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Thermal and dynamic mechanical properties of bio-based poly(furfuryl alcohol)/sisal whiskers nanocomposites

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Abstract In this study, bio-based nanocomposites of sisal whiskers-reinforced poly(furfuryl alcohol) (PFA) were prepared using an in situ polymerization method. Furfuryl alcohol (FA), which is a derived renewable monomer, was used to serve first as a solvent to disperse the whiskers and later as a monomeric precursor to produce PFA. Sisal whiskers were prepared via acid hydrolysis, which was followed by freeze-drying and re-dispersion of the dried whiskers in FA by sonication for 20 min. The polymerization process was catalysed using citric acid, which is also a renewable carboxylic acid found in citrus fruits. The effect of increased sisal whiskers loading on the thermal and dynamic mechanical properties of the nanocomposites was investigated using thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The TGA results showed slightly higher thermal stability for the nanocomposite samples compared to neat PFA. The DMA results showed that the incorporation of sisal whiskers imparts significant enhancement in the storage modulus of the PFA matrix. Moreover, the intensity of the tan δ peak at ~75 °C for the nanocomposites was remarkably reduced compared to that of neat PFA.

Keywords Poly(furfuryl alcohol) · Sisal whiskers · In situ polymerization · Biopolymer · Nanocomposites · TGA · DMA

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Introduction

The dwindling of fossil resources, the growing concerns about the environment and the ever-increasing prices of petroleum-based materials are some of the driving forces towards exploitation of renewable and eco-friendly materials. In recent years, bio-based polymer nanocomposites have attracted increasing attention as potential candidates to replace their existing petroleum-based counterparts. Possible applications of polymers from renewable resources and the perspectives for the future research have recently been reviewed in the featured article in Macromolecules by Gandini [1].

Owing to the advancement in technology, modifications of the naturally existing polymers and syntheses of novel new polymers from renewable monomers have been increasingly expanding. Poly(furfuryl alcohol) (PFA) is a crosslinked thermosetting polymer, which is produced via acid-catalysed polymerization of furfuryl alcohol (FA). FA is directly obtainable from the reduction of furfural, which is a renewable chemical produced from agricultural and forestry wastes [1, 2]. PFA has found successful applications and usage in different fields including metal-casting cores and moulds, corrosion resistant coatings, polymer concrete, wood adhesives and binders, sand consolidation and well plugging, materials possessing low flammability and low smoke release, modifier for natural fibre surfaces and precursor for glassy carbons and carbon nanocomposites [2–4].

Cellulose whiskers (CW) are bio-based nanofillers, which are produced from various agricultural, wood and animal resources through an acid hydrolysis method [5–7]. They have a lot of potential as reinforcing materials in polymer matrices due to their high surface area coupled with their good mechanical properties as well as their availability, renewability, recyclability and biodegradability [5–9].

Very few works [9, 10] have been published so far on composites comprising PFA and bio-based nanofillers. In general, the incorporation of these nanofillers was found to enhance the thermal stability of the PFA. However, to our best knowledge, a possible influence of CW on the viscoelastic properties of a PFA matrix has not been reported yet. In this study, completely bio-based nanocomposites of sisal whiskers-reinforced PFA were prepared via an in situ polymerization method. FA, which is a derived renewable monomer, was used to serve first as a solvent to disperse the whiskers and later as a monomeric precursor for the polymerization of PFA. Citric acid, which is naturally found in citrus fruits, was used to catalyse the polymerization process. The effect of increased sisal whiskers content on the thermal and dynamic mechanical properties of a PFA matrix was investigated.

Experimental

Materials

Sisal fibres were obtained from the National Sisal Marketing Committee in Pietermaritzburg, South Africa. Sulphuric acid (assay 95–99 %) was supplied by Merck Chemicals (Pty) Ltd. Sodium hydroxide pellets (assay 97 %) was supplied by Associated Chemical Enterprises (Pty) Ltd. Sodium hypochlorite was obtained from the local markets (JIK-household bleach, which contains sodium hypochlorite as an active ingredient with a concentration of 3.5 % (w/v), Reckitte Benckiser (Pty) Ltd., South Africa). FA (minimum assay 98 %) was purchased from Illovo sugar Ltd., South Africa. Citric acid monohydrate (assay 99.5 %) was supplied by Saarchem (Pty) Ltd., South Africa.

Preparation of sisal whiskers (nanofibres)

The sisal whiskers were prepared according to a procedure similar to that reported by Siqueira et al. [11]. Sisal fibres were cut with a Tecator sample grinder (Cyclotec-1093 sample mill, made in Sweden) until fine particulate fibres were obtained. The fibres were then treated with a 4 wt% sodium hydroxide solution at 80 °C in a water bath for 2 h under mechanical stirring. This treatment was done three times to remove other constituents than cellulose from the fibres. After each treatment, the fibres were filtered and washed with distilled water until all the akali was removed. A subsequent bleaching treatment was carried out to bleach the fibres. The solution used in this treatment consisted of equal parts of an acetate buffer (27 g of NaOH and 75 mL glacial acetic acid, diluted to 1 L using distilled water) and aqueous chlorite (1.7 wt% $NaClO_2$ in water). The bleaching treatment was performed at 80 °C for 4 h under mechanical stirring and was repeated four times. After each treatment, the fibres were filtered and washed with distilled water. The fibres were subsequently dried in an oven at 60 °C for 24 h. The dried fibres were ground to a fine powder using a Philips grinder (HR2021-400 W). Acid hydrolysis of the fine fibre powder was performed at 50 °C in a water bath, for about 50 min using 65 wt% sulphuric acid under mechanical stirring. The fibre content during all these chemical treatments was in the range 5–6 wt%. The suspension was diluted with ice cubes to stop the reaction. Successive washings in a centrifuge (HARRIER 18/80 refrigerated centrifuge, Model MSB080.CR1.K, made in the UK) at 10 °C and 5,000 rpm for 30 min were then performed. Dialysis (SnakeSkin® Pleated Dialysis Tubing-3,500 MWCO) against distilled water was done to remove the free acid in the dispersion. This was verified by determining the neutrality of the dialysis effluent. Complete dispersion of nanowhiskers was obtained by a sonication step using a Cole-Parmer Ultrasonic Processor (Model CP 505, 500 Watts). The dispersion was then filtered through a No. 1 fritted glass filter to remove residual aggregates, and then freeze-dried using a freeze dryer (Flex-Dry™ μP-Microprocessor Control, FTS Systems, Inc., USA).

Preparation of PFA/sisal whiskers nanocomposites

PFA nanocomposites were prepared by adding the freeze-dried nanowhiskers (1 and 2 wt%) to FA (40 g sample), as they are both hydrophilic, followed by a sonication step for 20 min, and then 5 phr citric acid monohydrate was added to the mixture to catalyse the polymerization process of FA. The mixture was heated at 85 °C under strong stirring for 8 h and then the resultant thick dark-brown material was transferred to the mould and subsequently heated in an oven, first at 70 °C for 2.3 h, and then the temperature was raised to 100 °C and the heating was continued for an additional 3 h. The final curing step was done by raising the temperature of the oven to 150 °C and the end of the curing was confirmed using differential scanning calorimetry (DSC) (no residual exothermic process was observed in the DSC curve [9, 12]). For comparison, pure PFA samples were prepared under the same conditions.

Characterization methods

Transmission electron microscopy (TEM)

The sisal whiskers suspension was examined using a transmission electron microscope, Philips (FEI) CM100 (The Netherlands), to confirm the separation of the nanofibres and to determine their dimensions. A drop of the diluted suspension was allowed to dry on a carbon-coated grid at ambient conditions and then the sample was stained using a uranyl acetate solution (2 wt%). The stained sample was observed using an accelerating voltage of 60 kV.

The morphology of the PFA-sisal whiskers nanocomposite was investigated on a Tecnai T20 transmission electron microscope at 200 kV with 20 eV energy slit to provide contrast. Since they were hard enough, the samples were cut cross-sectionally with the ultramicrotome. Sections, 100 nm thick, were collected on copper grids and investigated.

Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy

ATR-FTIR spectra of FA, pure PFA and its nanocomposite sample were obtained using a Perkin Elmer Spectrum 100 FTIR spectrometer. The samples were analysed over a range of 550–4,000 cm^{-1} with a resolution of 4 cm^{-1}. All the spectra were averaged over 8 scans.

Thermogravimetric analysis (TGA)

TGA was used to study the thermal stabilities of the sisal whiskers, neat PFA and its nanocomposite samples in a Perkin Elmer TGA7 thermogravimetric analyser. Samples with weights in the range of 5–10 mg were heated under a flowing nitrogen atmosphere (20 mL min^{-1}) from 30 to 800 °C at a heating rate of 10 °C min^{-1}, and the corresponding mass loss was recorded.

Differential scanning calorimetry (DSC)

DSC measurements were performed in a Perkin Elmer DSC7 differential scanning calorimeter in a nitrogen atmosphere. Samples were heated from 20 to 220 °C at a rate of 20 °C min^{-1}.

Dynamic mechanical analysis (DMA)

The dynamic mechanical properties (storage and loss modulus, as well as dissipation factor) of the samples were determined in a Perkin Elmer Diamond DMA dynamic mechanical analyser. The measurements were carried out in the dual cantilever-bending mode and the corresponding viscoelastic properties were determined as a function of temperature. The samples were heated under nitrogen flow (30 mL min^{-1}) from 25 to 190 °C at a heating rate of 3 °C min^{-1}, and at a frequency of 1 Hz.

Results and discussion

Morphological characterization of the sisal whiskers and nanocomposites

TEM was used to study the morphology of the obtained sisal whiskers and to determine their dimensions (length and diameter). Figure 1 shows the TEM micrographs of the sisal whiskers at different magnifications. It can be concluded that the process of acid hydrolysis coupled with sonication and filtration have successfully led to breakdown of the microfibres to produce the rod-like particles (whiskers). At higher magnification (Fig. 1b), it is possible to see the individual whiskers. The average length and diameter of the whiskers were 187 ± 17 and 15 ± 3 nm, respectively. The obtained value of average length is in agreement with that reported by Siqueira et al. [11], but the average diameter is slightly higher.

Figure 2 shows the TEM image of the cross-section of the composite sample with 2 wt% of filler. The sisal whiskers are apparently well dispersed in the PFA matrix. The image of the sample cross-section obtained at higher magnification (inset of Fig. 2) shows that the whiskers tended to group into bundles but the dispersion was relatively homogeneous.

FTIR spectroscopy

The polymerization of FA to produce PFA was confirmed using FTIR spectroscopy. In addition, FTIR analyses of PFA and its nanocomposite sample (98/2 w/w PFA/sisal whiskers) were also carried out to examine the possible interactions between PFA and sisal whiskers. The FTIR spectra of the three materials are shown in Fig. 3. The presence of the furan rings in all three spectra is proved by the absorption peaks at 3125, 1600, 1505, 1148, 1075, 1016, 885, 780, 730 and 600 cm^{-1} [13–15]. The aliphatic functional groups give rise to the bands at 2930, 1420 and 1377 cm^{-1}. The broad band at 3,322 cm^{-1} is assigned to the stretching vibration of both –OH end groups in PFA and to –OH groups in the monomeric FA. In the spectrum of PFA and PFA-whiskers nanocomposite, one can also notice two bands positioned at 1,713 and 1,560 cm^{-1} that are not present in the spectrum of the monomer. These bands, respectively, assigned to the carbonyl group stretching vibration of γ-diketones formed from hydrolytic ring opening of the furan rings and the skeletal vibration of 2,5-disubstituted furan rings, also indicate the resinification of FA

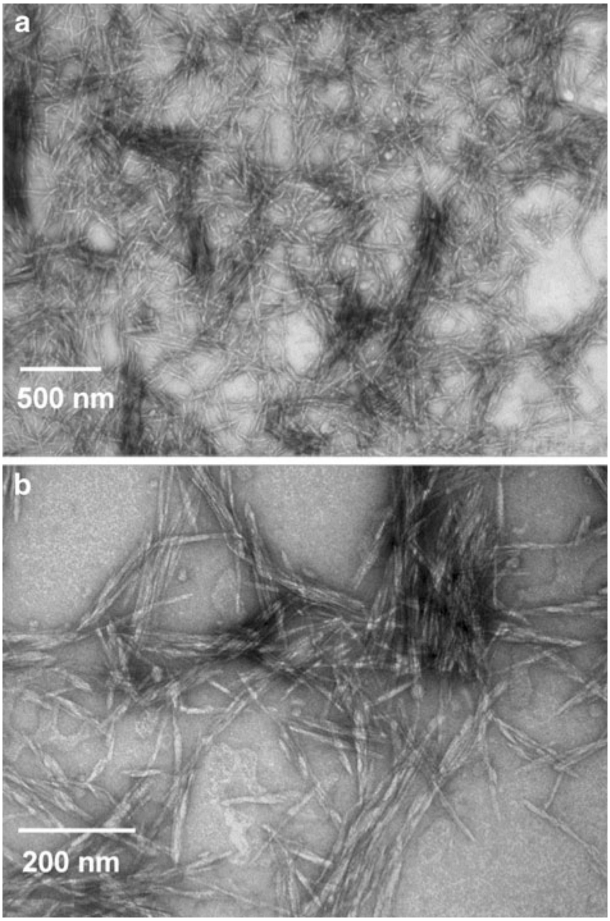

Fig. 1 TEM images of sisal whiskers

[9, 13, 15]. No significant changes between the absorption bands in the spectra of neat PFA and its nanocomposite sample could be noticed. This indicates that the curing process was successfully completed in the presence of sisal nanowhiskers, and that there was no chemical interaction between the matrix and the filler.

Thermogravimetric analysis (TGA)

Thermal degradation of neat PFA and its nanocomposite samples was studied using TGA. Figure 4 shows the mass loss of these samples as a function of temperature. In general, the incorporation of sisal whiskers slightly improves the thermal stability of the PFA in the temperature range studied here. It can also be noticed from Fig. 4 that the TGA curves show several degradation steps for all the samples. The first step starts above 200 °C and involves scission of the weaker chemical bonds [12]. The second degradation step occurs in the temperature range 320–400 °C, while

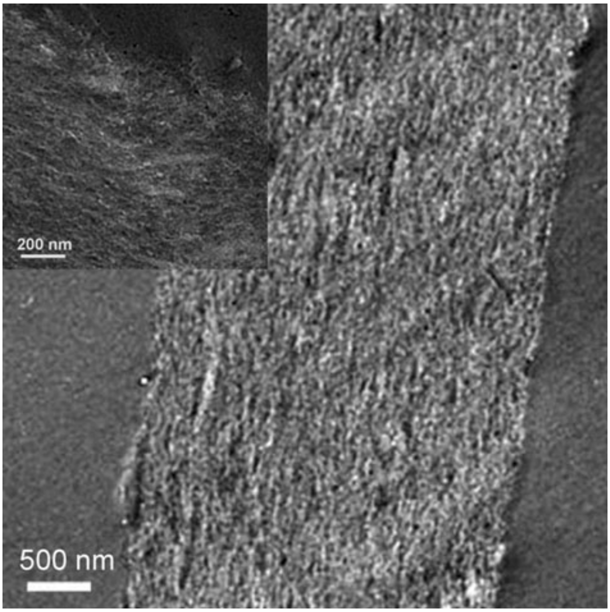

Fig. 2 TEM image of the cross-section of a PFA-sisal whiskers nanocomposite sample (98/2 w/w PFA/ sisal whiskers). The *inset* shows the cross-section at higher magnification

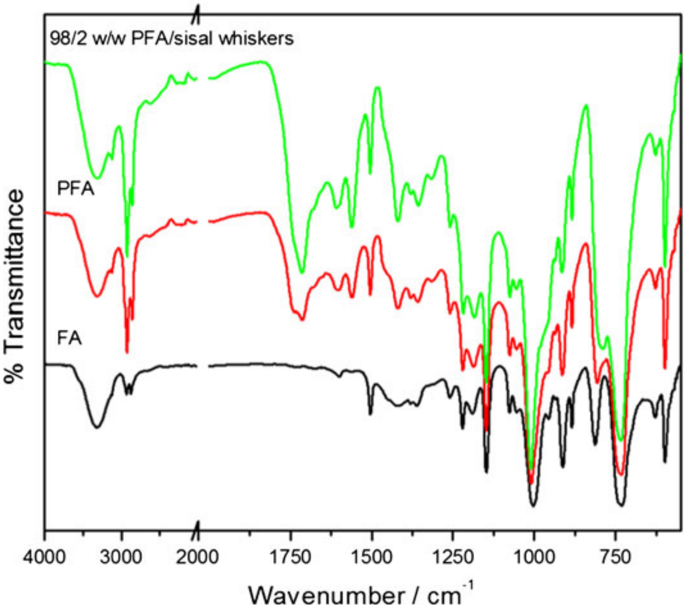

Fig. 3 ATR-FTIR spectra of the FA, neat PFA and PFA-reinforced sisal whiskers nanocomposite (98/2 w/w PFA/sisal whiskers)

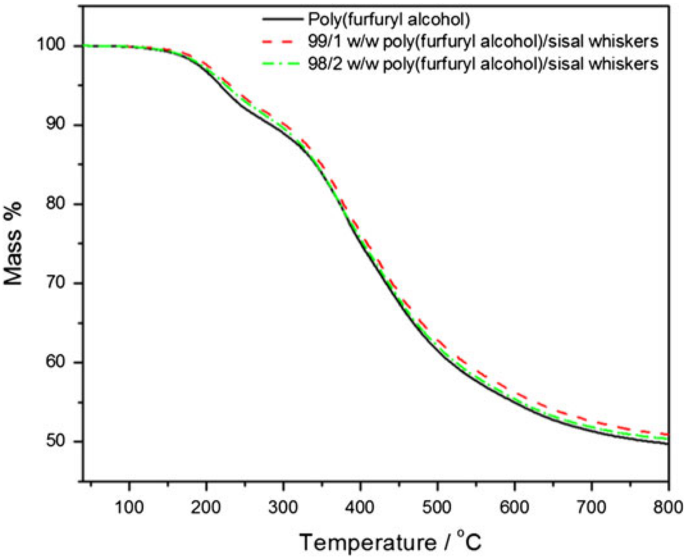

Fig. 4 TGA curves of the neat PFA and its nanocomposites

from 400 °C the mass gradually decreases. At the end of the measurement (800 °C), the observed mass losses for all the samples were about 50 %. Guigo et al. [12] identified the volatile compounds during thermal degradation of neat PFA using TGA–GC–MS. Their results showed a multi-step degradation pathway for the neat PFA. At lower temperatures, formation of alkylfurans (e.g. 2-methyl furan and 2-furfuryl-5-methylfuran) due to scission of both methylene and methyne links was observed. At higher temperatures, scission of furanic links form ketonic volatile compounds (e.g. acetone, 2-butanone and 2-pentanone). It is also important to mention that the thermal degradation of sisal whiskers starts above 200 °C (curve not shown) and the maximum rate of degradation appears around 350 °C. As the TGA curves of the pure PFA and the nanocomposites are almost identical (Fig. 4), it can be concluded that the sisal whiskers do not influence the degradation route of the matrix to a large extent. Other fillers influenced the thermal degradation of PFA in different ways [12, 15]. For example, the introduction of SiO_2 improved the thermal stability of the PFA matrix [12], while introduction of plasticized lignin reduced it [15]. It should be noted that PFA was also used for surface modification of sisal fibres in order to make them compatible with phenolic resins [16]. No significant changes in thermal stability of the fibres were noticed after modification with PFA.

Dynamic mechanical analysis (DMA)

The effect of the incorporation of sisal whiskers on the viscoelastic properties of PFA was investigated in the temperature range from 25 to 120 °C. The variation of the storage modulus (E') and loss tangent (tan δ) of the pure PFA and the PFA nanocomposites are shown in Fig. 5. As can be seen from Fig. 5a, although the whiskers content is relatively low, the storage modulus of the nanocomposites is significantly increased after introduction of the filler in the whole temperature range. The storage modulus of the nanocomposite sample with 2 wt% of sisal whiskers is almost three times higher than that of the neat PFA. This implies a strong reinforcement effect of the high-specific surface nanofiller, which was well dispersed in the FA during the sonication step. Later, during the polymerization of FA, the same state of dispersion was maintained in the final product leading to higher values of the storage modulus of the nanocomposites. Figure 5a shows a slight increase in the storage modulus (hardening) of the neat PFA and the nanocomposites at temperatures above ~140 and ~145 °C, respectively. Although DSC analysis showed no heat release by the samples at these temperatures, the results in Fig. 5a imply that some processes might not have been finished. Another explanation could be that the observed increase in modulus is a consequence of the first step of thermal degradation [17], which according to the TGA results in Fig. 4 starts around ~150 °C (note that the modulus starts to increase faster above this temperature and that the DMA measurements were carried out in air). It can be seen in Fig. 4 that the TGA curves of the composites were slightly shifted towards higher temperature with respect to that of the pure PFA. If we accept thermal degradation as a reason for the rise in modulus, the former result might explain why in the case of the composites this effect occurs at a higher temperature. In comparison with literature data, the effects of sisal whiskers on the storage modulus of PFA were slightly different from that reported for SiO_2 [12] and plasticized lignin [17] fillers, but in both of the mentioned studies it was observed that the storage modulus increased at higher temperatures (above ~150 °C).

The variation of tan δ of the PFA and its nanocomposites as a function of temperature is presented in Fig. 5b. The magnitude of the tan δ peak, related to the modulus drop, decreases after the introduction of sisal whiskers. The whiskers obviously improve the elasticity of the matrix and reduce the energy losses. On the other hand, the position of the relaxation peak (T_α), associated with the inelastic manifestation of the glass–rubber transition of the polymeric matrix, was shifted towards lower temperature after introduction of the filler (Fig. 5b). T_α can be directly related to the glass transition temperature (T_g) of the matrix as well as to the drop of the storage tensile modulus (i.e. mechanical coupling effect) [18]. In order to determine the glass transition temperature, we performed DSC analysis. However, the obtained DSC curves of the pure PFA and PFA nanocomposites were smooth showing no apparent phase transitions in the temperature range of 20–180 °C (the temperature range of DMA measurements). The softening transition of the pure PFA and the PFA nanocomposites was obviously too broad to be observed with this technique, probably due to the broad distribution of the lengths of polymer segments, the mobile entities that are activated during the transition. As the pure PFA and PFA nanocomposites showed similar DSC behaviour, the observed shift of the tan δ peak towards lower temperatures with increasing filler content should be attributed to a mechanical coupling effect [18].

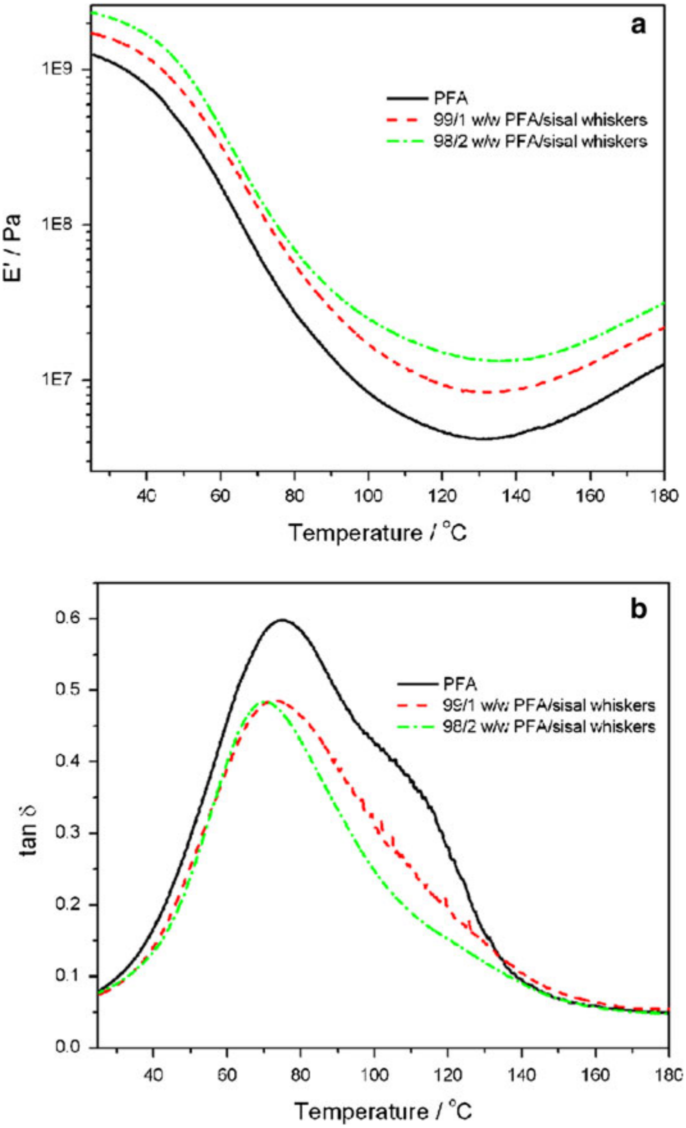

Fig. 5 DMA: **a** storage modulus and **b** tan δ curves for pure PFA and its nanocomposites

Conclusions

Bio-based nanocomposites of PFA and sisal whiskers were prepared by an in situ polymerization method and their thermal and dynamic mechanical properties were investigated. The resinification of FA was followed using FTIR spectroscopy. No chemical interaction between PFA and sisal whiskers could be noticed from the IR spectrum of the nanocomposite. TGA showed multi-step degradation behaviour for all the samples and the thermal stabilities of the nanocomposite samples were very slightly higher than that of the neat PFA. The effect of the sisal whiskers on the viscoelastic properties of PFA was examined using DMA. In comparison to neat PFA, all the nanocomposite samples showed significantly higher storage moduli and lower intensities of the tan δ peaks. At the same time, the position of the tan δ peaks of the nanocomposites was slightly shifted towards lower temperature due to a mechanical coupling effect.

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