Creep and dynamic mechanical behavior of PP–jute composites: Effect of the interfacial adhesion

Betiana A. Acha, María M. Reboredo, Norma E. Marcovich *

*Department of Chemical Engineering and Department of Materials Engineering, University of Mar del Plata (UNMDP),
Institute of Materials Science and Technology (INTEMA), National Research Council (CONICET), Av. Juan B. Justo 4302,
(B7608FDQ), Mar del Plata, Argentina*

Abstract

The dynamic mechanical response and the short term creep-recovery behavior of composites made from bi-directional jute fabrics and polypropylene were studied. In order to improve the compatibility of the polar fibers and the non-polar matrix, two alternatives were compared: the addition of coupling agents and the chemical modification of the fibers. In the first case, two commercial maleated polypropylenes and lignin, a natural polymer, were used. In the second approach, the fibers were esterified using a commercial alkenyl succinic anhydride. The degree of interfacial adhesion was inferred from the measured properties and confirmed by the observation of the composite fractured surface. The maleated polypropylenes acted as compatibilizers since they were able to join the fibers to the neat PP, locating themselves in the interphase region. On the other hand, a clear separation between fibers and matrix could be observed when lignin was used as compatibilizing agent and when the chemically modified fibers were used to prepare the composite. The creep deformation could be directly related to the interfacial properties. Bürgers model parameters were calculated from the creep part of the curves, and the recovery part was modeled using these values. A very good agreement between experimental data and theoretical curves were obtained in the creep region, although small discrepancies were found in the recovery part. The feasibility of the construction of a master curve (using the time–temperature principle) to predict long term creep behavior of the composites was investigated.
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1. Introduction

From some years new cellulosic fillers have attracted considerable interest for the reinforcement of thermoplastics polymers [1]. Among organic fillers, cellulose fibers offer a number of benefits as reinforcement for synthetic polymers since they have high specific strength and stiffness, low hardness, which minimizes abrasion of the equipment during processing, relatively low density, biodegradability and low cost on a unit volume basis [2]. Contrary to thermoplastic polymers, cellulosic fillers are predominantly polar

due the presence of polar groups on its different components and thus, easily absorb moisture. Thus, the development of methods for controlling the interfacial adhesion between chemically and physically incompatible phases has been the object of considerable effort [3]. Several techniques, ranging from grafting short-chain molecules onto fiber surfaces to coupling/adhesion promoting agents, have been reported [3–5]. Moreover, the utilization of sizing agents (generally those used mainly in the papermaking industry) was also presented as another very attractive method of modifying the fiber surface of natural fibers [6,7]. Several researchers [8,9] also indicated that lignin, a component of the wood and plant fibers, can be used as coupling agent, since it contains polar (hydroxyl) groups and non-polar hydrocarbon and benzene rings, and thus,

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* Corresponding author. Tel.: +54 223 481 6600; fax: +54 223 481 0046.
E-mail address: marcovic@fi.mdp.edu.ar (N.E. Marcovich).

it is expected to be able to improve the compatibility between cellulosic fibers and thermoplastic matrices. But until today, for PP-natural fibers composites, the utilization of maleated polypropylenes as coupling agents has proved to be the most effective way for improving interfacial adhesion [10–15].

Among all the natural reinforcing materials, jute appears to be a promising fiber due to its high toughness and aspect ratio in comparison with other natural reinforcements [16]. Moreover, jute fibers are easily available in the form of fabrics. The use of bi-directional fabrics instead of discontinuous fibers has the additional advantage of reducing the fiber agglomeration and possibilities the production of materials with same properties in two directions.

Traditional study of the mechanical behavior of fiber reinforced composites has been often restricted to a two-phase system. However, with the development of fiber-coating technology and with the introduction of cohesive or intermolecular bonding between fibers and the matrix, the effect of the interfacial zone (generally called the interphase) becomes also of practical importance for the determination of the overall behavior of the composite. This is especially true when the composite is to be used as a structural component whose long-term durability is of primary concern [17].

Polymer composites exhibit a time-dependent degradation in modulus (creep) and strength (creep rupture), as a consequence of the viscoelasticity of the polymer matrix [18]. The creep behavior of polymer matrix composites (PMC) is a critical issue for many modern engineering applications such as aerospace, biomedical and civil engineering infrastructure. Moreover, for natural fibers reinforced polymers, which are used mainly in applications where a light weight is more important than an exceptional resistance (i.e. decks, interior panels), the prediction of the creep performance is also interesting.

Recently, several works on polymer matrix composites creep behavior have been reported. Abdel-Magid et al. [19] studied the long-term creep behavior and creep-rupture properties of two systems of E-glass reinforced polymers. Raghavan and Meshiib [20] studied the creep rupture of continuous carbon-fiber-reinforced composites (AS4/3501-6) with fibers oriented at 10° and 90° to verify the predictive capability of the creep-rupture model developed by them. Govindarajan and coworkers [21] studied the influence of imperfections (voids) on the creep behavior of compression molded polymer/woven graphite fiber composites at elevated temperatures. Doh et al. [22] studied the creep behavior of liquefied wood–polymer composites based on low-density polyethylene (LDPE), high density polyethylene (HDPE), and polypropylene (PP). However, creep studies that take into account the changes in the adhesion between polymeric matrix and natural fibers are scarcely found [23,24].

In this work, the interfacial adhesion between jute and PP was modified in two ways: by the addition of coupling agents to the PP matrix (i.e. using a modified matrix) and by treating chemically the fibers (i.e. using less polar fibers) with a commercial alkenyl succinic anhydride prior to composite preparation. The effect of the interface fiber–matrix on the composite creep behavior and dynamic mechanical properties was investigated.

2. Experimental

2.1. Materials

Commercial bi-directional jute fabrics were used as reinforcement. The properties of jute fibers were presented in a previous paper [25]. A polypropylene (PP) homopolymer (Petroquimica Cuyo) was used as matrix. The interfacial adhesion between fibers and matrix was modified using two commercial maleic anhydride grafted polypropylenes (PPMANs), supplied by Eastman Kodak, as coupling agents: Epolene G3003 (1.4% of maleic anhydride, $Mw = 52,000$) and Epolene E 43-wax (8.2% of maleic anhydride, $Mw = 9100$) and using a commercial lignin (Curan 2711 P, powder), kindly supplied by Lignotech, Sweden.

Jute fabrics were also esterified in order to modify its compatibility with the matrix using a commercial alkenyl succinic anhydride (ASA, Lasar 2019 CE, Akzo Nobel). The fabrics were first dried at 70 °C in a vacuum oven until constant weight was reached. The esterification reaction was carried out by immersing the fabrics in a solution of acetone containing 96 g/l of Lasar and catalyst (4-dimethyamino-pyridine, Fluka, 8.75 g/l) and then heating at reflux temperature (56.5 °C) during 4 h. The esterified fabrics were then separated from the acetone solution and intensively washed with distilled water in order to eliminate the unreacted materials. Finally, the fabrics were dried again at 70 °C in a vacuum oven until constant weight was achieved. The ester content of the ASA modified jute was calculated from the saponification values using the techniques described elsewhere [26,27], indicating that there were 0.29 moles of ASA attached to 1 kg of treated jute (∼105 g ASA/kg treated jute).

Mixtures of PP and PPMAN or lignin were blended in a heated intensive mixer at 180 °C for 10 min. Films from PP, PP/PPMAN and PP/lignin blends were obtained by compression molding using a hydraulic press at 180 °C and 7.4 MPa. To prepare the composites, layers of jute fabric were sandwiched between the films. The samples were compression molded at 180 °C and 7.4 MPa for 25 min. The jute fabrics were dried in a vacuum oven at 70 °C overnight before the preparation of the composites.

Composites with 25 wt% (based on the total weight) of jute were prepared, as follows:

PPJ: made from neat PP.
PPJA: made from esterified jute fabrics and neat PP.
PPJL: made from PP modified with lignin (5 wt% of lignin, based on total weight).
PPJE: made from PP modified with Epolene E-43 wax (5 wt% of E-43 wax, based on total weight), and

PPJG: made from PP modified with Epolene G3003 (3, 5, 7 and 9 wt% of G 3003, based on total weight).

PPJ composites with different jute content (ranging from 9 to 30 wt%) were also prepared.

Before testing, all composites were annealed in an oven for 1 h at 100 °C and then slowly cooled into the oven to room temperature to release the residual thermal stresses.

2.2. Creep tests

A Perkin Elmer dynamic mechanical analyzer (DMA 7) was used in creep-recovery experiments to measure deformation as a function of time. The tests were carried out using three point bending geometry with a specimen platform of 15 mm length. The applied static stress was 4000 kPa for the creep step and then the composite was allowed to recover under 4 kPa. The relative low stress applied during creep (15% of the tensile strength of the neat PP, 10% of the tensile strength of the PPJ with 25% of jute) was selected to ensure the linearity of the viscoelastic behavior [23]. Generally, the temperature was fixed at 50 °C, although some tests were performed at different temperature. Composites were stabilized at 50 °C during 15 min before testing.

2.3. Dynamic mechanical tests

Viscoelastic properties, such as storage modulus (E') and mechanical damping parameter ($\tan\delta$), as a function of temperature were measured in a Dynamical Mechanical thermal Analyzer (ExplorTM 150 N, Gabo Qualimeter, Ahlden, Germany). The measurements were carried out in tensile mode using rectangular specimens of dimensions 50 mm × 10 mm × 3 mm over a temperature range of −100 °C to 150 °C, at a heating rate of 1 °C/mim, under nitrogen flow. The samples were scanned at a fixed frequency of 10 Hz, with a static force of 20 N and dynamic force of 10 N.

2.4. Scanning electron microscopy

The morphologies of composite samples were studied using a JEOL 35 CF EM scanning electron microscope. Micrographs were obtained from the fracture surface of selected specimens. The surfaces were previously coated with gold to avoid charging under the electron beam.

3. Results and discussion

3.1. Creep behavior

Fig. 1 shows the short term creep tests performed on PPJ composites prepared with different jute concentrations. It is noticed that the creep deformation decreases as the jute content increases, as expected from the addition of a
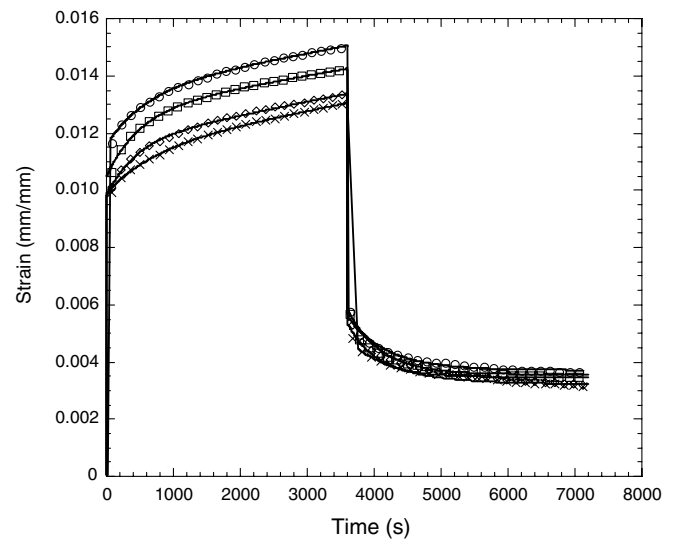

Fig. 1. Experimental creep-recovery curves (symbols) and fitting with the four elements model (lines) for PPJ composites. Jute content (wt%): ○ 9; □ 17; ◇ 25; × 30.

rigid reinforcement into a viscoelastic matrix, although the creep deformation of samples containing 25 or 30 wt% of reinforcement is practically the same. This indicates that no additional reinforcement is obtained using more than 25 wt% of fibers. The four parameters of Eq. (2) were calculated for each creep curve and they are shown in Table 1. The theoretical curves are also included in Fig. 1, as continuous lines. It can be noticed that the agreement between experimental and theoretical predictions is very good for the creep part of the curve, with small discrepancies appearing only in the recovery part. From the parameters reported in Table 1, it is observed that the immediate deformation (σ_0/E_0) and the slope of the steady state creep zone (σ_0/η_2) decrease as jute concentration increases.

Fig. 2 shows the creep-recovery curves of composites made from 25 wt% of jute with different interfacial adhesion between the fibers and the matrix. The highest creep deformation is exhibited for the composites prepared from ASA esterified samples (PPJA), followed for that of the composites that contain lignin (PPJL). PPJ composites exhibit an intermediate creep strain and the deformation of the samples prepared with both PPMAN as compatibilizers shows the lowest values. This behavior can be directly

Table 1
Bürger model parameters for PPJ samples with different jute concentrations

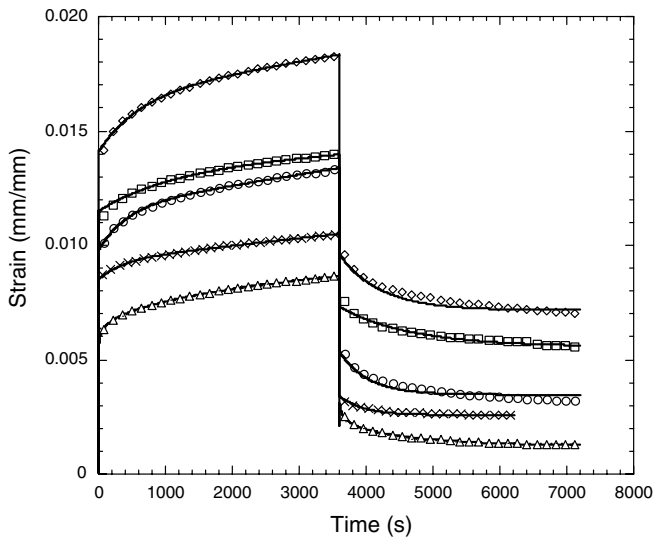| Jute (wt%)	E_0 (Pa × 10^8)	E_1 (Pa × 10^9)	η_1 (Pa s × 10^{12})	η_2 (Pa s × 10^{12})
9	3.45	2.143	1.282	8.998
17	3.81	1.766	0.886	9.642
25	3.96	2.252	1.367	9.731
30	4.04	2.617	1.535	9.912

Fig. 2. Experimental creep-recovery curves (symbols) and fitting with the four elements model (lines) for composites made from 25 wt% of jute. ○ PPJ; □ PPJL; ◇ PPJA; × PPJE; △ PPJG.

related with the interfacial adhesion. As the compatibility between the two phases is improved, the filler–matrix interaction increases and leads to the development of a stronger interface, which greatly improves the creep behavior [23]. In order to corroborate this, the interfacial region of the composites was observed by SEM and the micrographs obtained are shown in Fig. 3. Fig. 3a (PPJA) shows that there is a significant gap between the fiber and the matrix, i.e. the fiber is practically separated from the polymer. Moreover, the fiber surface is smoother than that of the untreated fiber (Fig. 3c, PPJ composite). Although the esterification reaction was conducted in order to increase

the fiber–matrix compatibility, the opposite happened. Probably the length of the ASA chains attached to the fiber surface was too short (about 20 C atoms) to effectively entangle with PP chains or the polarity of the modified fibers was still too high compared with that of the matrix. Besides, the natural roughness of the fibers decreased with the chemical modification and thus, the possibility of mechanical interlocking decreased too, contributing also to reduce the interfacial strength. Fig. 3b shows the interfacial region of PPJL composites. The free space between the fiber and the PP still appears and it is similar to that found in PPJ samples, indicating that the lignin did not act as a good compatibilizer for this system. Moreover, the matrix of PPJL samples is darker than that of the other composites, because the lignin was homogeneously distributed in the whole composite and not located preferably at the fiber–matrix interface. In this case, instead of performing as a compatibilizer for PP-Jute composites the added lignin is acting as a rigid particulate filler.

The fiber surface is also clean (free of adhered PP) in the composites made without compatibilizers (Fig. 3c), confirming the poor bonding between the fibers and the PP matrix. On the other hand, Fig. 3d and e show a layer of matrix evenly distributed onto the fiber surface and the fibers are practically joined to the matrix due to the enhanced interfacial adhesion and better wetting. From the morphology shown in these composites, a complex response to creep testing is expected, since reinforcement of well-bonded fibers contributes to enhance stiffness of composites [28]. These composites exhibit an excellent compatibility between both phases, being the Epolene G3003 the coupling agent that induces the best creep performance, probably because its molecular mass is higher
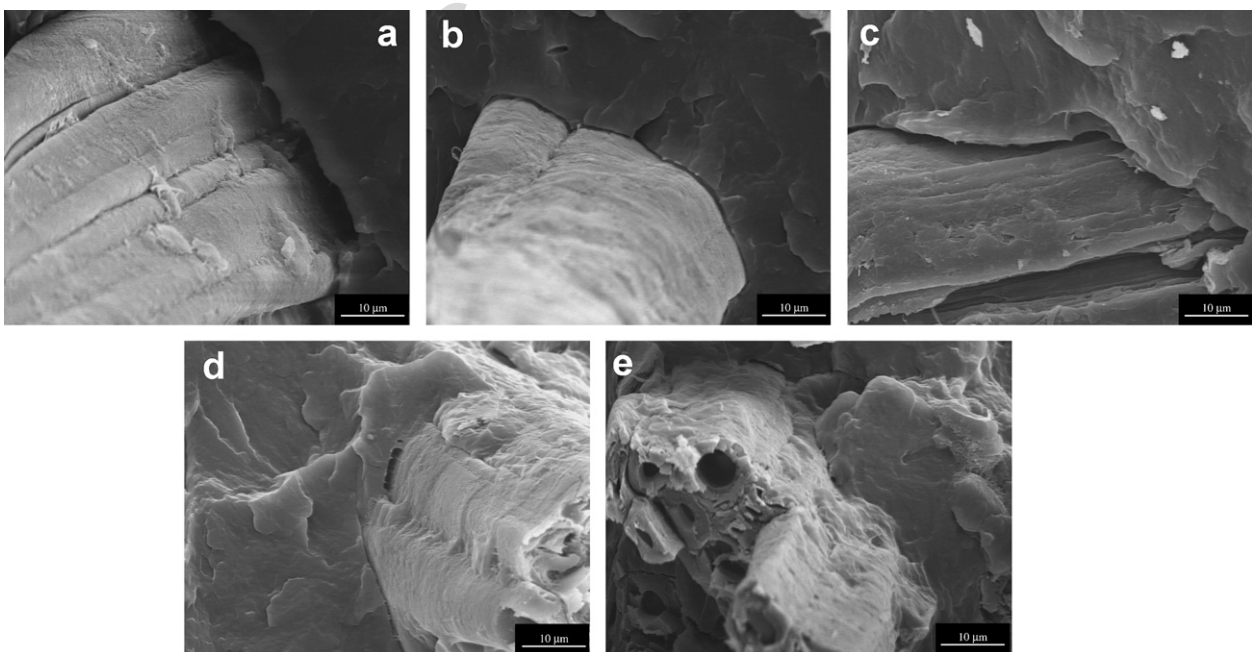

Fig. 3. Scanning electronic micrographs for composites made from 25 wt% of jute. (a) PPJA; (b) PPJL; (c) PPJ; (d) PPJE; (e) PPJG.

than that of the E 43-wax (Mw 52000 vs 9100, supplier data) and thus the entanglements formed with the PP matrix are more tight than those formed between the E 43-wax and the matrix. Even more, it was found that the presence of a low molecular weight PPMAN in a PP matrix could enhance the ability of the polymer to undergo a glass–rubber transition [29] and would behave like a lubricant. In terms of creep response of semicrystalline polymers, this means that a relatively higher deformation should be expected. On the other hand, the maleic anhydride content of the Epolene G3003 is lower than that of the E43-wax. However, from SEM observations it seems that not a high concentration of maleate groups was necessary to saturate the fiber surface –OH groups. This point will be further analyzed.

Table 2 shows the fitting four parameters calculated for the composites with different interfacial adhesion. From these data, it can be noticed that E_0 increases as interfacial adhesion increases and so does η_2, with an important exception for the PPJL composite. In this case, the slope of the steady state creep curve is the lowest (i.e highest η_2), which it is expected if a particulate filler (lignin) is incorporated to the polymeric matrix [23]. The fitting curves are also included in Fig. 2 and it is observed again the good fitting of the experimental creep curves and the ability to predict the recovery (Eq. (3)) of the samples using the calculated parameters for the creep zone.

Fig. 4 shows the creep behavior of composites containing 25 wt% of jute and different concentrations of one of the compatibilizing agents (Epolene G3003). The creep deformation is practically the same using 3 or 5 wt% of compatibilizer, but increases significantly if a higher concentration is used. Fig. 5 shows the SEM pictures of the fractured surface of these composites. It is noticed that there is a small free space between the fiber and the PP, and that the fiber surface does not show adhered matrix when only a 3 wt% of Epolene G3003 is used. This is an indication that a higher concentration of compatibilizer is needed to saturate the fiber surface –OH groups and that the interface quality can be further improved. On the other hand, there are no differences between the features exhibited by the composites made with 5 wt% or more compatibilizer, indicating that a 5 wt% is enough to saturate the fiber surface.

Due to the introduction of the maleic anhydride in the PP, the maleated polypropylenes are polymers less regular
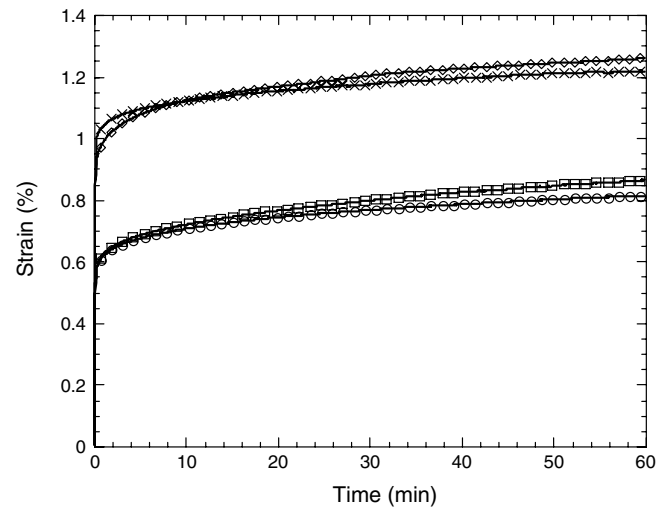

Fig. 4. Experimental creep curves composites for containing 25 wt% of jute and different concentrations of Epolene G3003. ○ 3%; □ 5%; ◇ 7%; × 9%.

than the unmodified PP, and thus, their ability to crystallize decreases with the degree of grafting. However, in semicrystalline polymers, the degree of crystallinity extremely influences the creep behavior [30–32]. In the present case, the increase in the creep deformation with G3003 content can be explained taking into account that the interfacial adhesion was not further improved (respect to that obtained using 5%) but the degree of crystallinity of the modified matrix decreased with the excess of compatibilizing agent [33]. Thus, the creep deformation increased as the excess of PPMAN increased because matrix crystallinity decreased.

In order to predict the long term behavior, creep tests at different temperatures were performed on PPJG samples. Fig. 6 shows the strong temperature dependence of creep behavior of these composites. As expected, as the temperature increases, the sample deformation increases. The creep curves shown in Fig. 6 were shifted according to the TTS principle, selecting 60 °C as the reference temperature, and the resulting master curve is shown in Fig. 7. Plotting the master curve in a log–log scale, a straight line should be obtained. However in this case, several experimental points of each individual creep curve deviate from the expected linear viscoelastic behavior, giving a rather poor long term prediction. To predict the long term behavior from short term measurements, it is generally assumed that the polymer does not change its structure with time, so the TTS principle holds. In the case of composite or complex materials, this assumption cannot be taken as valid a priori, but instead its applicability to evaluate particulate, laminate and fiber reinforced composites [23,34–37] was investigated in recent years, with satisfactory results. On the other hand, it was suggested that the existence of imperfections and discontinuities in the material can enhance its nonlinear viscoelastic response [38]. In the present case, the deviations from the expected linear viscoelastic behavior can

Table 2
Bürger model parameters for compatibilized composites made from 25 wt% of jute

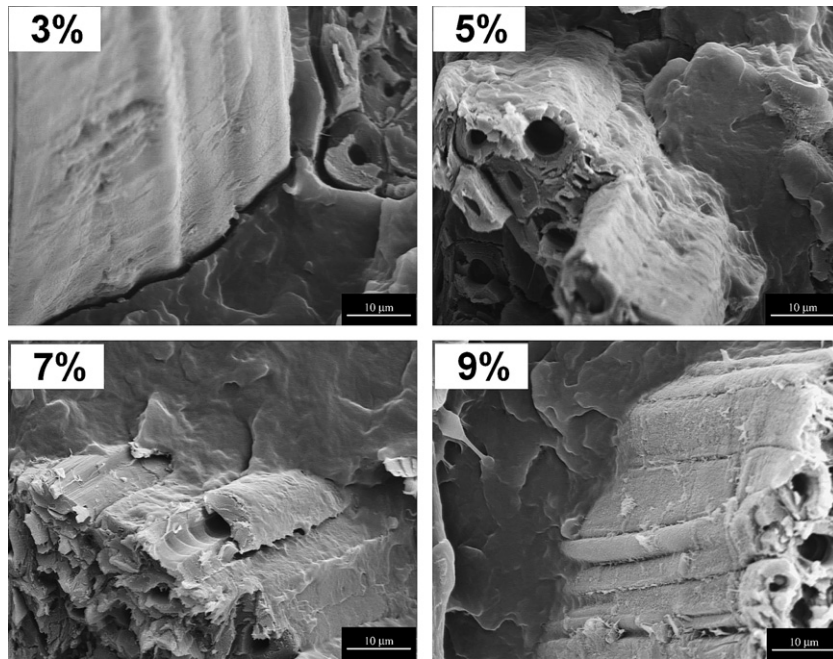| Sample	E_0 (Pa $\times 10^8$)	E_1 (Pa $\times 10^9$)	η_1 (Pa s $\times 10^{12}$)	η_2 (Pa s $\times 10^{12}$)
PPJA	2.84	1.64	1.010	7.940
PPJL	3.48	2.30	2.478	18.12
PPJ	4.08	2.13	0.906	8.42
PPJE	4.71	4.79	1.724	12.27
PPJG	6.35	3.49	2.194	11.62

Fig. 5. Scanning electronic micrographs for composites made from 25 wt% of jute and different concentrations of Epolene G3003.
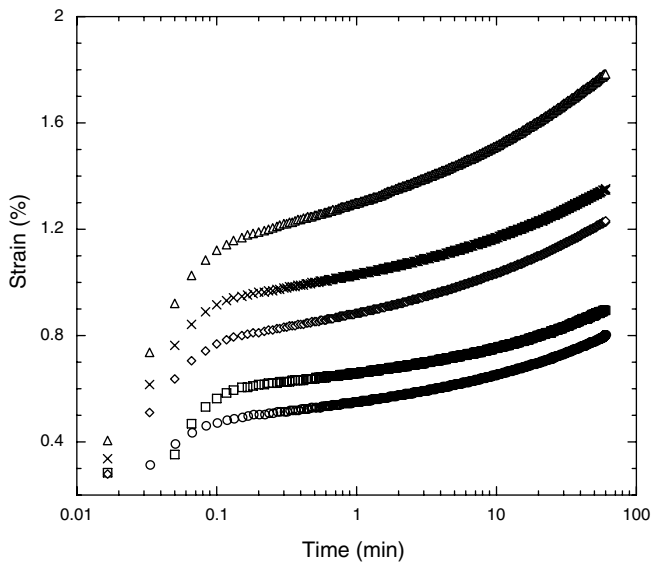

Fig. 6. Experimental creep curves for PPJG composites at different temperatures. ○ 40 °C; □ 50 °C; ◇ 60 °C; × 70 °C; △ 80 °C.
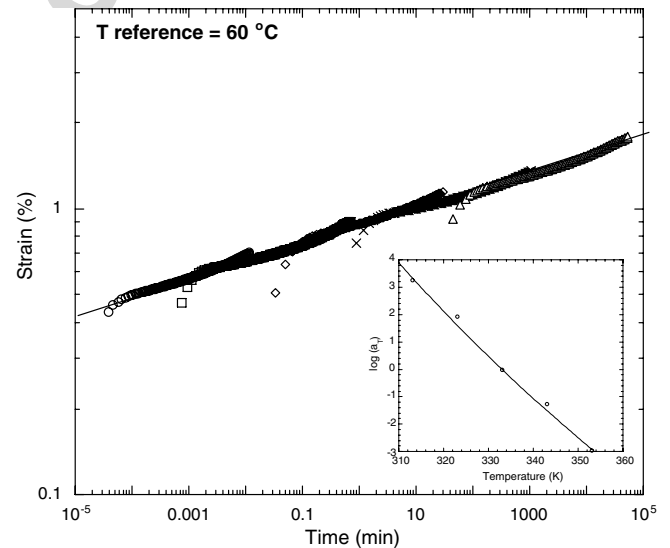

Fig. 7. Master curve constructed from the short-term creep data for the PPJG composite. The reference temperature is 60 °C. ○ 40 °C; □ 50 °C; ◇ 60 °C; × 70 °C; △ 80 °C.

be attributed to specimens inhomogeneities because, being jute a natural reinforcement, the number and diameter of fiber yarns and so the mechanical resistance could vary from fabric to fabric, leading to specimens with different creep resistance.

Although these deviations, the shift factors were plotted as a function of the temperature (inset in Fig. 7), and the WLF constants could be obtained as $C_1 = 43.9$ and $C_2 = 282.4$. The shift factors for complex materials such as polymer blends or composites have been shown to be dependent on the properties of the individual components

and do not always obey Eq. (4) [39]. Even though, in this case, the values of the WLF constants are within the range reported for other polymers [39,40].

3.2. Dynamic mechanical behavior

Fig. 8 shows the changes in the storage modulus versus temperature of composites prepared with 25 wt% jute and neat polypropylene. The dynamic modulus of the pure PP is lower than those of the composites in the whole
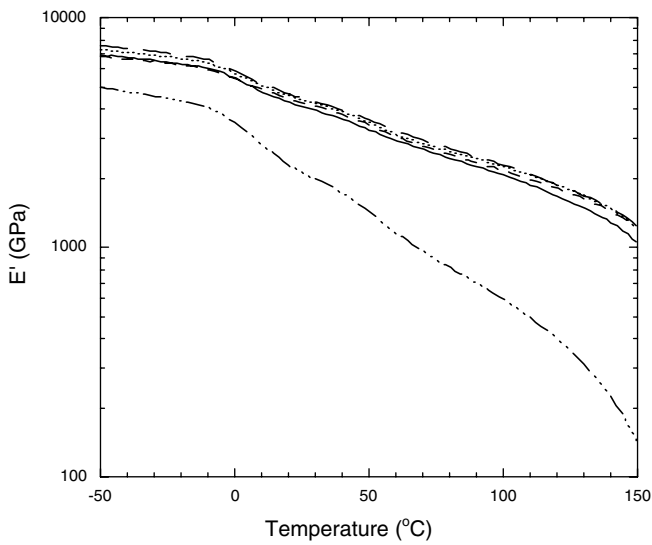
Fig. 8. Storage modulus (E') versus temperature for jute composites and pure polypropylene. —··—PP; —— PPJ; ——— PPJG; - - - - PPJL; ······PPJA.

Fig. 9. Tan δ versus temperature for jute composites and pure polypropylene. —··— PP; ——PPJ; ——— PPJG; - - - - PPJL; ······ PPJA.

temperature range, but the difference increases as the temperature increases. In all cases a sharp drop in E' from -10 to about $0\,^{\circ}\mathrm{C}$ is observed. This change is the relaxation of the amorphous phase of the PP, which goes from glassy state to the rubber one. After that, E' continues to fall, but with a higher slope than in the glassy zone. At about $100\,^{\circ}\mathrm{C}$ the pure PP reaches the melt region although all the composites still behave as rubbery materials. The reinforcing effect of jute fabric is evident. The effectiveness of fillers on the moduli of the composites can be represented by a coefficient C such as [41,42]:

$$C = \frac{(E_{\mathrm{g}}/E_{\mathrm{r}})_{\mathrm{comp}}}{(E_{\mathrm{g}}/E_{\mathrm{r}})_{\mathrm{resin}}} \tag{1}$$

where E_{g} and E_{r} are the storage modulus values in the glassy and rubbery region, respectively. The higher the value of the constant C, the lower the effectiveness of the reinforcement. The measured E' values at -30 and $50\,^{\circ}\mathrm{C}$ were employed as E_{g} and E_{r}, respectively. Although the values obtained for the different composites are practically the same ($C = 0.6–0.63$), it is interesting to notice that they are much lower than those obtained for cellulosic short fibers based composites, i.e. 0.96 for 30 wt% banana fiber–polyester resin as reported by Pothan et al. [41] indicating that a better reinforcement effect can be achieved using a woven fabric.

On the other hand, small differences are observed between the different fiber treatment or coupling agent additions. The PPJG composite presents slightly higher E' in the whole range of temperature than that of the PPJ sample. This behavior is the result of the PPMAN attached at the jute fibers surface, which can form entanglements with the PP chains of the matrix, improving the interfacial adhesion in the composite. This increased adhesion at the interface leads to an increase in the interfacial stiffness achieved through a more intense fiber–matrix
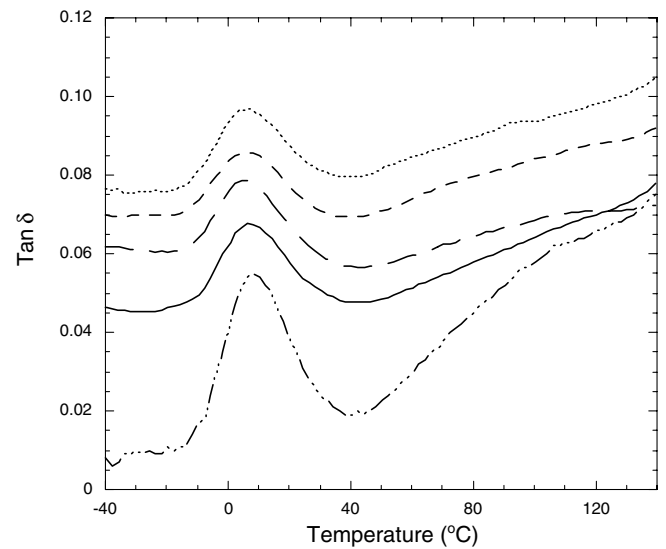
interaction, as it was observed by other researchers [43]. The other composites exhibit an intermediate behavior (between PPJ and PPJG performance).

Fig. 9 shows the changes of tan δ versus temperature of jute composites and pure PP. The peaks of most composites are broader than that of the matrix. This behavior suggests that there are molecular relaxations in the composites which are not present in the pure matrix. The molecular motions at the interfacial region generally contribute to the damping of the material apart from those of the constituents [44,45]. Thus, the observed broadening may be explained as due to the difference in the physical state of the matrix surrounding the fibers in comparison to the rest of the matrix [46]. Hence, the width of the tan δ peak is indicative of the increased volume of the interface. Table 3 shows the peak width at half height of the samples from the damping curve. The peak width is found to be maximum for the composite containing lignin. As it was explained above, it was found that lignin acts as a filler, instead as a coupling agent in this system. Moreover the surface area of lignin particles is higher than the corresponding for jute fabric. Thus, increasing the concentration of the filler increases the interface contribution [47]. On the other hand, the peak width is minimum for the PPJG composite, even narrower than that of the pure matrix. As it was noticed also by other researchers [48] a composite with poor interface bonding tends to dissipate more energy than that with good interface bonding. In the PPJG composite the coupling agent increases the fiber matrix adhesion causing lesser molecular mobility in the interfacial region.

Table 3
Tan δ peak characteristics

Material	PP	PPJ	PPJL	PPJA	PPJG
Width (°C)	23.2	25.0	25.5	24.5	22.5

The beneficial effects of maleated polypropylene on the strength properties of cellulose fiber polypropylene composites have been attributed to the esterification reaction between cellulosic fiber hydroxyl groups and anhydride functionality of maleated PP [41–49].

The molecular mobility associated with glass–rubber transition is complicated and not yet completely understood in semicrystalline polymers [29–50]. The presence of the fibers adds also complexity. The transition related with glass transition takes place at 8.3 °C for the pure PP, and this peak occurs at higher temperature than the corresponding peaks for the composites. The uncompatibilized composite and those made using coupling agents (lignin and G3003) exhibit the maximum in tan δ at about 6.4 °C. Several factors need to be considered to understand transitions occurring in these composites, but taking into account that the PPJ samples behave in the same way that compatibilized samples do, we attribute this effect to the materials present on fiber surface. Commercially available jute fabrics have a surface coating that is added to the fibers to facilitate the woven–weaving procedure and to protect the fibers from surface abrasion caused by handling and fiber–fiber contacts. This coating is a low molecular weight wax, which would be sheared off from the fibers and added to the matrix. This sheared material could also include hemicelluloses, oils and other surface extractives that are inherently present in the fibers and contributes to reduce the transition of the pure PP.

On the other hand, the glass–rubber transition of the PPJA composite is even lower (4.2 °C) than those of the other composites. In this case, the fiber surface coating was almost completely removed during fiber esterification, because it is soluble in acetone. But it is possible that the removal of unreacted ASA after fiber treatment was not complete. Thus, being the ASA a low molecular weight wax, with lubricant effect on the higher molecular weight matrix polymer, the small amount that can be present on fiber surface after successive washings could reduce the transition temperature by enhancing the ability of the polymer to undergo a glass–rubber transition.

3.3. Other considerations

Although in this study we try to keep fixed many of the parameters that affect the mechanical and thermomechanical behavior (reinforcement concentration, aspect ratio, thermal treatments, etc.) the behavior of composite systems based on polymeric matrices is complex and can be influenced by other factors (apart from interfacial interaction) that we were not able to control. For example, the crystallinity (crystal size and orientation of PP crystals) is a key determinant of composite properties, as demonstrated by Salemane and Luyt [51], who indicated that the addition of maleic anhydride grafted PP to PP/wood flour composites led to an increase in PP crystallinity, but a decrease in lamella thickness. These authors also pointed out that these results are dependent on the filler particle size and PPMAN

content. Transcrystalline growth could also take place (though a very low concentration is expected for our system). Moreover, the complete melting and continuity of the PP in the surfaces of the composites is also important. The morphology of the compression molded thermoplastic composites differs from the bulk to the surface since the surfaces are the first to solidify. Although a thermal treatment was applied to the composites after preparation and before testing (for releasing residual thermal stresses), it is possible that it was not enough to produce the same morphology along the thickness of the sample.

4. Conclusions

The creep-recovery behavior of jute-PP composites was studied and modeled using the four parameters approach. Creep deformation decreases as jute content increases, but the reduction of the deformation using fiber concentrations larger than 25% is only marginal.

Both, creep tests and scanning electronic micrographs, confirmed that the interfacial adhesion between the jute and the thermoplastic matrix was enhanced when maleated PP were used as compatibilizers. However, the interface formed when using G3003 copolymer was the best and consequently, PPJG composites displayed the most reduced creep deformation. The use of the TTS principle to predict long-term creep deformation was attempted; however, the resulting master curve was not entirely satisfactory.

Dynamic mechanical tests confirmed that the interphase between fiber and matrix was modified by the addition of compatibilizers, and also by using chemically treated fibers. They also revealed that the polymer reinforcement effect obtained using woven fabrics is much better than the one that can be achieved using short fibers.

Acknowledgements

Appendix

The Bürgers model, a combination of Maxwell and Kelvin–Voigt elements [52], is one of the most used models to predict creep behavior because it is described by a differential equation whose response to an applied stress can be easily solved analytically [24]. When using four elements, the resulting equation is the following:

$$\varepsilon(t) = \sigma_0/E_0 + \sigma_1/E_1(1 - e^{-tE_1/\eta_1}) + \sigma_0/\eta_2 \qquad (2)$$

where σ_0 is the applied stress, t is the time, E_0, E_1 are the modulus of both springs and η_1, η_2 are the viscosities of both dashpots. In a similar way, the four parameters model can be applied to calculate the recovery of a sample

previously subjected to a constant load for a period of time. In this case, the resulting equation is the following:

$$\varepsilon(t') - \varepsilon(t) = \varepsilon(t') - \{\sigma_0/E_0 + \sigma_0/E_1(1 - e^{-(t-t')E_1/\eta_1})\} \quad (3)$$

To predict the long-term behavior of polymeric materials it is necessary to know whether a linear or nonlinear viscoelastic theory should be used. The material is said to be linearly viscoelastic if stress is proportional to strain at a given time, and, in this case the linear superposition principle holds. Most materials are nearly linear over certain ranges of the variables, stress, strain, time and temperature, and nonlinear over larger ranges of some of the variables [53]. If the polymer behavior is linear viscoelastic in the range of study, it is a general practice that the test results from accelerated conditions would be extrapolated up to one order of time using the principle of time–temperature superposition (TTS). Thus, the creep curves obtained at different temperatures would be superposed by horizontal shifts along a logarithmic time scale (log a_T) to obtain a master curve. The shift factor (a_T) can be correlated with temperature using the relationship suggested by Williams et al. [54] (WLF equation), as described in Eq. (3):

$$\log(a_T) = -C_1 \cdot \frac{(T - T_0)}{C_2 + (T - T_0)} \quad (4)$$

where T_0 is the reference temperature and C_1 and C_2 are constants that depend on the material. This expression is usually valid for polymers over the temperature range $T_g < T < T_g + 100\,^\circ\text{C}$ (where T_g is the glass transition temperature).

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