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Environmental ageing studies of chemically modified micro and nanofibril phenol formaldehyde composites

Bibin Mathew Cherian[a,*], Alcides Lopes Leão[a], Marcia Rodrigues de Morais Chaves[b], Sivoney Ferreira de Souza[c], Mohini Sain[d], Suresh S. Narine[e]

[a] Department of Natural Resources, São Paulo State University (UNESP), Botucatu 18610-307, São Paulo, Brazil
[b] Centre of Applied Sciences, University of Sagrado Coração (USC), Bauru, São Paulo, 17011-160, Brazil
[c] Department of Nanoscience and Advanced Materials, Universidade Federal do ABC (UFABC), Santo André 09210-170, São Paulo, Brazil
[d] Centre for Biocomposites and Biomaterials Processing, University of Toronto, Toronto, Ontario M5S 3B3, Canada
[e] Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, Peterborough, Ontario K9J 7B8, Canada

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ABSTRACT

Cellulose micro and nano fibrils were extracted from banana macro fibres and chemically modified using sodium hydroxide, formic acid, 3-methacryloxy propyltrimethoxy silane. These untreated and chemically treated fibrils were incorporated into PF resin and the specimens were prepared. The composites were subjected to long-term water ageing, thermal ageing soil burial and outdoor weathering. The mechanical properties are reduced under all ageing conditions. The present study investigates the effects of different types of ageing on macro fibre, microfibril and nanofibril reinforced PF composites. The effect of chemical modifications of fibres on the degradability of the composites at different environments also has been analysed.

1. Introduction

The progress of the industrial sector for the production of consumer goods is dependent on the development of new materials. Properties as superior mechanical strength, thermal, and low specific weight are usually required. In this context, the use of vegetable fibres (e.g. banana fibre) as reinforcing agents for polymeric materials is of great importance, once they contribute to the mechanical strength improvement, and they contribute to turn the composite more environmentally sustainable. Therefore, several studies are needed to determine the best conditions of processing, use and disposal of composite materials. To contribute to this field, the present study brings lights over new findings on the behaviour of fibre-resin composites under different conditions, through the environmental ageing studies of chemically modified macro, micro and nanofibril phenol formaldehyde composites.

The environmental degradation of polymeric materials includes thermal, mechanical, photochemical, radiation, biological, chemical degradation, etc. Most of the natural fibres are stable up to 300 °C. Hence incorporation of natural fibres into plastics changes the environmental stability. Phenolic resins are highly heat resistant, and they find applications in aerospace as ablative heat shields for protection of space vehicles. Incorporation of natural fibres accelerates the thermal degradation process. Composite components have also to survive in a range of different environments of moisture and temperature. Relative humidity can vary from 0% to 100%. Temperatures for most uses range from 40 °C to 70 °C, although the military aircraft has to withstand temperatures up to 130 °C in flight and even greater around engines. The effect of these temperatures on composite properties needs to be known and ideally predicted (Espert et al., 2004). Mohd Ishak et al. (2001) found that the immersion of rice husk–polypropylene (PP) composites in water resulted in a reduction in tensile properties, the extent of which depended on the water immersion temperature. This was attributed to interfacial degradation and also to microstructural changes in rice husk that reduced its efficiency in acting as a reinforcer. The incorporation of cellulose fibres into polymeric matrices increases the water sorption ability of the composite due to the highly hydrophilic nature of the cellulosic fibres which support water permeability. It has been reported that long-term water exposure of composites fabricated from silane-treated fibres can cause a significant decrease in the mechanical properties. Megiatto et al. (2009) worked on thermoset matrix reinforced with sisal fibres. They observed minimum water uptake in the treated composites and attributed it to better fibre/matrix adhesion. The effects of environmental ageing on the mechanical properties of

* Corresponding author. Tel.: +55 14 3811 7162 7163; fax: +55 14 3811 7202.
E-mail address: bmcherian@gmail.com (B.M. Cherian).

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bamboo/glass-fibre-reinforced PP hybrid composites were studied by Thwe and Liao (2003). Thwe and Liao (2002) also found that property retention in both bamboo-fibre composites and bamboo/glass hybrid composites with a maleic anhydride modified PP matrix was better than that with PP. They found that hybridising more durable glass fibres with bamboo fibre was an effective way to improve the durability of natural-fibre composites under environmental ageing. Hill and Abdul Khalil (2000) reported that acetylation and silanisation protect the coir and oil palm reinforced polyester composites from deterioration in mechanical properties upon environmental exposure. The effect of environmental ageing can be minimised by applying the hydrophobic morphology at the fibre matrix interface and the resin rich layer on the outer face of the composites (Singh et al., 2000). The cross-sectional area of the composite becomes the main absorption face. Each fibre was found to be surrounded by the phenol formaldehyde (PF) resin as they can penetrate through individual fibres. The water penetration and diffusion are mainly through the fibre–matrix interfacial region and the cross-sectional portions of the fibre by capillary mechanism. This mechanism involves flow of water molecules along the fibre–matrix interface, followed by diffusion from the interface into the matrix and fibres. In cellulose–phenol formaldehyde, enormous compatibility is achieved at this interfacial region due to the high hydrophilic nature of the phenolic resin and cellulose fibres. Thus, the gap width is comparatively lower in phenolic composites.

Alonso et al. (2011) studied the thermal stability and thermal degradation kinetics of phenol–formaldehyde (PF) and lignin–phenol–formaldehyde (LPF) resol resins using thermogravimetric analysis (TG) in air and nitrogen atmospheres in order to understand the steps of degradation. The results indicate that 30 wt% ammonium lignin sulfonate (lignin derivative) as filler in the formulation of LPF resin improves the thermal stability in comparison with PF commercial resin. The structural changes of both resins during thermal degradation were studied by Fourier transform infrared spectroscopy (FTIR), with the results indicating that PF resin collapses at 300 °C whereas the LPF resin collapses at 500 °C. In the present study chemically modified cellulose micro and nanofibre PF composites were developed and investigate the effects of different types of ageing on macro fibre, microfibril and nanofibril reinforced PF composites. The effects of chemical modifications of fibres on the degradability of the composites at different environments were also analysed.

2. Experimental

This study involved the isolation of cellulose fibres, their surface modification, and use as reinforcing agent in composite PF. The effects of chemical modification on the degradability of the fibre-composites were evaluated by ageing under different conditions, as described in this section and summarised in the Table 1.

2.1. Isolation of cellulose fibrils

The isolation of cellulose fibrils was based on the methodology developed by Cherian et al. (2008), using steam explosion and chemicals to bleach and hydrolyse the fibres.

2.1.1. Isolation of cellulose microfibrils

Microfibrils were separated from banana fibres (macro) obtained from local sources. The fibres obtained from the pseudo stem of the plant were subjected to alkali treatment in 2% NaOH followed by the steam explosion. During the steam explosion, the pressure was maintained at 138 kPa. The fibre was further retained under the same conditions for 1 more hours. The fibres were taken out and washed several times with water. It was then bleached with a solution of 27 g NaOH in 75 mL glacial acetic acid along with sodium hypochlorite and water. The pH of the solution was 4.5. The fibres were filtered, washed and then kept in an air oven at 60 °C for 1 h. This was further powdered in a mixer.

Table 1
Summary of the experimental procedure of fibres treatment, the composites preparation and the environmental ageing study.

Fibres treatment design	
Alkali	NaOH (10 g/L)/ethanol 120 min/78 °C/oven dried 60 °C
Formic acid	HCOOH (99%) 40 min/20 °C/oven dried 70 °C
Vinyltrimethoxysilane	$H_2C{=}CHSi(OCH_3)_3$ + ethanol/water 6:4 90 min/20 °C/oven dried 60 °C

Composites design

Fibres	Treatment	Composites			
		Composition		CM	RTM
Macrofibres	No	wt% fibre	Fibre length (mm)	X	X
		30	10, 20, 30, 40		
		4, 10, 20, 30, 40, 50	30	X	X
	Yes (all treatments)	40	30	X	X
Microfibres	No	7, 10, 15, 20, 25	–	X	–
	Yes (all treatments)	4, 10	–	X	–
Nanofibres	No	2, 4, 6, 8, 10, 12	–	X	–
	Yes (all treatments)	4, 10	–	X	–

Ageing design	
Cold water	Immersion on distilled water/27 °C/14 days
Boiling water	Immersion on boiling water/2 h
Thermal	Air oven/120 °C/10 days
Burial	Burial in natural soil/6, 12, 18 months
Outdoor weathering	Exposure to natural weathering (local climate conditions) 6 and 12 months