

Novel Cellulose Ester–Poly(Furfuryl Alcohol)–Flax Fiber Biocomposites

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ABSTRACT: Composites based entirely on renewable materials with flax fibers as reinforcement and cellulose acetate butyrate (CAB) as the matrix were prepared by compression molding. Scanning electron microscopy of the fracture surfaces showed insufficient penetration of the matrix into the fiber mat. Rheological measurements indicated that this was caused by the high melt viscosity of CAB. Various amounts of furfuryl alcohol (FA) were added to the matrix to control the melt viscosity of CAB. The melt viscosity was decreased dramatically by the introduction of FA, which acted as a CAB solvent and facilitated the impregnation of the flax fiber mats. The mechanical and dynamic thermal properties of composites based on flax mats and various amounts of CAB and FA were investigated. The addition of FA to CAB and the polymerization of FA resulted in a linearly increased modulus and an increase in the maximum fiber stress (strength) of flax composites but a decreased toughness.

Dynamic mechanical thermal analysis (DMTA) showed that CAB/poly(furfuryl alcohol) (PFA) matrices were miscible because the glass-transition temperature (T_g) in the resulting blends occurred between the T_g of the homopolymers. DMTA also showed that increasing the amount of FA in the matrix substantially increased the storage modulus of the composites at temperatures lower than 80°C. It was possible to tune the storage properties of the composites through the addition of appropriate amounts of FA to the matrices. The CAB/PFA matrix showed behavior between that of thermoplastics and thermosets because of the miscibility and affinity of its components. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 337–345, 2003

Key words: composites; biomaterials; viscosity; dynamic mechanical thermal analysis; mechanical properties

INTRODUCTION

In recent years, interest in composites based on renewable materials has grown tremendously because of greater environmental awareness.^{1,2} The advantages of natural materials, such as those that are light weight, low price, and have low abrasion to equipment, are now even more attractive because of the progress that has been made in fiber development, the genetic engineering of plants to produce a variety of new polymers and fibers, the chemistry of natural compounds, and so on. This has broadened the horizons for the design of new materials.^{3–5} Traditionally, the use of renewable materials in composites has been restricted to cellulose fibers, which serve as reinforcement in synthetic polymeric matrices (see refs. 6–10 and the references therein). The new generation of cellulosic composites being developed in several laboratories around the world is based on entirely renewable components. Examples of these biocomposites

are cellulose/(polyhydroxyalkanoates),^{5,11,12} cellulose/starch,^{5,13,14} and cellulose/poly(lactic acid).⁵

Natural composites, such as wood and bone, represent advanced materials with properties that are adequate for their intended use.¹⁵ These materials behave differently when they are separated from the living organisms, which is reflected in their lack of response to environmental changes. Natural composites consist of a polymeric matrix reinforced with either fibers or crystallites. They are hierarchically organized with a high degree of order on the different scales from micro and nano to Ångström levels and are a source of inspiration in the design of materials that will be termed *intelligent* in the near future because they will be able to respond differently to different, special environments. There are hopes that these intelligent materials also be self-repairing and be able to be destroyed on demand.

The matrices that make up natural composites are not easy to mimic. Although natural polymers, such as lignin, hemicelluloses, starch, chitosan, and proteins, are readily available, they are often modified during the isolation process. These materials yield stiff matrices with a high modulus, making it necessary to use plasticizers when toughness is required.^{5,13,14,16–18} Thermoplastics based on renewable sources, such as

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the polymers mentioned previously, either as natural polymers or as sources of monomers, are under intense development for special applications that call for biocompatibility and biodegradability.^{10,19–21}

The molecular structure of cellulose provides a building block in plants because of the rigidity of the cellulosic chains. The rigidity originates from the hydrogen bonding of the free hydroxyl groups in the glucose repeating unit within and between chains. The stability of the superstructure that is formed (microfibrils and fibrils) comes mainly from the ability to form hydrogen bonds. As a consequence, cellulose is not a thermoplastic but degrades on heating before the theoretical melting point is reached. Breaking the hydrogen bonds by solubilizing and reacting the free hydroxyl groups yields a polymer that is thermoplastic. Cellulose ethers and esters are examples of such derivatives that have extensive industrial uses. It is possible to prepare a wide variety of materials whose properties depend on the degree of substitution, the length of the chain of the derivatizing agent, and the degree of polymerization of the cellulose chain.^{22,23}

Although the major applications of cellulose esters are automotive coatings, lacquers, printing inks, and so on, they have been used in selected composite systems, such as ceramics,²⁴ conducting polyaniline–cellulose composites,^{24,25} and nanocomposites where microcrystalline cellulose acts as a reinforcement.^{18,20} In the latter case, the cellulose microcrystals are perfectly embedded in the cellulose ester matrix due to a partial derivatization of the cellulosic fibers that allows thermal deformability and enhanced mechanical properties in the reinforced composites. These properties vary with the degree of substitution of the hydroxyl groups. However, cellulose acetate matrix–flax fiber reinforced composites have shown poor mechanical properties because the degree of impregnation of the matrix into the reinforcing fiber has not been sufficiently high because such parameters as fiber preparation, fiber matrix bonding, and the viscosity of the matrix at the processing temperatures have not yet been optimized.²⁶

Furfuryl alcohol (FA) is a product of the acid–thermal transformation of biomass-based pentoses such as xylans whose traditional applications include foundry cores and molds, polymer concretes, coatings for corrosion resistance, wood adhesives and binders, materials with low flammability and smoke release, and graphitic electrodes from carbonaceous products.²⁷ FA polymerizes under acid conditions and heat and ultimately yields crosslinked resins. Nguyen and Zavarin²⁸ reported the graft polymerization of poly(furfuryl alcohol) (PFA) of different viscosities; they found that the higher the viscosity was, the better the grafting was. It was also found that the FA monomer did not graft on wood fibers.²⁸ Other studies have investigated the binding of wood with FA and PFA.²⁹

This study evaluated the properties of composites based on flax fibers, cellulose ester, and FA prepared by compression molding.

EXPERIMENTAL

Materials

Cellulose acetate butyrate (CAB; CAB-553-0.4) was kindly supplied by Eastman Chemical Co. (Kingsport, Tennessee). It possessed the following characteristics, according to the company and as tested with the ASTM standard test for CAB (D707-98): viscosity = 0.114 Pa s, acetyl content = 2.0%, butyryl content = 46%, hydroxyl content = 4.8%, melting point = 150–160°C, glass-transition temperature (T_g) = 136°C, density = 1200 kg•m⁻³, and number-average molecular weight = 20,000.

Flax fiber mats were kindly supplied by Flex Prop Production AB (Halmstad, Sweden). Flax mats were retted and nonwoven needled with a grammage of 1750 g•m⁻² and had a single-fiber diameter of 23 μm. This material is widely used in the automotive industry.

FA (>98% purity, density = 1135 kg•m⁻³, and boiling point = 170°C) was a clear colorless to clear yellow liquid of low viscosity. It was generously supplied by Perstorp AB (Gustafsberg, Sweden) and was used as received.

Maleic acid and maleic anhydride (>99% purity; Fluka AG, Chemische Fabrik, Buchs, Germany) were used as received.

Methods

Viscosity measurements and dynamic mechanical thermal analysis (DMTA) tests

Viscosity measurements were made in a Rheometrics dynamic analyzer (RDA II) (Piscataway, NJ) at different temperatures in a parallel-plate geometry. The strain was kept constant at 10% during frequency sweeps (0.1–80 Hz). Viscosity measurements were also made with temperature sweeps (20–200°C) at 1 Hz and 10% strain. Dynamic thermal mechanical tests were done in a Rheometrics apparatus with temperature sweeps (2°C step) in the range of 25–200°C at 1 Hz.

Composite preparation

CAB/FA mixtures were prepared by the addition of the required amount of FA to CAB and by stirring to achieve a homogeneous clear solution or paste. Composites with a flax fiber content of 50 wt % were prepared by the addition of CAB/FA mixtures, catalyst, and acetone (evaporated afterward under vacuum) to improve the impregnation of the flax mat. Composites consisting of FA and CAB/FA were pre-

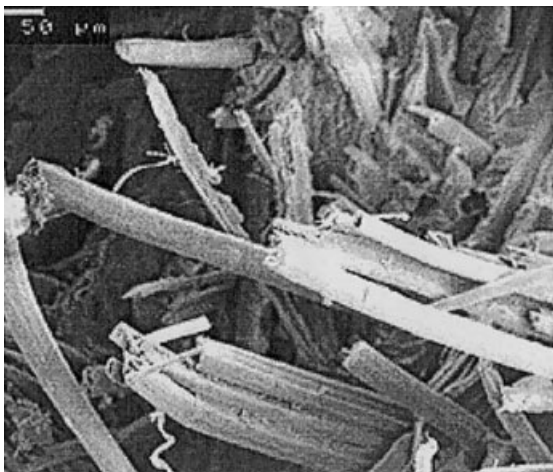


Figure 1 CAB-flax fracture surface micrograph.

polymerized in an oven by ramping of the temperature from 25 to 120°C at a rate of 3°C/min for about 30 min and were pressed according to the following schedule:

1. Flax-FA composites: The impregnated mat was brought to 80°C and a pressure of 8.89×10^5 Pa; the temperature was then increased to 120°C at 1.33°C/min, which took 30 min. The composite was brought to atmospheric pressure to release

byproducts from the polycondensation of FA. The pressure was increased to 22.2×10^5 Pa, and the temperature was ramped from 120 to 150°C at 1.5°C/min. The composites were cooled to room temperature under pressure (22.2×10^5 Pa). After cooling, the composites were placed in an oven at 100°C overnight to ensure that all the FA was cured or evaporated.

2. Flax-CAB-FA composites: The same procedure was followed, but the temperature was raised to 155°C (instead of 150°C) to melt the CAB.
3. Flax-CAB composites: The prepolymerization step was omitted, and the composites were pressed directly at 22.2×10^5 Pa and 155°C.

Mechanical tests

Composites were conditioned at 23°C and at 50% relative humidity for at least 40 h and tested according to two ASTM standard test methods: D 790-97 (flexural properties of unreinforced and reinforced plastics and electrical insulating materials) and D 6110-97 (charpy impact resistance of notched specimens of plastics).

Scanning electron microscopy

Scanning electron micrographs of the gold-sputtered fracture surfaces of the composites were taken with an

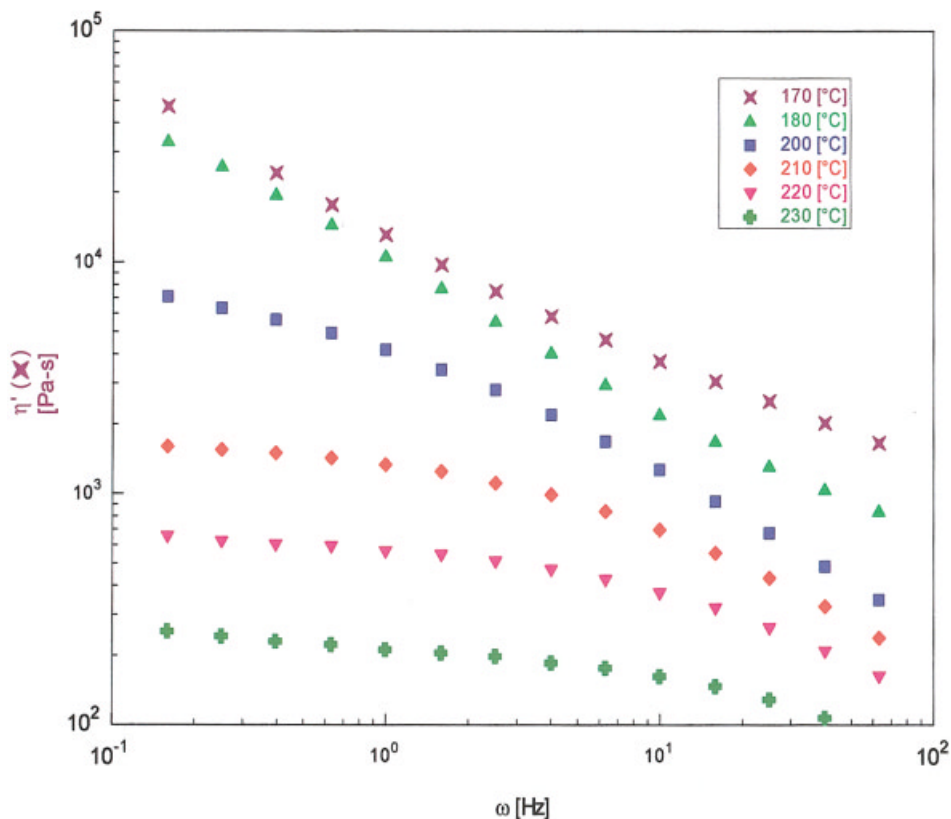


Figure 2 Viscosity of CAB as a function of frequency at different temperatures.

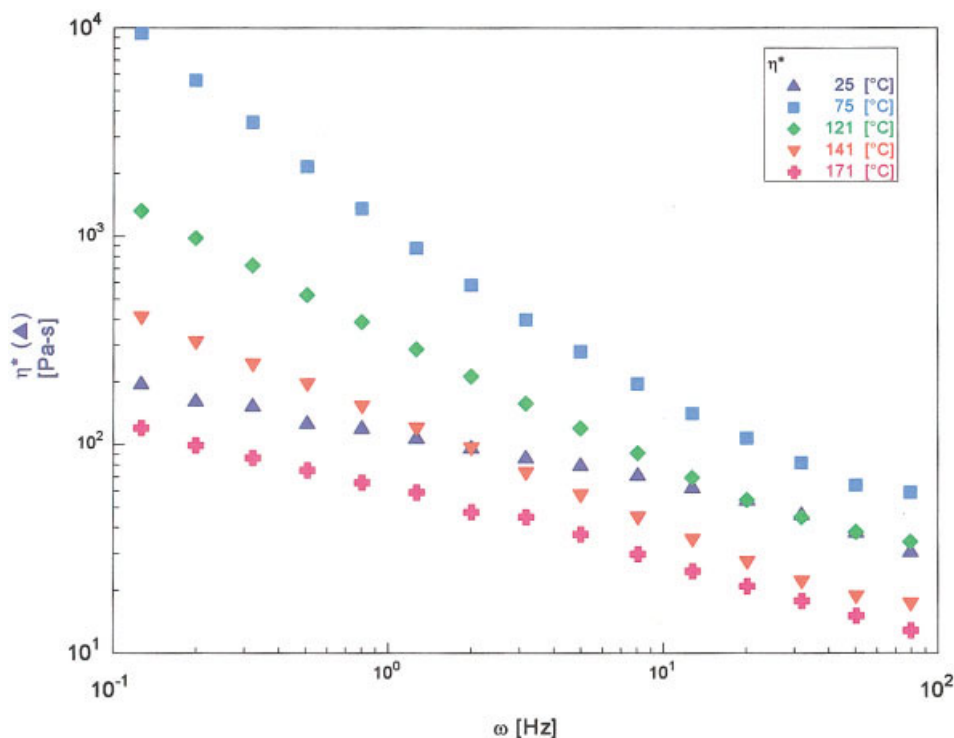


Figure 3 Viscosity of CAB–FA solutions at 50% CAB content as a function of frequency at different temperatures.

electronic microscope (Zeiss model DSM 940 A, Oberkochen, Germany) at 15 kV working energy.

RESULTS AND DISCUSSION

CAB–flax fiber composites

CAB was added as a powder and spread into the flax mat. The composite was then prepared by hot pressing at 170°C and 8.89×10^5 Pa. Figure 1 shows the fracture surface of the CAB/flax composite. The bundles of flax fibers that were pulled out from the matrix were evidence of the lack of wetting of the fibers by the matrix. One possible explanation is an insufficient flow of the CAB melt at that processing temperature.

Viscosity measurements

A series of rheological measurements was made with CAB to investigate its viscosity under different temperatures and shear rates. These are shown in Figure 2. For a given temperature, an increase in the shear rate decreased the viscosity, especially at lower temperatures. Temperature itself reduced the viscosity by several orders of magnitude; for instance, the viscosity of CAB at 170°C and 0.1 Hz (5×10^4 Pa s) was reduced to about 250 Pa s by increasing the temperature to 230°C at the same shear rate. A good impregnation of CAB into the flax mat could be obtained at this temperature. However, temperatures higher than 190°C promote the degradation of lignocellulosic fibers.²

Polymeric matrices are often dissolved to improve the impregnation of the reinforcing material. We evaluated various polymerizable solvents based on renewable resources.³⁰ FA was found to dissolve CAB. Dissolving CAB in FA produced a light yellow viscous liquid whose viscosity depended on the amount of CAB in the samples, the temperature, and the shear rate. Figure 3 shows the viscosity of CAB/FA as a function of the shear rate and temperature at 50% CAB content. The value of the viscosity at room temperature and low shear rate was around 200 Pa s, which is sufficiently low for both resin-transfer-molding and compression-molding processes. At low shear rates, increasing the temperature increased the viscosity to a maximum of 10^4 Pa s at a temperature of 75°C. The viscosity decreased at higher temperatures. The solubility of CAB was improved at temperatures higher than room temperature, as seen by the greater viscosity. However, there may be several explanations for the decreased viscosities at temperatures higher than 75°C. Although FA requires an acid catalyst to polymerize, the availability of hydroxyl reactive groups in CAB might have triggered the formation of oligomers at relatively low temperatures, which could lead to phase separation and could decrease the viscosity. The viscosity decreased to lower values at 171°C, which were lower than those observed at room temperature, even though that was the boiling point of the FA monomer. Regardless of the temperature, an increase in the shear rate decreased the viscosity,

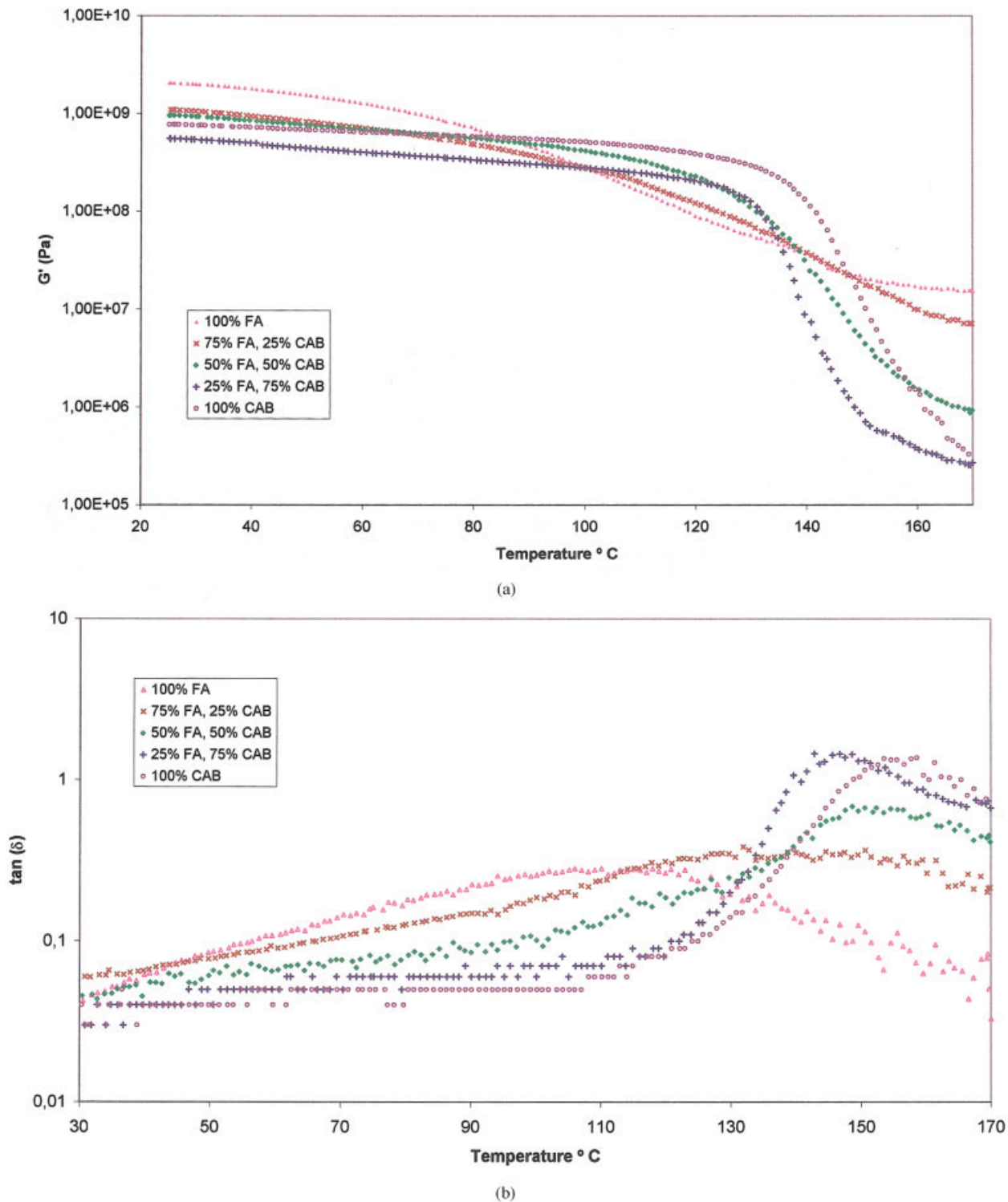


Figure 4 (a) G' and (b) damping behavior of unreinforced matrices.

illustrating the shear thinning character of the CAB/FA mixture.

The viscosity of CAB at a concentration of 25% as a function of temperature and shear rate was also recorded. Behavior similar to that of CAB/FA at a concentration of 50% was observed in this sample. At 25 $^{\circ}\text{C}$, the viscosity of the sample was around 80–100

Pa s and was not greatly affected by the shear rate. However, increasing the temperature increased the viscosity up to a maximum at 50 $^{\circ}\text{C}$. A further rise in temperature above 50 $^{\circ}\text{C}$ decreased the viscosity. Increasing the shear rate reduced the viscosity back to the lower values. The improvement in the solubility of CAB in the FA monomer at higher temperatures re-

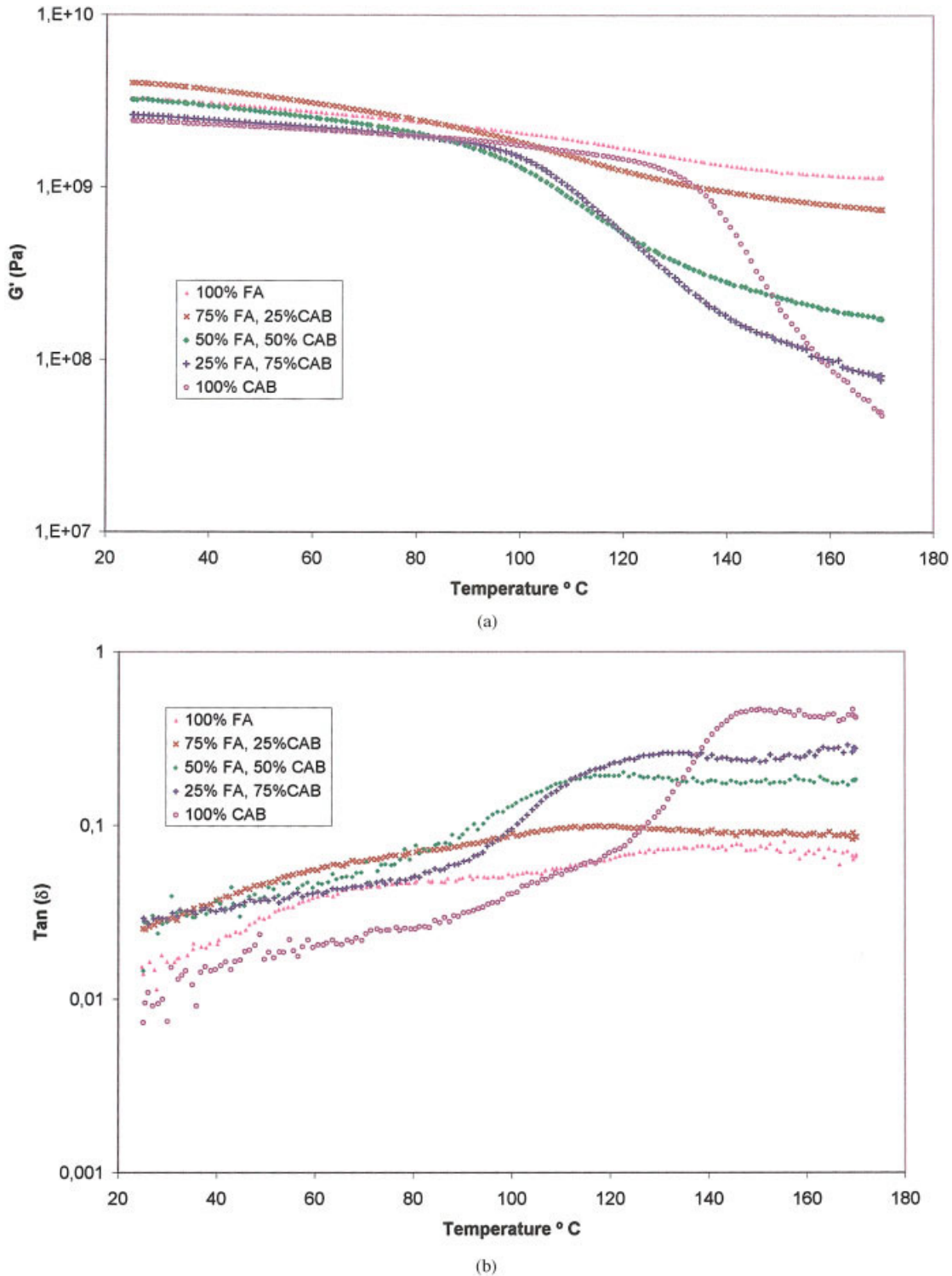


Figure 5 (a) G' and (b) damping behavior of reinforced matrices.

sulted in an increased viscosity. Oligomer formation and subsequent phase separation were probably responsible for the decrease in the viscosity. The shear rate also affected the viscosity regardless of the temperature, and there was a thinning effect at high FA concentrations as well.

DMTA of CAB/PFA matrices and flax composites

The dynamic thermomechanical properties of matrices and flax composites were studied after the curing of FA. FA polymerizes through condensation reactions under acidic conditions that ultimately yield a black

crosslinked resin.^{27,28} The curing of FA resin is further improved in the presence of nucleating particles that have a large surface area and a sufficient amount of reactive groups, such as acidic hydroxyl groups.³¹ Curing times of 30 min are sufficient to obtain a degree of polymerization between 300 and 700 furan units.³¹

Figure 4 shows the shear storage modulus [G' ; Fig. 4(a)] and the damping behavior [Fig. 4(b)] of the unreinforced matrices. As shown in Figure 4(a), G' of PFA was greater than all the other matrices up to a temperature of about 80°C; the slope then changed, and G' decreased to values lower than the matrices that consisted of both PFA and CAB. The less stiff behavior of the PFA matrix at temperatures higher than 80°C was due to the main relaxation process that takes place under a broad temperature range. When the matrix was composed of both CAB and PFA, the system became stiffer with increased amounts of PFA, although their storage modulus was lower than that of neat CAB. It is likely that the presence of oligomers and unreacted monomer would plasticize the matrix as illustrated by Figure 4(a) at 75% CAB. In that case, only 25% FA lowered G' over the whole range of temperature.

The damping behavior of the matrices is shown in Figure 4(b), which reveals a broad T_g peak for PFA at about 105°C and distinctive T_g peaks for the CAB/FA matrices. The T_g values were between those of the neat polymers, which indicated the miscibility of the system.³² The resultant single T_g of the matrices followed a modified version of the Gordon–Taylor equation that describes T_g as a function of blend composition and accounts for strong interactions or crosslinks. It can be described by³³

$$T_g = (W_1T_{g1} + kW_2T_{g2})/(W_1 + kW_2) + qW_1W_2$$

where W is the mass fraction of each component and k and q are adjustable parameters. In this case, $k = 1.4$ and $q = 1.8$ (q accounts for crosslinks in the blends, and k is related to the components of the blends in terms of their change in the cubic expansion coefficient at the T_g and their specific volumes³³). The fact that PFA and CAB were miscible or compatible explained the behavior of the composites. As shown in Figure 4(b), the $\tan \delta$ peak for the different matrices also changed in size, and it was smaller for the PFA matrix because of the restriction of chain mobility caused by the crosslinks. The broadening of the $\tan \delta$ peak on addition of PFA was most likely due to inhomogeneity of the crosslinks within the material.

The viscoelastic properties of the reinforced composites are shown in Figure 5. G' of the reinforced matrices is shown in Figure 5(a). The flax-reinforced PFA matrix showed a typical curve for a reinforced thermoset without severe transitions under the whole temperature range studied. Increasing the thermoplastic content decreased the stiffness of the composites at lower temperatures, although the slope of the curves of the composites changed at about 30°C before the change in neat CAB. This change could be related again to the main relaxation process undergone by PFA in the temperature range. Changes in the T_g of the composites are shown in Figure 5(b), which shows the $\tan \delta$ of the composites. There was a clear T_g distinction in the composites with up to 50% CAB content and their decrease in T_g , which followed the relationship mentioned for the unreinforced matrices. For larger PFA contents, the T_g 's were not distinctive.

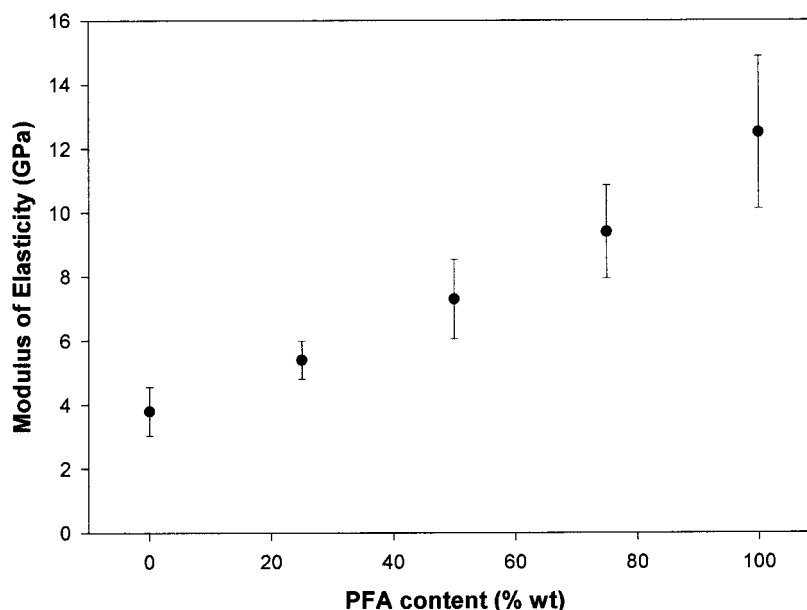


Figure 6 Modulus of elasticity of CAB–FA composites as a function of FA content.

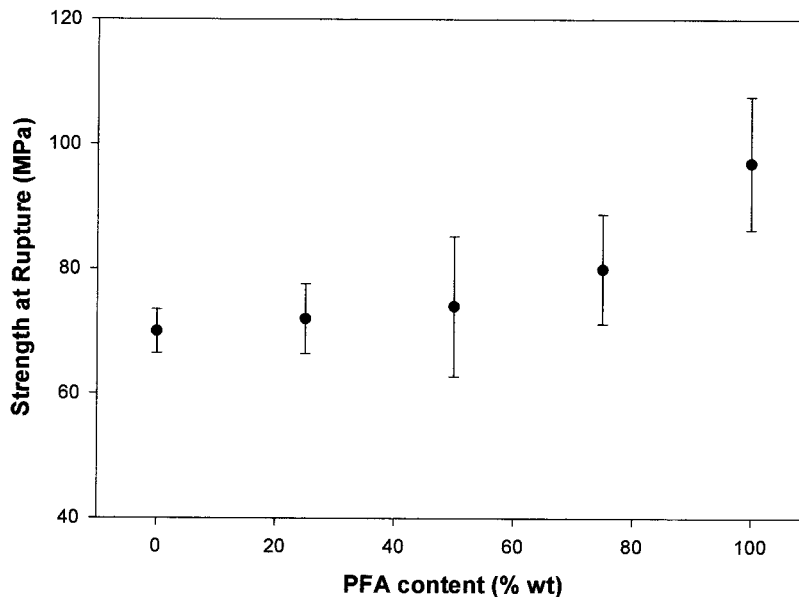


Figure 7 Modulus of rupture (bending strength) of CAB-FA composites as a function of FA content.

Comparison with unreinforced matrices showed that the composites had a larger storage modulus (ca. one order of magnitude) because of the addition of fibers. Also important were the facts that at temperatures lower than 80°C, increasing the amount of FA in the matrix also substantially increased the storage modulus of the composites and that the stiffness of the composites could be tuned by the addition of appropriate amounts of FA to the matrices, thus achieving composites with behaviors between thermoplastic and thermoset.

Mechanical properties of the composites

Flexural and charpy impact strength properties of PFA-CAB-flax composites are shown in Figures 6, 7, and 8. In Figure 6, it is shown that the modulus of elasticity increased linearly with addition of FA, which was consistent with DMTA data at room temperature. Because of the formation of a highly crosslinked matrix composite from a thermosetting material such as PFA, a threefold increase in modulus was achieved when the matrix was composed only of

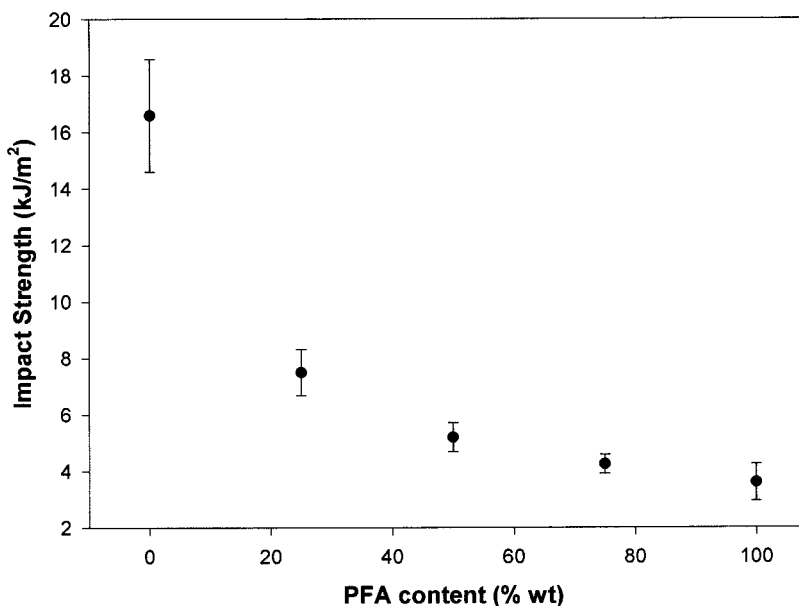


Figure 8 Impact strength of CAB-FA composites as a function of FA content.

PFA, as compared with CAB matrices. Hence, stiff composites could be achieved by the use of only PFA as the matrix component. Figure 7 shows that the strength at rupture was substantially increased when the matrix was composed only of PFA; any other improvement would be negligible when one considers the rather high standard deviation registered in these experiments. However, the network formation of PFA had a direct effect on increasing the bending strength of such composites because it increased up to 40% over CAB-flax composites. Figure 8 shows that the impact strength of the composites decreased to more than half when PFA was included as a component of the matrix at 25 wt %. The impact strength decreased only slightly at greater PFA contents. It is thus important to emphasize that additions of FA to CAB-flax composites increased the modulus at the expense of impact strength.

CONCLUSIONS

Composites materials can be prepared exclusively from renewable sources such as cellulose fibers and cellulose esters as matrix. The processability of CAB was substantially improved by the addition of FA. CAB/FA solutions at 50 and 25 wt % CAB resulted in viscous liquids at room temperature. Their viscosity increased when the temperature was increased to 75 and 50°C, respectively. CAB/FA solutions showed a shear thinning effect. Efficient wetting of flax fibers with CAB/FA blends was achieved at low temperatures. DMTA of the matrix samples at different PFA contents revealed a single T_g in each of them. The T_g detected for each matrix was between those of the homopolymers, indicating a miscible system. Reinforcement of the matrices with flax fibers increased the storage modulus and retained the characteristics of the unreinforced matrices. The mechanical properties of composites made with CAB/PFA blends showed that the addition of FA increased the modulus of the composites and the strength at rupture but decreased its impact strength because of the network formation of PFA.

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