinal fiber architecture within the used fiber types.

screw rotational speed 120 rpm). Additionally, the machine's hopper was heated to 80°C and rinsed with nitrogen gas with $\sim$ 4 L min^{-1} (N$_2$ $\geq$ 99.999 vol%, Air Liquide Deutschland, Düsseldorf/Germany). Further detailed processing conditions are described elsewhere.[24,25]

Testing Method

To test the topography of the fiber surface, micrographs in scanning electron microscopy (SEM) were taken. A CamScan MV 2300 scanning electron microscope with a wolfram cathode emission gun with acceleration voltage of 10 kV was used. The samples of fibers were sputtered with thin gold film of several nanometers in thickness.

The stiffness of the manufactured test specimens were tested in a tensile test according to DIN EN ISO 527. The test was carried out on a Zwick/Roell UPM 1446 universal testing machine. The testing velocity of 1 mm min^{-1} for estimating the tensile E-modulus was applied. The test results were summarized with the help of the computer-supported software testXpert®. The following values represent the average of 10 separate measurements. Standard injection molded tensile bars type 1 A were used.

Storage modulus, loss modulus, and loss factor were determined by using Q 800 Dynamical Analyzer from TA Instruments. All measurements were done in a multi-frequency-strain modus in a dual-cantilever clamp under nitrogen atmosphere. Frequencies used were 1, 3, and 10 Hz at the amplitude of 10 μm and heating rate of 3 K min^{-1}. Rectangular specimens with the dimension of 35 mm $\times$ 10 mm $\times$ 4 mm (length, width, thickness) were used.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

Because of influence of the fiber surface on the mechanical response of the composites all fibers have been characterized by SEM (Figure 1). As the fiber diameter and surface topography (roughness, defects, etc.) vary along the length, different position and several fibers have been taken. For each fiber type three different SEM microphotographs are depicted.

As it can be seen, the geometry and surface topography of the fibers differ significantly. There is not only a variation between different fibers types, but also a visible varying appearance within separate groups of natural fibers. For instance, considerable differences in fiber diameter for abaca can be noticed. In addition, the surface roughness of natural fibers indicates an increased value of dissipative energy due to higher friction in the interfacial region. In contrast, the man-made cellulose fiber is distinguished by very smooth surface and fine fiber diameter. In consequence, the effect of friction at the interphase is reduced compared to rough natural fibers.

It is also well known that reinforcing fibers are exposed to thermo-mechanical damage during compounding. As a consequence, the resulting fiber length varies depending on the fiber performance, e.g. stiffness and elongation at break, and processing parameters. The fiber shortening during processing influences the overall mechanical behavior of the composites. In general, the shorter the fiber length, the lower the mechanical resistance. The lignocellulosic fibers can also defibrillate with resulting decrease of the fiber diameter. In this particular case, the mechanical parameters increase due to smaller cross
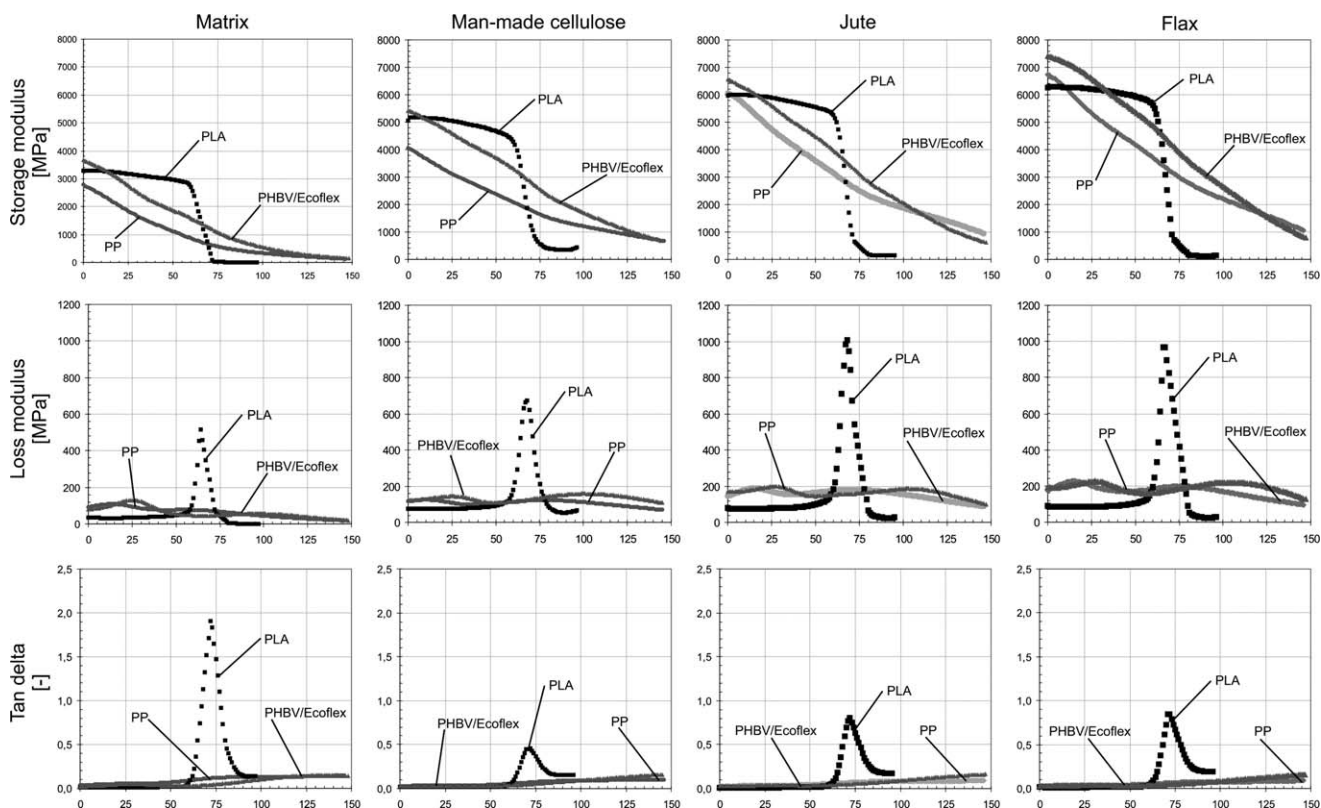
Figure 2. Chosen DMTA thermographs; frequency 1 Hz, the *X*-coordinate: temperature in °C.

dimensions of the fiber and improved distribution of the separated filaments. All these aspects were investigated and published by authors in their previous work.[25]

Storage Modulus and Composites Stiffness

Figure 2 shows the change in storage modulus (E'), loss modulus (E'') and tan delta (tan δ) derived from DMTA. Typically, the storage modulus increases when fibers are added. That is caused by a stiffening effect of reinforcing fibers and significantly reduced viscous constituent. As a result the composite remains stiffer and the polymer flow is restricted. These tendencies correspond with the E-modulus ascertained in the tensile test (Table II).

The storage modulus in the glassy state is determined predominantly by the strength of the intermolecular forces and the way the polymer chains are aligned.[16] In the case of composites, the storage modulus is additionally a function of fiber stiffness and content. The highest values of E' are achieved with natural fibers, especially with jute. The addition of man-made cellulose leads, similar to the quasi-static tensile test, to a slightly lower increase of the stiffness.

Although the initial E-modulus of jute is relatively low (Table III), the composite stiffness achieved with this fiber represents the highest values. As discussed in the previous section, the fiber stiffness depends strongly on the final size of the cross-section, whereas the fiber strength is a function of the fiber length. Both fiber diameter and length are affected during compounding. In the end, the composite properties are related to the initial fiber performance and the processing history of the composite. A detailed discussion regarding the influence of processing on the fiber-size distribution and resulting mechanical behavior of composites was published elsewhere.[25]

Man-made cellulose provides much higher strengths and significantly improved impact behavior.[4–6,24] Unfortunately, the stiffness may be insufficient for several applications. The solution could be a hybrid composites made of both, man-made cellulose and native natural fibers (e.g., see Figure 3).

At temperatures above 60°C (glass transition of PLA), the storage modulus of PLA decreases rapidly. The typical drop for amorphous thermoplastics is due to amorphous phase, which dominates the storage modulus at higher temperatures. Below their softening temperature amorphous polymers are rigid. During heating they soften in the region of glass transition temperature and, in consequence, the viscosity above T_g decreases without any distinct melting point. This behavior indicates that PLA was solidified into an amorphous state by quenching during injection molding. Pothan et al.[16] consider that the banana fibers in unsaturated polyester have larger effect on the storage modulus above T_g than below it. They observed that the difference in storage modulus of unreinforced polyester compared to its composites is noticeably higher at temperatures exceeding T_g. It is, however, taking into account unsaturated resins only, and not like in the present study, where the polyester is an aliphatic thermoplastic. In PLA, no crosslinkages occur and the decrease in modulus continues even though reinforced with fibers.

Table II. Comparison of DMTA Results and Tensile E-Modulus

Matrix	Fiber	Tensile E-modulus (GPa) +23°C	Storage modulus at 1 Hz (GPa)			Glass transition derived from E'' (°C)		
			+23°C	+50°C	+80°C	1 Hz	3 Hz	10 Hz
PP	–	1.5 ± 0.0	1.9	1.1	0.5	+14	+15	+17
	Cellulose	3.7 ± 0.1	3.2	2.4	1.7	+11	+12	+13
	Abaca	4.9 ± 0.1	5.5	4.2	2.7	+15	+17	+19
	Flax	4.8 ± 0.1	4.8	3.6	2.3	+16	+17	+18
	Jute	5.8 ± 0.5	5.4	4.2	2.8	+15	+16	+18
PHBV/Ecoflex	–	2.1 ± 0.1	2.9	1.9	0.9	−23/+26	−21/+27	−18/+30
	Cellulose	4.4 ± 0.3	4.7	3.7	2.3	−26/+25	−24/+28	−22/+32
	Abaca	4.4 ± 0.1	4.4	3.4	2.1	−23/+27	−21/+30	−18/+32
	Flax	5.3 ± 0.2	5.7	4.5	2.8	−23/+26	−21/+29	−18/+32
	Jute	7.0 ± 0.1	6.7	5.4	3.6	−22/+28	−20/+28	−17/+32
PLA	–	3.4 ± 0.2	3.2	3.0	0.01	+64	+64	+65
	Cellulose	5.8 ± 0.1	5.0	4.7	0.4	+68	+69	+70
	Abaca	8.0 ± 0.3	5.7	5.4	0.1	+66	+66	+67
	Flax	8.0 ± 0.6	5.9	5.5	0.2	+67	+69	+71
	Jute	9.6 ± 0.3	6.2	5.9	0.2	+66	+67	+67

Finally, due to increased temperature, an increased chain motion can be observed, resulting in decreasing storage modulus. Especially, at temperatures around and higher than T_g the chain segments or even entire polymer chains movement occur.[28]

Since the storage modulus remains on a very low level, the test for PLA ends at 90°C. It is obvious that due to secondary crystallization of PLA at temperatures above 90°C, an increase in the crystallinity and consequently in the storage modulus would be seen.[18,29–33] Moreover, if it had been possible to continue the experiment at higher temperatures, the modulus should be expected to level the rubbery plateau, before falling again in the viscous region.

Compared to an amorphous PLA the peaks in tangent delta, loss modulus, and the decrease in E' are less pronounced for PP and PHBV composites. Semi-crystalline PHBV and PP show continuous but gentle decline in storage modulus with increasing temperature. Furthermore, PHBV blend with Ecoflex shows noticeable higher values compared to PP. First, at increased temperature the curves draw near to each other due to

increased freedom of rotation in the main chain. As a result, the mobility of polymer chains increases and the stiffness given by storage modulus decreases continuously.

The presence of crystalline domains or reinforcement could also act as a physical "crosslinking," decreasing the mobility of amorphous regions and consequently increasing the stiffness of the composite at higher temperatures, while the decrease is rapid in the amorphous PLA, when the glass transition temperature is exceeded. Moreover, in PP composites transcrystallization takes place affecting the interaction on the fiber surface and consequently changing the composite ability of stress transfer.[34] In the case of PP, great attention should be paid to the addition of MAH-g-PP. This coupling agent improves adhesion on the fiber surface and develops better compatibilization of highly polar cellulose to unpolar PP.[14,35]

Loss Modulus

The loss modulus tends to be higher for composites with natural fibers indicating higher dissipative energy. In general, the higher the loss modulus in comparison to storage modulus, the more mechanical loss in the material. The increased loss

Table III. Engineering Properties of Natural Fibres[26,27]

Fiber	Density (g cm⁻³)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation to break (%)	Diameter of elementary fibre (μm)
Flax	1.40	800–1500	60–80	1.2–1.6	15–25
Jute	1.46	400–800	10–30	1.8	12
Abaca	1.50	980	27–32	–	10–30
Man-made cellulose	1.49	885	27	12	12
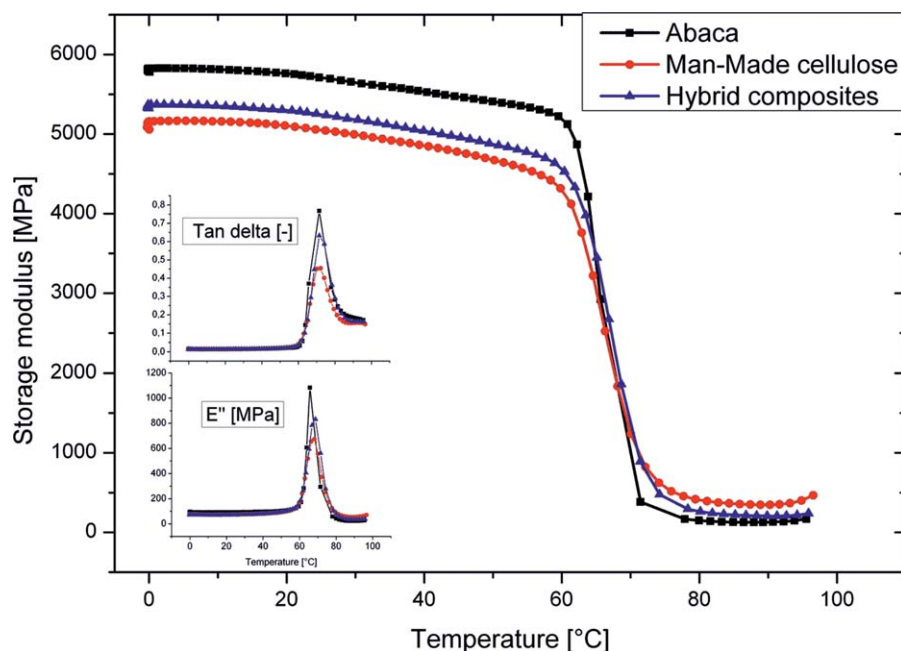
Figure 3. An example of DMTA of hybrid composites; PLA reinforced with Abaca/man-made cellulose (composition 70/15/15). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modulus corresponds to enlarged friction between fiber and matrix during cycling–loading. In addition, fiber–fiber interaction takes place further increasing the friction, and in consequence enhancing the dissipative energy. This effect is more likely for rough natural fibers than for flat man-made cellulose (Figure 1). The smooth and very fine fibers of man-made cellulose rather slide on each other, which leads to lower energy dissipation into heat. This hypothesis is confirmed when considering the change of E'' and tan δ of the PLA hybrid composite (inserts in Figure 3).

Because of the blends made of two thermodynamically immiscible components of PHBV and Ecoflex, the T_g values derived from the loss modulus show two different peaks ($T_{gEcoflex} = -23°C$, $T_{gPHBV} = +25°C$) (Figure 4).

A typical increase in T_g with increasing stress frequency can be observed (Table II). At higher frequencies, the material response on the applied strain is delayed (viscoelastic behavior). In consequence, the relaxation peaks occur at higher temperatures.

In addition, broadening of the transition region for both PP and PHBV/Ecoflex composites takes place (Figure 4). It is more likely due to the effect of the relaxation process within the composites in the mean of reinforcing fibers. This effect appears in semi-crystalline polymers only. For that reason we conclude that the change is related with rearrangement in amorphous areas between crystalline domains[14] and/or with higher ability of PP and PHBV to trans-crystallization, which affects the time–temperature depended relaxation behavior.[18] Furthermore, PP and PHBV/Ecoflex show again a drop in E'' at temperatures around 80 and 100°C, respectively. The molecular motion of viscoelastic materials is still being discussed and seems to be not fully understood.[18,31] The obvious transition of PHBV composites at increased temperature can be related either to movement

toward the T_g of the dry cellulose, which is $\sim$200°C or to approaching the melt region of the matrix.[14,18] Another explanation is a thermally initiated secondary crystallization (or trans-crystallization), which occurs within the discussed temperature range[31,36–38] and can be induced by fibers. The peak of PP can be related to α-relaxation.[32,35]

**Mechanical Damping**

Mechanical losses are often referenced to damping. For that reason the damping performance of materials in relation to their stiffness (tan $\delta = E''/E'$) is a good explanation for the overall material damping. A highly viscose PLA, especially near to its T_g, is characterized by the highest damping signal compared to rigid natural fiber reinforced composites. Whereas, tan δ for PHBV and PP increases continuously with increasing temperature, indicating a continually decline of the viscosity. As a result, material damping increases. Similarly for the loss modulus, the tan δ is noticeably higher for natural fiber reinforced composites compared to man-made cellulose composites. With regard to greater amount of dissipative energy, the heat development is higher and the decreasing viscosity increases the mechanical damping expressed by tan δ.

The fiber reinforcement shows no obvious influence on the glass transition temperature for semi-crystalline PHBV and PP composites (Table II), which agrees with the prior results.[17,38,39] A little shift to higher temperatures for PLA composites compared to the unreinforced PLA can be observed. Most likely, the reinforcing fibers affect the chain movements and/or lead to trans-crystallization on the interphase.

**Effectiveness of Fibers on the Moduli**

The effectiveness of reinforcing fibers on the moduli can be described by coefficient C determined by eq. (1).[16,18,40]
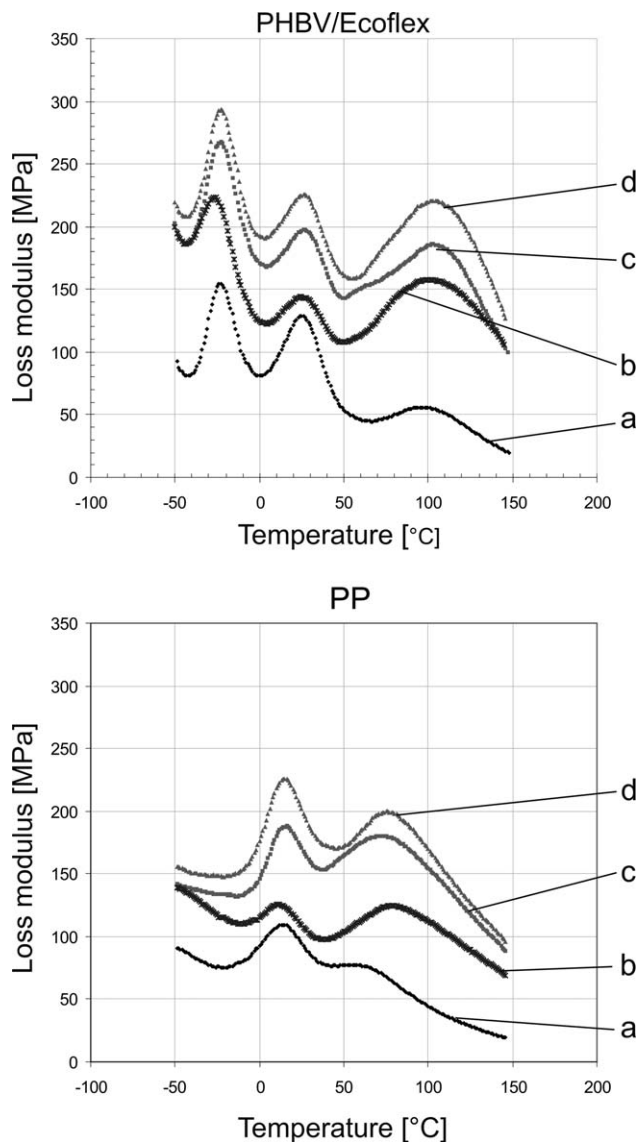
Figure 4. Loss modulus of PHBV/Ecoflex (70/30) and PP with natural fibers (30% by weight), frequency 1 Hz; (a) matrix, (b) man-made cellulose, (c) flax, (d) jute composites, respectively.

$$C = \frac{(E'_g/E'_r)\,comp}{(E'_g/E'_r)\,resin} \qquad (1)$$

where E' is the storage modulus and the sub-indexes "g" and "r" correspond to glassy and rubbery state, respectively. Basically, the lower the C coefficient the higher the effectiveness of reinforcement. However, the C coefficient corresponds only to storage modulus, without any direct relation to composite strength. It describes the ability to disturb the increasing motion of polymer chains in composites at elevated temperatures. Therefore, "C" is a function of fiber load, type, and size distribution as well as fiber–fiber interaction and fiber–matrix interfacial adhesion. In addition, this coefficient depends on the polymer nature, e.g. branched, crosslinked, amorphous, or semi-crystalline polymer.
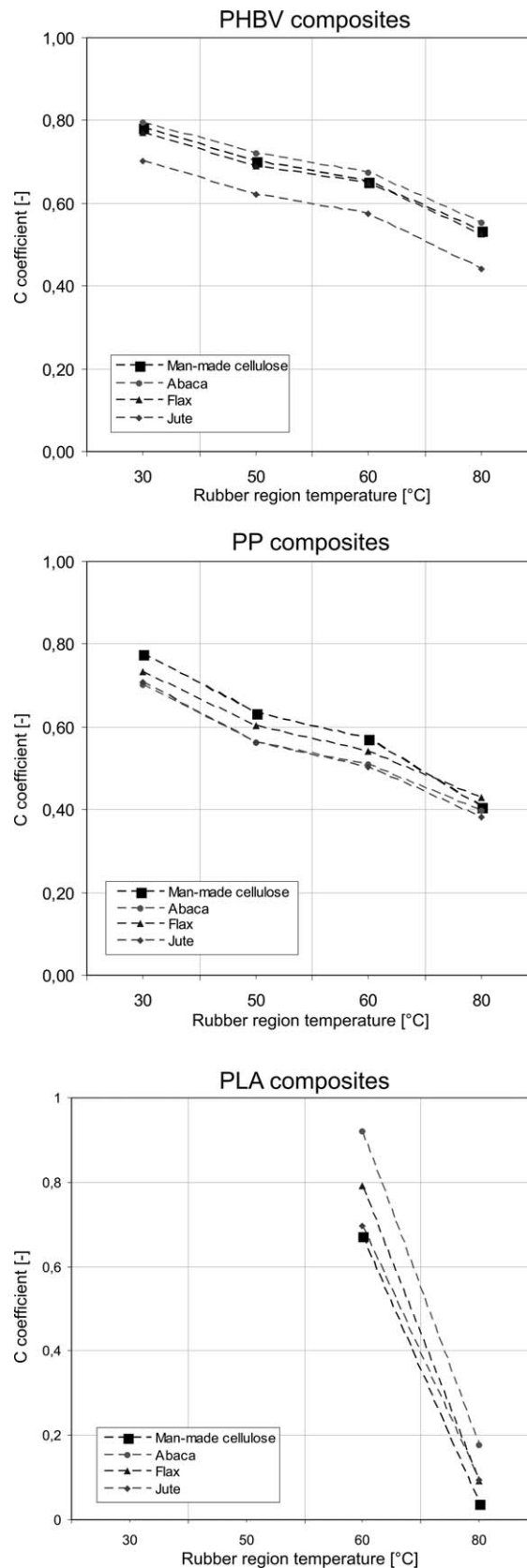
Figure 5. C coefficient of composites.

In Figure 5, the C coefficients for semi-crystalline PP and PHBV/Ecoflex as well as amorphous PLA composites are presented. For both semi-crystalline polymers, the E_g' was set at $-45°C$ and the E_r' for the rubbery region was measured at four different temperatures 30, 50, 60, and 80°C. Both parameters, E_g' and E_r', are results from the traces performed at the frequency of 1 Hz.

It is obvious that the "C" depends not only on the aforementioned criteria but it is also a function of the reference temperature. Furthermore, the C coefficient decreases with increasing temperature indicating enhanced effectiveness of the fiber at elevated temperatures. It is due to induced motion at the molecular level. Under such conditions, the polymer loses the ability to elastic response and the viscose behavior begins to dominate. In consequence, the storage modulus of the polymer decreases, while the stiffness of the fiber remains unchanged in the considered temperature range, increasing the effectiveness of fibers on the composite moduli. In this temperature range, natural fibers do not undergo any thermal induced transitions and behave almost perfectly elastic.

Acha et al. estimated C values for PP with 30 wt% jute as 0.6–0.63,[18] where the jute fibers were used in the form of fabric. The authors discuss that a better reinforcement effect can be achieved with fabrics. However, the textile form of reinforcing fibers disables the processing via injection molding. In Ref. [16] dynamic mechanical analysis of unsaturated polyester with banana fibers was investigated. The estimated C coefficient for systems with 30 wt % fibers was 0.96 indicating lower ability to stress transfer as in the present study. Similarly in Ref. [41] the C values, between 0.75 and 1.07, depending on fiber load, were achieved.

It is interesting that the tendency for compatiblized PP is different than for PHBV/Ecoflex. It is most likely due to the use of MAH-g-PP. For instance, abaca shows much lower C values in PP composites than in biopolymer systems indicating improved interfacial adhesion. Further explanation is the higher shrinkage of PHBV compared to PP, which damages the interphase. Finally, PP is a mono-matrix system in comparison to the PHBV blend with PBAT.

The C coefficient seems to be applicable for semi-crystalline or crosslinked polymers. Regarding some amorphous polymers like PLA a rapid drop in storage modulus at T_g and the near to perfect elastic nature of cellulosic fibers above glass transition of the matrix lead to very small values of the C. For instance, the C coefficient of PLA composites, estimated at 0°C for E_g' and at 60 and 80°C for E_r' drops significantly. This is why the correlation (1) for amorphous polymers is only relevant at temperatures just above T_g. At $T >> T_g$ the given formula predicts a very good effectiveness of fibers on moduli, although the absolute composites elastic response expressed by E' is already noticeably reduced. At higher temperatures, the polymer flow is dominant and the effectiveness of fibrous reinforcement, taking into account the overall composites performance, is negligible.

CONCLUSIONS

The tested biocomposites clearly show better or comparable characteristic values to the "common" natural fiber reinforced PP. The fibers typically cause an increase in storage modulus, loss modulus, and a lowering of damping, which is a result of better stress transfer, affected chain mobility, and fiber elastic response at increased temperatures.

The highest stiffening effect was achieved by reinforcing all matrix materials with jute. This is due to the change in fiber shape after compounding (shortening and defibrillation). In addition, all lignocellulosic fibers stiff the structure more evident than man-made cellulose, which is a clear effect resulting from different fiber performances.

Semi-crystalline PHBV/Ecoflex shows a comparable performance to PP composites. PLA composites show much higher mechanical characteristic values than PP counterparts; however, the material loses the ability to stress transfer as soon as the glass transition temperature is exceeded. Therefore, the combination of thermally untreated PLA and cellulose fiber is usable as engineering material only at temperatures up to 50–60°C (short-term).

The estimated C coefficients show an obvious dependence on the fiber type and coupling agent. Further, the C coefficient seems to be only applicable for semi-crystalline thermoplastics and their composites. Due to the rapid drop in storage modulus for amorphous polymers, the C can only be applied at temperatures near to T_g.

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