INVESTIGATION ON THE EXISTENCE OF PHYSICAL-CHEMICAL INTERACTION BETWEEN EPOXY MATRIX AND FIBRILLATED CELLULOSE IN NANO / MICROCOMPOSITES

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Abstract. *The physical-chemical interactions between microfibrillated cellulose (MFC) and epoxy resin (EPX), using acetone (A), and isopropyl alcohol (IA) as MFC dispersants, have been investigated via DSC and FTIR-MIR analyses. DSC results showed that cellulose reached its maximum catalytic effect on the polymerization and curing of the epoxy matrix at the weight percentage of 0.75. On the other hand, isopropyl alcohol promoted, alone and in the presence of MFC, substantial generation of water connected to the polymeric network, harming the chemical reactions mentioned above. The spectroscopic analysis did not indicate the existence of chemical bonds between EPX and MFC, contrary to the propositions of previous literature. Optimal rheological conditions attained for that cellulose content in the EPX-MFC-AC liquid mixture was inferred as responsible for the maximum reaction yield in the composite system, probably accompanied by pseudo-cure provided by a small water content formed this composite system.*

1. INTRODUCTION

The growing need for sustainable, low cost, tailorable materials, has stimulated the design, development and manufacture of semi-structural composites using plant-based fibers [1].

Microfibrillated cellulose (MFC) exhibts a multi-scale fibrillar structure, with fibrils diameters ranging from micrometers (10 μm) to nanometers (10 nm) [2]. MFC is easy and inexpensive to obtain from abundant natural renewable sources, with a high specific mechanical performance (i.e., per unit mass), nontoxic, biodegradable, therefore being a potential candidate for such applications.

The use of MFC as a strengthening and toughening phase of EPX matrices is as well-known practice and has been used by one of the author’s (JRT) research group in the field of Materials Engineering [3,4].

In this context, aiming at designing structural engineering materials for automotive, wind power, and even aeronautical applications, while still maintaining in good measure the use of vegetable fibers, EPX-MFC matrices applied in hierarchical composites reinforced with glass and carbon fiber, seems to be very attractive approach in the technological development of high-performance materials incorporating natural fibers.

Considering that the matrix phase must protect the reinforcing phase against environmental effects, it is essential to characterize the interaction between EPX and MFC species forming the intended composite matrix, which will largely define its physical and chemical stability, as well as its curing characteristics relative to the neat resin. This subject is discussed in the preliminary study now reported.

It is worth mentioning that, without exception, researches aiming at manufacturing EPX-MFC hybrid composites call for the chemical modification (functionalization) of cellulose in order to make it compatible with the inherently hydrophobic polymeric matrices. However, the chemical functionalization methods are invariably complex, slow, costly, and with a high potential for negative environmental impact; furthermore, frequently employed freeze-dried processing of cellulose is not less onerous [5-11].

In view of these cons, and in the search for a stable EPX-MFC composite in terms of hygroscopic, thermal, and mechanical behaviors, in addition to exhibiting an attractive cost-benefit ratio, this work employs, respectively, acetone and isopropyl alcohol as dispersing liquids for raw MFC, which invariably is supplied in the form of aqueous suspension.

2. MATERIAL AND METHODS

2.1. Materials

The aqueous pulp suspension of MFC (from pinus hardwood) at 10% (w/w) was provided by Borregaard^{TM}. EPIKOTE MGS RIMR (diglycidyl ether of bisphenol A-DGEBA) resin, and EPIKURE MGS RIMH 037035C (polyoxide propylene diamine) curing agent, composed the EPX system supplied by Hexion^{TM}, which suggests cure at room temperature for 36 h, followed by post-cure at 70°C for 5 h.

2.2. Methods

Solvent exchange: The as-received MFC suspension was further diluted and subjected to water exchange for polar organic solvents, respectively, acetone (A) and isopropyl alcohol (IA), via liquid-liquid extraction. After partial solvents evaporation, the gel dispersions A-CEL and AI-CEL had their concentrations adjusted to, respectively, 0.5, 0.75 and 1% by weight of MFC. *Preparation of nano/microcomposites*: To obtain the systems, now called EPX-DGEBA/A-CEL and EPX-DGEBA/IA-CEL, the gels were respectively added to the EPX resin in a heating bath (60ºC for A, and 80ºC for AI) under mechanical agitation. While stirring with the heating off, the curing agent was added. For reference purposes, the process was reproduced using neat resin (EPX), containing acetone (EPX-A), and isopropyl alcohol (EPX-IA).

The obtained compounds were then evaluated by: (i) Differential Scanning Calorimetry (DSC) with dynamic measurements of enthalpy of the liquid samples analyzed in TA Instruments® model DSC 2910 equipment operating with a continuous flow of nitrogen fed at a rate of 20 ml.min$_{-1}$, under a heating rate of 10°C.min$_{-1}$, from room temperature to 250ºC. The curing enthalpies were obtained by integrating the respective curves of released energy during the resin crosslinking exothermic reaction, (ii) Infrared Spectroscopy (FTIR-MIR) using 500 μm thick solid films partially cured at room temperature and postcured in an oven at 70°C for 5 h. FTIR spectra were obtained in Perkin Elmer® equipment, Spectrum 100 Spectrophotometer, using the attenuated total reflectance (ATR) method with scanning at wavelengths from 600 to 4000 cm^{-1}, in a resolution of 4 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Differential Scanning Calorimetry (DSC)

Table 1 shows the enthalpy values for the neat EPX resin and respective composite systems. Since different liquid sample volumes were used for the systems containing, respectively, A and IA solvents, the corresponding enthalpy percentage values were obtained considering the respective base condition, namely, 0% MFC, which means the EPX-solvent mixtures.

For the EPX-DGEBA/A-CEL system at MFC concentrations of, respectively, 0.5 and 0.75%, the cure enthalpy was higher than the pure EPX resin, indicating a crosslinking process favored by the MFC until a limiting amount of dispersed MFC.

In fact, the catalytic effect of cellulose on the acceleration and efficiency of EPX resin curing has been pointed out by researchers [12-19] as an unequivocal result of covalent bonds formed between the two substances, although functionalized cellulose and/or very higher filler content than this study was employed by the authors.

Table 1 - Enthalpy values for the studied composite systems.

MFC Content (%)	EPX-DGEBA/AC-CEL (J/g)	EPX-DGEBA/IA-CEL (J/g)
0	620 (100%)	347 (100%)
0.5	682 (110%)	306 (88%)
0.75	705 (114%)	313 (90%)
1.0	602 (97%)	317 (91%)

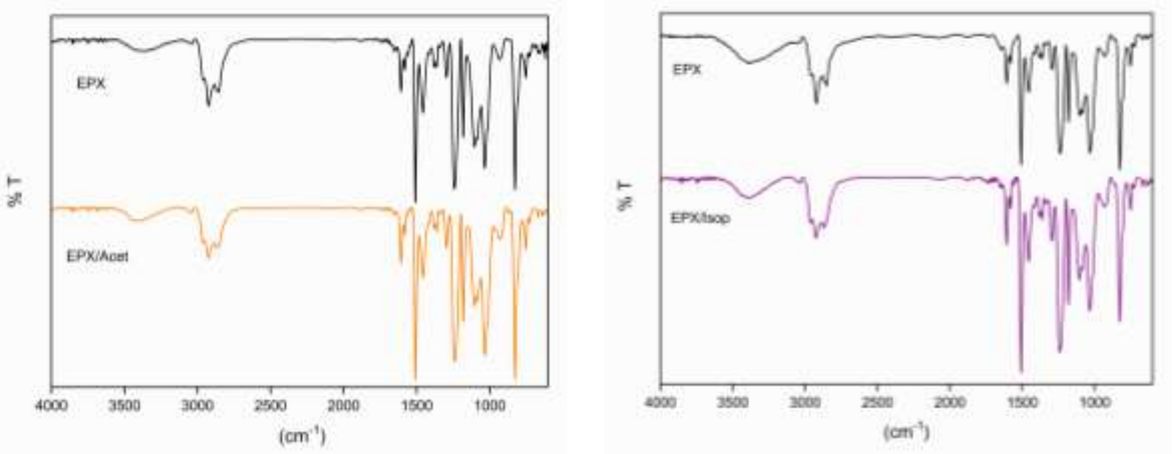
For the EPX-DGEBA/IA-CEL system, cellulose disfavored the resin cure reaction, probably due to the presence of one OH group in the solvent molecule, which binds to the hydroxyl group of EPX and/or MFC, forming bound water and compromising the curing process, even in the presence of MFC.

3.2. Fourier Transform Infrared Spectroscopy (MIR – FTIR)

The MIR – FTIR spectra of neat EPX, and with additions of, respectively, AC and IA solvents, are shown in Figure 1, while Figure 2 shows the spectra of the respective systems containing MFC in various amounts in the composites.

Initially, it is important to highlight the characteristic bands of the epoxy resin associated to its main functional groups: ~ 3400 cm^{-1} (OH) and (NH), ~ 1250 and ~ 1040 cm^{-1} (aromatic ether group), 920 cm^{-1} (COC epoxide), and 830 cm^{-1} (CH aromatic ring) [20-23], all present in the spectra below. The absence of the band between 920-910 cm^{-1} is the main difference between cured and uncured EPX resin.

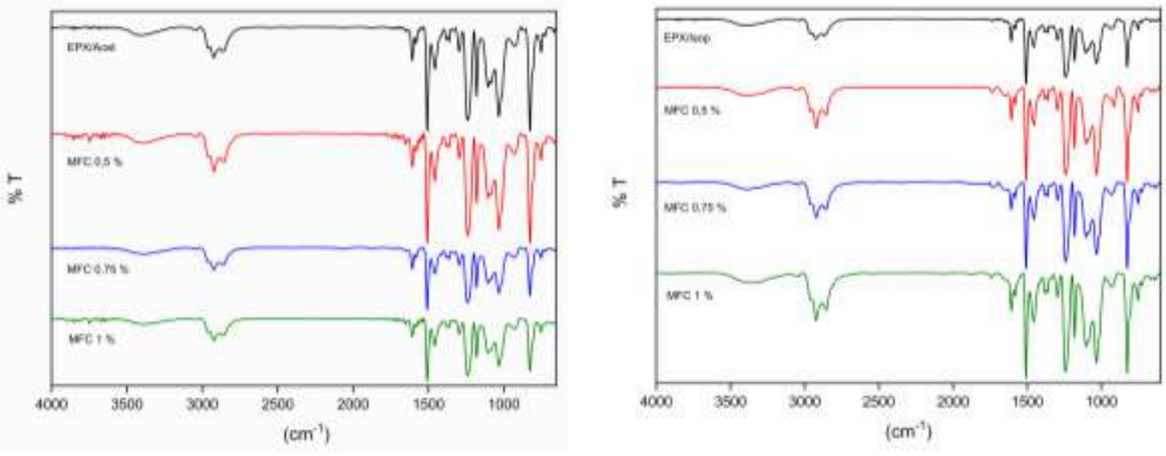
The addition of acetone (Fig.1a) shifted the band around 3400 cm^{-1} (OH) to higher frequencies, suggesting free volumes (nano voids) in excess, or molecular dispersions with no interaction with bounded hydrogen. This, in principle, would imply in only slightly negative effect on the polymerization and subsequent curing processes, insofar as water, in low proportions, may promote the diffusion of reactive molecules, as well as act as a pseudo-agent of cure of EPX [25-28].



(a) (b)

Figure 1 - Solvents effects on DGEBA curing process: (a) Acetone, (b) Isopropyl alcohol.

On the other hand, the isopropyl alcohol (Fig.1b) displaced the OH band to lower frequencies, indicating that hydrogen from the solvent molecules bounded to specific places along the polymeric network, forming linked water to the resin, which is confirmed by the peak present at 1740 cm^{-1} and the absorption bands in the region of 1740 to 1650 cm^{-1} present also an increase in the half-width and relative intensity. This water deactivates EPX crosslinking sites, reducing its degree of conversion, that is, the curing efficiency.



(a) (b)

Figure 2 - Photophysical behavior of (a) EPX-DGEBA/AC-CEL, (b) EPX-DGEBA/IA-CEL nanocomposites.

As it does not have a hydroxyl group, acetone does not interact with resin OH [29], and its smaller molecular volume, compared to isopropyl alcohol, only minimally impairing the interaction between reagents for polymerization, with little effect on the availability of epoxide curing sites.

The presence of a band at 933 cm^{-1}, associated with a shoulder at 865 cm^{-1}, for both solvents used, might indicate possible incomplete cure of the resin. In the complete cure of EPX, the band centered in 933 cm^{-1} disappear, decreases in intensity, or yet changes to higher values, or even divides itself, while the shoulder at 865 cm^{-1} fades away. Another possible indicator of the epoxy resin conversion would be the appearing of a band around 1650 cm^{-1}, related to the formation of an imino group of the curing agent [30], which is indeed observed in all the cases, signaling that the incompleteness of the curing step, if it occurred, may not be as significant in some circumstances.

In the EPX-DGEBA/A-CEL system (Fig.2a), in the cellulose concentrations of, respectively, 0.5% and 1.0%, there was an increase in the full width at half maximum of the OH band (3400 cm^{-1}) with shifts to lower frequencies compared to pure resin and with 0.75% MFC. This behavior signals the development of hydrogen bonds between MFC and EPX, forming water connected to the polymeric network, impairing the cure due to the disorganization of the chain during curing and leading the composite to plasticization.

In the EPX-DGEBA/IA-CEL system (Fig. 2b), the OH band shifted to smaller wave numbers in all cellulose concentrations, indicating a greater tendency for bound water formation in this composite system. The appearance, in all MFC concentrations in the EPX-DGEBA/IA-CEL system, of the band around 1740 cm^{-1} (absent in EPX-IA) are related to the stretching of the C = O bond of aromatic ester groups and is possibly related to some oxidation process. There is also an increase in the half-width of the band around 1607 cm^{-1}, which can be associated to the aromatic C=C group of the resin, as well as OH groups.

The solvent exchange process for both systems studied probably resulted in some type of interaction between the MFC and the EPX, which can be inferred by the displacement of the OH band to greater or lesser wave numbers, by the appearance of bands around 1740 cm^{-1}, due to the presence of the band of the epoxide group centered on 933 cm^{-1}, and the disappearance of the shoulder at 858 cm^{-1} [31] in some of the nano/microcomposites studied.

In the EPX-DGEBA/A-CEL system, particularly at a MFC concentration of 0.75%, it can be inferred, through previous results of rheometry [3], that cellulose has acted effectively to reduce the viscosity of the mixture compared to the pure resin, increasing its gel time, allowing better dispersion and spatial configuration of the MFC, in addition to greater diffusion and better interaction between the reagents [32]. As a result, a greater effectiveness of strong intermolecular interaction (hydrogen bonding) between the hydroxyl groups of MFC and resin epoxide must have been established.

On the other hand, in all cellulose concentrations for the EPX-DGEBA/IA-CEL system, spectral changes (particularly at 1740 cm^{-1} - carbonyl region) indicate the probable occurrence of hydrogen bonds between the OH groups of the MFC and resin [33], in addition to the contribution of the solvent (which also has an OH group), forming bound water and undermining the cure process. In addition to the spectral changes of the functional groups OH and C = O, the widening and increasing intensity of the bands in the C-O region (1300-1000 cm^{-1}) confirm that more water has been generated by the additional presence of the MFC in the EPX-IA mixture, as suggested by the DSC results.

Under these conditions, multiple hydrogen bonds formed between OH groups, resulting in water attached to the resin network, would form bridges between the structural segments, which may result, as in the case of free water [22-25], in secondary crosslinking, or pseudo cure [34,35].

According to the results obtained by the FTIR technique and reported above, it can be concluded for the non-occurrence of chemical bonds between the EPX matrix and MFC reinforcement phases, since no significant or noteworthy changes were observed in the spectra evaluated, besides those expected on the basis of typical functional groups, and interactions between them. In the absence of those bonds, the greater polymerization and curing efficiency of EPX containing MFC previously dispersed in acetone (proven herein by DSC) was most likely due to favorable rheological conditions for diffusion and interaction between EPX reagents, as promoted by reduced viscosity and longer gel time of the resin, which are optimized at 0.75% MFC [3], possibly associated with pseudo-curing effects of water formed in the EPX reticulate.

In the casual existence of the covalent bonds inferred literature (ie, never directly proven), its non-identification in the present study could be justified due to the low concentration of MFC in thecomposites, and, consequently, a density of bonds below the threshold of sensitivity and resolution of the equipment used.

It must be emphasized that the premises, analyzes, and results presented here must be corroborated by other spectrometric techniques (e.g., XPS), as well as by mechanical, thermal and thermomechanical tests.

4. CONCLUSIONS

i. Acetone (A) did not interact effectively with the resin to generate a by-product that could harm its polymerization and curing processes.
ii. Isopropyl alcohol (IA) significantly reduced the curing kinetics and degree of conversion of EPX resin by forming bound-to-resin water through reaction between their hydroxyl groups.
iii. The addition of 0.75% microfibrillated cellulose (MFC) dispersed in acetone to EPX provided favorable rheological conditions for polymerization and curing of the resin, leading to the effectuation of more hydrogen bonds between the matrix and reinforcement phases.
iv. The addition of MFC dispersed in IAto EPX impaired both the polymerization and curing processes at a larger extent than the presence of the solvent only, since bound-to-resin water was much more prolific in the former case.

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