



Accelerated weathering of unbleached and bleached Kraft wood fibre reinforced polypropylene composites

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ABSTRACT

In this paper, combined moisture/ultraviolet (UV) weathering performance of unbleached and bleached Kraft wood fibre reinforced polypropylene (PP) composites was studied. Composites containing 40 wt% fibre with 3 wt% of a maleated polypropylene (MAPP) coupling agent were fabricated using extrusion followed by injection moulding. Composite mechanical properties were evaluated, before and after accelerated weathering for 1000 h, by tensile and impact testing. Differential scanning calorimetry (DSC), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) were also carried out to assess the changes occurring during accelerated weathering. Bleached fibre composites initially showed higher tensile and impact strengths, as well as higher thermal stability and greater crystallinity. During accelerated weathering, both unbleached and bleached fibre composites reduced tensile strength (TS) and Young's modulus (YM), with the extent of the reduction found to be similar for both unbleached and bleached fibre composites. Evidence supported that the reduction of TS and YM was due to PP chain scission, degradation of lignin and reduced fibre–matrix interfacial bonding.

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1. Introduction

The incorporation of lignocellulosic materials as a reinforcing component in polymer composites has received increased attention, particularly for price driven and high volume applications. This development reflects several advantages of lignocellulosic fibres over their inorganic counterparts, including lower density, reduced abrasiveness to expensive moulds and mixing equipment, as well as being less expensive. Moreover, lignocellulosic based fibres are derived from renewable resources [1]. Wood fibre is the most widely used lignocellulosic fibre for reinforcing plastics. In fact, there are a wide variety of different wood fibres pertaining to different species and processing conditions. The Kraft process is the most widely used for pulping, which is a partly mechanical and partly chemical process producing strong fibre. In the Kraft pulping process, after de-barking, wood chips are heated in a solution of NaOH and Na₂S under pressure, during which time a large amount of lignin (the substance that make tree cells wood 'hard' and 'woody' rather than soft), hemicellulose, pectin and other non-cellulosic compounds are removed from the wood. The pressure is then released suddenly, causing the fibre to quickly separate within the chips. The fibre pulp is washed with water to remove the pulping chemicals and non-cellulosic compounds from the fibre, so

that they do not interfere with further processing steps. A sieve is used to remove knots and clumped-together undigested fibres from the pulp. Bleaching is also commonly used to increase the brightness of pulp which largely removes the remaining lignin, as well as other non-cellulosic compounds from the wood fibre, in a two stage process. Firstly, the pulp is treated with NaOH in the presence of O₂, such that NaOH removes hydrogen ions from the lignin and O₂ breaks down the polymer, then, the pulp is treated with ClO₂, followed by a mixture of NaOH, O₂ and H₂O₂ and finally, again with ClO₂ to remove the remaining lignin [2]. Typically, unbleached Kraft fibres consist of 65–75% cellulose, 17–32% hemicellulose, and 3–8% lignin, compared to bleached pulp with 70–80% cellulose and 20–30% hemicellulose and ≤1% lignin [3]. Removal of lignin from fibre has the potential to increase fibre–matrix adhesion within a composite due to the more open or rougher fibre surface, allowing for increased physical bonding with the matrix [4].

There are many applications of wood plastic composites (WPC) present in everyday life. Wood fibre/polypropylene (PP) composites are used in cars behind the vinyl facings on doors, consoles and seat backs. Residential construction applications include windows, sidings, and roof tiles. Many window and door manufacturers are considering WPC as alternatives to solid wood in cladding components [5]. In North America, building products, particularly decking, account for 75% of the total WPC market [6]. As the outdoor applications of WPC become more widespread, the durability of these products against weathering, particularly UV and moisture

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becomes of concern. UV exposure can cause changes in the surface chemistry of the composite, also known as photodegradation, which may lead to discoloration, making the products aesthetically unappealing [7–9]. Furthermore, prolonged UV exposure may ultimately lead to loss in mechanical integrity [9]. In addition, absorption of moisture can lead to the degradation of the fibre–matrix interface leading to poor stress transfer, resulting in a reduction of mechanical and dimensional stability [10].

Table 1 shows the cell wall polymers in natural (wood) fibres in order of importance for a range of different properties including UV, moisture as well as biological degradation. Lignin is considered to be most responsible for UV degradation, whereas, hemicellulose is suggested as more important for moisture and biological degradation [11].

The photodegradation mechanisms of wood and plastic separately are complex but well documented in the literature. The photodegradation of PP is mainly due to photo-oxidation promoted by UV irradiation [12]. The most likely oxidation reactions caused by UV radiation are represented in Fig. 1 [13]. For these reactions, O_2 is used up before it can diffuse to the interior, so that degradation is concentrated near the surface, even in polymers in which high UV levels are present in the interior. The photo-oxidation process also takes place mainly in amorphous regions because of their higher permeability to O_2 [13–15]. Schematic representation of PP molecules after extensive photodegradation is shown in Fig. 2 [13]. As previously detailed, lignin is the component of wood most responsible for UV degradation. This occurs via many different pathways; ultimately, they all lead to the formation of chromophoric groups, such as carboxylic acids, quinones and hydroperoxy radicals which have a characteristic yellow colour [16–18] commonly associated with aging of paper.

Moisture diffusion in polymeric composites has been shown to be governed by three different mechanisms [19,20]. The first involves diffusion of water molecules inside the microgaps between polymer chains. The second involves capillary transport into the gaps and flaws at the interfaces between fibre and the matrix. This is as a result of poor wetting and impregnation during the initial manufacturing stage. The third involves transport of microcracks in the matrix arising from the swelling of fibres.

The long-term behaviour of materials due to environmental influences can be evaluated by real time observations of the materials exposed to natural conditions for several years [21]. However, research programmes lasting 10 years or more are rare for organizational and economic reasons. Accelerated aging tests have potential for assessing long-term behaviour. However, there are a number of variables to consider including exposure time, UV exposure as radiant energy over a specific wavelength range, and water exposure as a number of cycles or in time. To allow the best

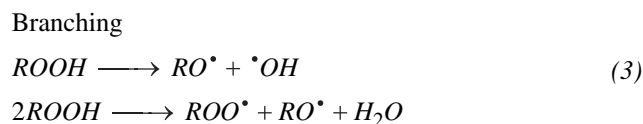
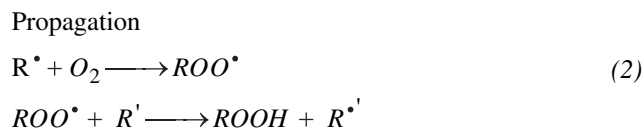
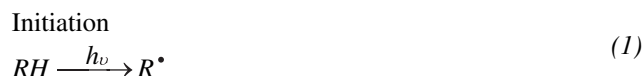


Fig. 1. Oxidation reactions initiated by UV radiation [13].

comparison between studies, it is recommended that performance after weathering be reported after a specific radiant exposure, commonly termed the time integral of irradiance [22]. Weathering in the presence of water, enhances the rate of degradation of WPC; wood cell walls swell when penetrated by water, facilitating light penetration further into the wood providing sites for further degradation [17]. Furthermore, washing a degraded surface with water exposes new surfaces for degradation. Weathering of WPC including periodic water spraying, results in a cyclical erosion of the surface as the lignin is degraded and subsequently washed away, exposing more lignin to degradation. Washing can also remove water soluble extractives that impart colour to wood [22].

Research on the degradation of wood fibre reinforced polyolefin composites has focused mainly on changes in appearance and mechanical properties [7–9]. Seldén et al. [23] studied UV aging of PP/wood fibre composites without water spray and found that the wood fibre composites displayed a maximum 20% reduction in flexural strength and almost retained initial impact strength. The degradation of the composites was restricted to a thin surface layer, owing to the screening effect of the wood fibres. The degraded layer had a chalky appearance, due to degradation of the PP matrix, leading to extensive surface cracking. The rate of degradation of the PP matrix was approximately twice as high in samples with 50 wt% wood fibres, compared to samples with 25 wt% fibres, owing to the higher number of chromophores in the former. Nicole and Matuana [24] reported that mechanical degradation of wood fibre/HDPE composites by UV was greatly accelerated by moisture effects.

Overall, however, little work has provided insight into the influence of fibre chemistry of wood fibre reinforced polyolefin composites before and after UV exposure [25] particularly in the

Table 1
Cell wall polymers responsible for the properties of lignocellulosics in the order of importance [11]

Strength	Moisture absorption
Crystalline cellulose	Hemicellulose
Non-crystalline cellulose	Non-crystalline cellulose
Hemicellulose + lignin	Lignin
Lignin	Crystalline cellulose
Thermal degradation	Ultraviolet degradation
Hemicellulose	Lignin
Cellulose	Hemicellulose
Lignin	Non-crystalline cellulose
	Crystalline cellulose
Biological degradation	
Hemicellulose	
Non-crystalline cellulose	
Crystalline cellulose	
Lignin	

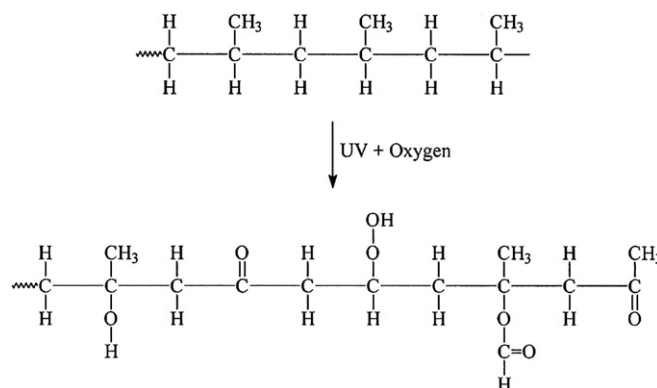


Fig. 2. PP molecules after extensive photodegradation [13].

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