Hygrothermal behaviour of epoxy resin nanocomposites reinforced with microfibrillated cellulose

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Abstract

Monitoring of water content and prediction of absorbed water in nanocomposites reinforced with microfibrillated cellulose (MFC) are of great importance for its potential use in the automotive, textile, packaging and coating industries, as those materials can be prone to hygrothermal degradation. Gravimetric analysis allows one to determine the mass changes of a given material from dry to wet conditions and estimate its water absorption capacity over time, which controls many of its physical, chemical and mechanical properties. This work aims at evaluating the water content in neat epoxy resin (EPX) and its nanocomposites reinforced with MFC. Since MFC is highly hydrophilic, its compatibility with greatly hydrophobic EPX matrix may strongly depend upon the chemical nature of the MFC solvent during the cellulose incorporation in the thermoset polymer. In this study, acetone (AC) and isopropyl alcohol (IA) are proposed cellulose solvent in order to manufacture EPX-based nanocomposites with different filling concentrations, namely, 0.5, 0.7% and 1 wt%. Gravimetric results indicated that AC is far superior to IA due to the strong tendency of the later solvent in impairing EPX cure.
Keywords: epoxy resin, hygrothermal behaviour, microfibrillated cellulose, nanocomposite.

Introduction

In view of the current scenario regarding natural, abundant, sustainable, environmentally friend, low-cost, and renewable materials, the incorporation of MFC in EPX resin presents itself as a great advance. When MFC is dispersed into EPX, the resultant material is called polymeric nanocomposite due to the fillers´ nanosize [1]. Thermoset EPX resin has particularly found a huge niche in technological and innovative industrial branches, like automotive, aerospace, petrochemical, and wind energy [2]. In this regard, hygrothermal behaviour of natural fibre-reinforced composites must be deeply studied before they are put to operate in moisture prone environments, since the filling agent, as well as its interface with the polymer matrix can severely undermine its semi-structural or structural load-bearing capacity. This is especially important because EPX resin is hydrophobic by nature, while MFC is intrinsically hydrophilic, and their interaction are not well understood though interface define to a great extent the physical-chemical-mechanical properties of the nanocomposite.

In this study, acetone (AC) and isopropyl alcohol (IA) were employed as cellulose solvent in manufacturing EPX-based nanocomposites with different minimally processed, neat MFC concentrations. Gravimetric analysis was performed to infer which of the two organic polar solvents is better in preventing, or mitigating the tendency of the materials to deteriorate when operating in high-moisture environments. The results here reported will effectively aid the interpretation of further analytical techniques, such as infrared spectroscopy, differential scanning calorimetry, and thermogravimetry.

Experimental Procedure

Hexion™ provided both the diglycidyl ether of bisphenol-A (DGEBA) epoxy resin and cure agent poly(propylene oxide) amine. Curing was carried out at 70°C for 5 h. Microfibrillated cellulose (MFC) Exilva F 01-V at 10 wt % in water paste form was supplied by Borregaard™. Two classes of nanocomposite were manufactured, namely, EPX-MFC-AC and EPX-MFC-IA, were AC and IA refers to acetone and isopropyl alcohol utilized as solvent during incorporation of MFC in EPX at weight percentages of 0.5%, 0.75% and 1%, respectively. Small samples were cut, pre-dried and weighed in a high-precision analytical balance accurate to E-5 g, then immersed in deionized water at 60° in an Erlenmeyer flask stored in Isotemp™ oven model 285A. During 6 months, the samples were periodically retrieved from the flasks and weighted, so that the respective gravimetric curve could be plotted [3][4].

Results and Discussion

Figure 1 shows that the EPX resin exhibits good hygrothermal stability during practically the whole period of hygrothermal test.
On the other hand, EPX-MFC-AC nanocomposites exhibit increasing water absorption with the immersion time, with the rate of moisture gain proportional to the MFC content, though 0.5 and 0.75% MFC present a noticeably similar behaviour. Besides the water sorption by the cellulose, which is related to the strong affinity between them (hydrogen bonds associated to van der Waals dispersion forces) [5], the liquid can also be confined due to potentially reversible interaction of water with specific segments of the matrix, and/or by water distributed in microvoids [6], when plasticization can occur, associated or not with physical ageing and chemical modification of the epoxy resin [7][8][9].
At the final stages of the long-term aging tests, the vast majority of the materials present pronounced weight loss, which is compatible with irreversible water trapping in the resin network, followed by polymer chain degradation by hydrolysis, leading to resin dissolution and mass loss [6][10][11], implying in loss of mechanical properties [12][13].

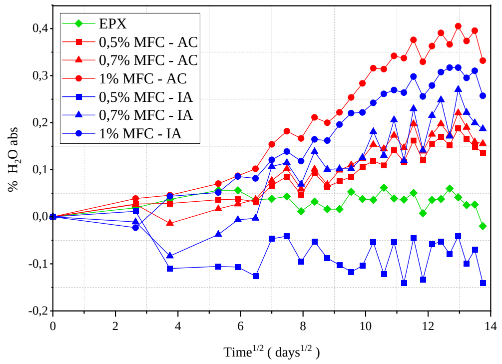

Figure 1. Moisture absorption percentage vs square root of immersion time for neat EPX resin and its nanocomposites obtained via AC and IA routes, respectively.

Figure 1 also indicates that EPX-MFC-AI composites with 0.5 and 0.75% MFC begin losing mass already in the early stages of immersion yet, probably due to matrix dissolution. This process lasts approximately 40 days for 0.5% and 15 days for 0.75% MFC. This suggests, particularly for the former composition, that some failure in the resin curing process during manufacture [10], which has been determined through FTIR analysis by [14] as a result of water formation due to IA interaction with both epoxy reagents and MFC filler, respectively, therefore impairing both polymerization and cross-linking reactions. From the moment the two above referred formulations attained the minimum weight onwards, they began to absorb water, indicating the possibility of further curing in-situ due to incomplete cure and/or slow cure kinetics [10].

Conclusions

EPX matrix nanocomposite systems obtained via MFC dispersed in AC has shown superior performance to the neat EPX resin and their counterparts synthesized via IA route, with the exception of the highest cellulose content. Degradation mechanisms have been inferred for most of the materials at the final stage of the hygrothermal/aging tests, and in-situ curing of IA-derived nanocomposites with low and intermediate MFC contents has been deduced. The obtained results, along with those reported in [14] regarding FTIR, DSC, TGA, DSC, AFM, SEM, will for sure elucidate physic-chemical events determining the mechanical performance of this class of composite materials.

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