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STUDY OF CYANOETHYLATED ALFA FIBER REINFORCED COMPOSITES BY DYNAMIC MECHANICAL ANALYSIS

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Introduction

Fiber-filled composites are widely used in numerous applied areas by the rational selection of both fiber and resin [1–2]. Since the eighties, the greater emphasis has been rendered in the development of fiber-filled composites based on natural vegetal fibers [3-5] with a view to replace glass fibers either totally or in part for various applications. The scope for using vegetal fibers instead of the traditional glass fibers stems from the lower specific mass and workable specific modulus of the vegetal fiber.

Moreover, their much lower cost and the renewable nature make them attractive for use as a reinforcing material in fiber-filled composites.

Table I. Properties of vegetal and glass fibers [6]

	Density	Specific tensile strength (GPa)*	Specific tensile modulus (GPa)**	Relative price
Vegetal fibers	0.15-1.2	1.6-2.95	10-130	1-8
Glass fibers	2.6	1.35	30	10–14

* Tensile strength/density
** Tensile modulus/density

In spite of the various desirable properties of the vegetal fibers to act as a reinforcing material, their commercial utilization in fiber-filled composites has not gained much success.

The main reasons of the failure are the poor wettability and adhesion characteristics of cellulosic fibers towards many commercial synthetic resins, resulting in the poor strength of the composite. Moreover, their hydrophilic nature induces the poor environmental resistance [7–8].

Therefore, attempts have been made to overcome the limitations of cellulosic fibers through their chemical modification [9–10].

The object of the present article is to study the effect of cyanoethylation of the alfa fiber on improving its suitability as a reinforcing material in the unsaturated polyester resin-based composite.

Alfa is the Arabic name of the *Stippa Tenacissima* plant. It is constituted of stalks that can attain 1.20 m in length. Alfa is a heterogeneous polymer; apart from cellulose (45%), the alfa fiber contains 25% hemicellulose and 23% lignin as major constituents [11–12].

The mechanical properties of the modified alfa-polyester composite (MAC) were studied by performing traction tests in the first step, and using a dynamic mechanical thermal analyzer in the second step.

Materials and chemicals

Long alfa fibers were extracted from the alfa plant stalks. The alfa stalks were treated with a (3N) sodium hydroxide solution for 2 hours with reflux, washed with water and then bleached for 1 h in a NaOCl solution (40%) at 25°C. After that, the fibers were thoroughly washed with water, dried at 105°C for 4 h and finally carefully carded.

The general-purpose unsaturated polyester resin (USP) was obtained from the NESTE Chemicals; the styrene content was about 38%. The laboratory reagent-grade acrylonitrile was used in this study without further purification.

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Cyanoethylation of alfa fibers

Cyanoethylated alfa fibers were prepared by using the procedure described by A. K. Saha and Col and reported earlier [13].

20 g of dry extracted alfa fibers were impregnated for 2 minutes with a 4.0% (w/w) sodium hydroxide solution at room temperature and the fibers were then hydro extracted by centrifugation until the weight became 40 g. The alkali-soaked fibers were steeped in 400 ml of acrylonitrile for different periods of time, namely, 1-2-3-4-5 h at room temperature. After the stipulated time of reaction, the fibers were thoroughly washed with 5% acetic acid and finally with distilled water. The fibers were then dried at 105°C until constant weight was obtained.

Some properties of the unmodified alfa fibers, the cyanoethylated alfa fibers and the cured unsaturated polyester resin are given in table II.

Table II. Properties of fibers and unsaturated polyester resin (cured)

Sample	Moisture regain (65% at 25°C)	Tensile strength (MPa)	Tensile modulus (GPa)	CV (%)
Unmodified alfa fiber	7.00	240	22.8	60
Modified alfa fiber (RT, 1h)	3.75	106	4.62	70
Modified alfa fiber (RT, 2h)	3.30	100	6.25	34
Modified alfa fiber (RT, 3h)	3.20	85	5.26	43
Modified alfa fiber (RT, 4h)	3.00	73	5.26	66
Modified alfa fiber (RT, 5h)	3.00	87	5.29	30
USP resin cured	-	60	3.5	-

RT denotes the reaction time for cyanoethylation.

Fabrication of composite sheets

In all the experiments, the fiber content of 10% by volume was maintained. A weighted amount of the polyester resin, admixed with 2% catalyst (methyl ethyl ketone peroxide and cobalt octoate) was poured in one side of the mould. A layer of uniaxially oriented alfa fibers was dipped into the resin, and the two faces of the mould were pressed together. The composite was cured at 80°C for 2 h.

A wax polish was applied on both sides of the mould for easy release and to obtain a superior surface finish of the pressed sheets. After the stipulated time of curing, the laminate was taken out and trimmed.

Measurements

The test samples (250 x 25 x 2 mm) were cut from the alfa-polyester laminated sheets for the traction proof tests. The tensile strength and the tensile modulus of composites were measured by a ROYLLD type machine according to ISO 527 standard.

The DMA measurements were carried out on a METTLER TOLEDO DMA/ SDTA861e machines with the test samples with dimensions of the size (30 x 10 x 2 mm).

In DMA, the test specimen was clamped between the ends of two parallel arms mounted on the low-force flexure pivots allowing the motion only in the horizontal plane. The samples in a nitrogen atmosphere were measured in the fixed frequency mode, at an operating frequency of 10 Hz and a heating rate of 5°C per minute. The samples were evaluated in the temperature range from 40 to 180°C.

The tensile fracture surfaces of the composite samples were studied visually and with a scanning electron microscope.

Traction Tests

Figures 1 and 2 depict, respectively, the curves of the tensile strength and the tensile modulus versus RT of modified alfa-polyester composites (MAC).

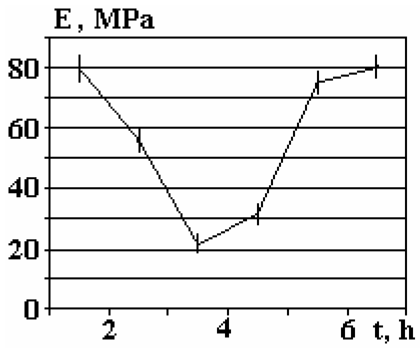


Fig. 1. Tensile strengh of modified alfa-polyester composites versus RT

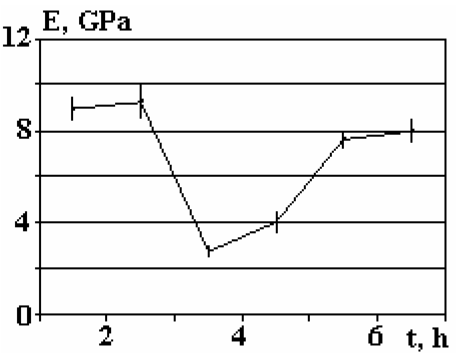


Fig. 2. Tensile modulus of modified alfa-polyester composites versus RT

The curves indicate that the mechanical performances of MAC have been drastically reduced for the low extents of cyanoethylation. Nevertheless, the second branch of the curves suggests an improvement in mechanical properties until finding again initial performances for RT= 4 and 5 h.

The much decreased tensile strength and tensile modulus of the MAC was foreseeable in view of the fragility of the cyanoethylated alfa fibers used. For a better understanding of the subsequent improvement of mechanical properties for increasing RT, we proposed to study both unmodified alfa-polyester composites (NAC) and MAC by using a dynamic mechanical analyzer.

Dynamic mechanical analysis

Dynamic mechanical tests, in general, give more information about a composite material than other tests. The dynamic tests, over a wide range of temperature and frequency, are especially sensitive to all kinds of transition and relaxation processes of the matrix resin and also to the morphology of the composites. The dynamic mechanical analysis DMA also provides the reliable information about the glass transition temperature T_g of a fiber filled composite.

In the technique, a sinusoidal load is usually applied to the sample, and a real modulus E' and an imaginary one E" are measured. The real and imaginary moduli represent the elastic and viscous behaviour of the sample, respectively. Their ratio E"/E' defines the loss tangent or damping $\tan\delta$. This quantity can relate to the impact properties of the material. Generally, the $\tan\delta$ peak is near to T_g. Figure 3 depicts the DMA curves of the storage moduli E' versus temperature of one NAC and three MAC.

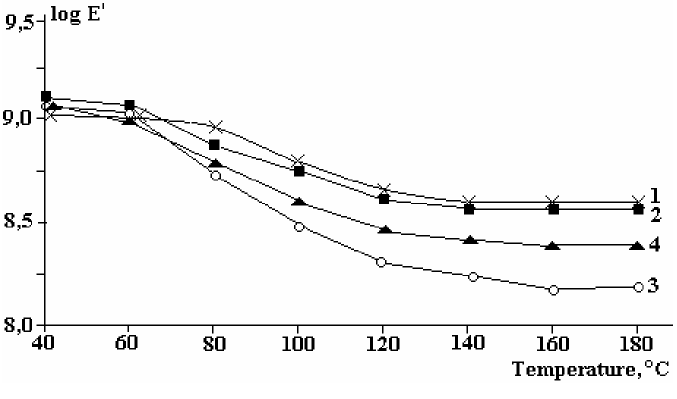


Fig. 3. Storage modulus E' versus temperature of one AC and three MAC

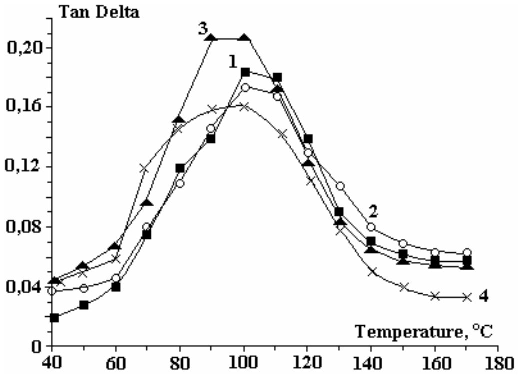
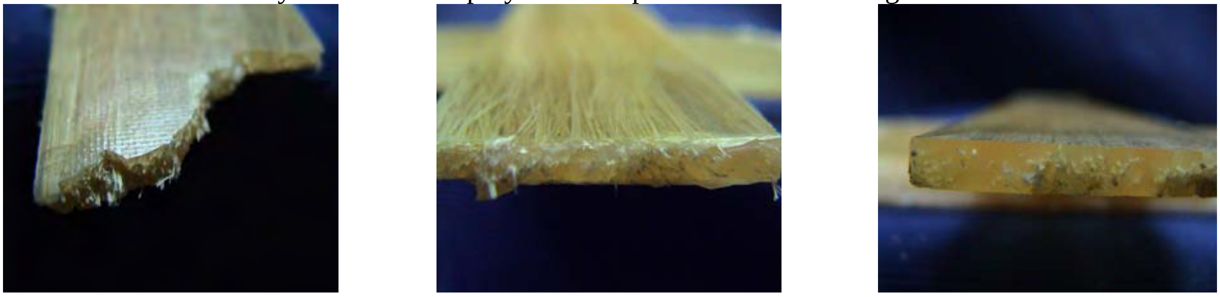


Fig. 4. Tan δ versus temperature of one NAC and three MAC

The curves indicate that the initial storage modulus value E' of all the three modified alfa-polyester composites and the unmodified alfa-polyester one are the same. It is also evident from figure 3 that in all cases, the storage moduli values of MAC at any temperature are very near to that of NAC. It is seen from table II that there are large differences in modulus values between the modified and the unmodified alfa fiber; the modified alfa fibers are markedly less stiff than the unmodified ones. In spite of this, NAC and MAC show the comparable mechanical performances. It appears that the fragility of the used fibers has been compensated by the greater interfacial bond strength between the matrix resin and the fiber. The hydrophilic nature of the alfa induces the poor wettability and adhesion characteristics with USP resin, and the presence of moisture at the alfa - resin interface promotes the formation of voids at the interface. Thus, the presence of moisture and voids at the interface weakens the bonds and produces a composite of lower stiffness and strength. The presence of moisture in the system may result from diffusion of atmospheric moisture through the matrix on the subsequent aging. On the other hand, owing to cyanoethylation, the moisture regain capacity of the alfa fiber is much reduced; moreover, the compatibility with unsaturated polyester resin is improved and a strong interfacial bond with the matrix resin is produced.

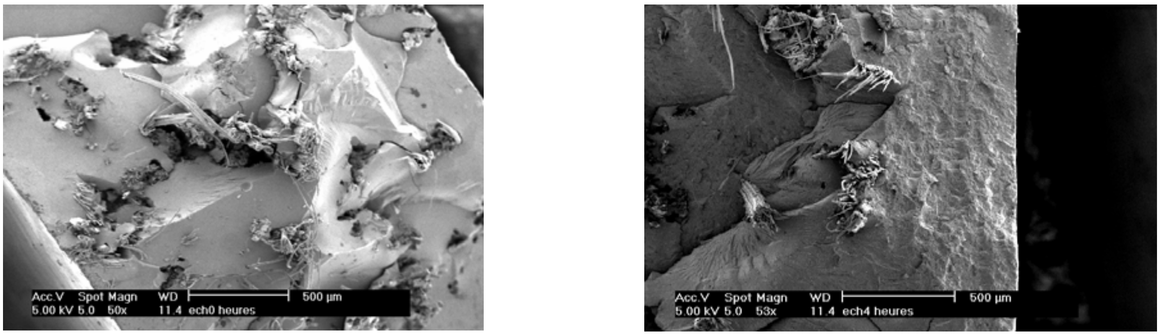
Figure 4 shows $\tan\delta$ versus temperature plots for one NAC and three MAC composites. It is evident from figure 4 that there is no much difference in the height of the $\tan\delta$ peak for all the four composites, including NAC. This indicates that all the four composites possess the same order of the damping capability. As the temperature of the $\tan\delta$ peak is near T_g, the small increase in T_g values of MAC compared to the NAC suggests a slight increase in the stiffness of the fiber-matrix interfacial zone due to the improved fiber-matrix interaction, which reduces the molecular mobility in the interfacial zone [14].

The visual examination and scanning electron micrographs of the fractured surfaces [15] of both unmodified and chemically modified alfa-polyester composite are shown in figures 5 and 6.



RT=0 h RT= 1 h RT=3 h

Fig. 5. Tensile fracture surfaces for various RT values



a *b*

Fig. 6. Scanning electron micrographs of tensile fracture surfaces of (a) unmodified and (b) chemically modified alfa-polyester composites

The MAC shows the excellent retention of resin on broken fiber ends, while an unmodified sample shows uncoated fibers and holes in the matrix. Thus, the indication of the better fiber-matrix bonding in the case of cyanoethylated alfa is further supported by the scanning electron microscopy study.

Conclusions

In spite of the fragility of the cyanoethylated alfa fibers compared to the unmodified ones, both NAC and MAC manifest the same order of mechanical properties: T_g, $\tan\delta$ and E' values are very close in the two cases. Fragility of the fibers is compensated by the better interfacial bonds between the fibers and the matrix.

1. Cyanoethylation of alfa fibers reduces their moisture regain capacity and improves their compatibility with the unsaturated polyester resin.
2. The scanning electron micrographs of the fracture surface of the samples reveal the improved bonding at the interface between the cyanoethylated fiber and the polyester resin

Other smooth chemical modification techniques have to be explored in future to improve or at least maintain the mechanical characteristics of the studied fibers, such as esterification with fatty acids, silanation or polyvinylacetylation.

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Summary

Cyanoethylation of long alfa fibers was studied, and these chemically modified fibers were used to manufacture alfa-polyester composites. The dynamic mechanical thermal properties of an unsaturated polyester resin (cured) and of composites of unmodified and chemically modified alfa-polyester were studied using a dynamic mechanical analyzer over a wide temperature range. The data suggest that in spite of the fragility of the cyanoethylated alfa fibers compared to the unmodified ones, both unmodified and modified alfa-polyester composites manifest the same order of mechanical properties: T_g, $\tan\delta$ and E' values are very near in the two cases. Fragility of fibers is compensated by the better interfacial bond between the fibers and the matrix. The scanning electron micrographs of the fracture surface of the samples reveal the improved bonding at the interface between the cyanoethylated fiber and the polyester resin.