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High performance natural rubber composites with a hierarchical reinforcement structure of carbon nanotube modified natural fibers

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ABSTRACT

A simple and facile method for depositing multiwall carbon nanotubes (MWCNTs) onto the surface of naturally occurring short jute fibers (JFs) is reported. Hierarchical multi-scale structures were formed with CNT-networks uniformly distributed and fully covering the JFs (JF–CNT), as depicted by the scanning electron microscopy (SEM) micrographs. The impact of these hybrid fillers on the mechanical properties of a natural rubber (NR) matrix was systematically investigated. Pristine JFs were cut initially to an average length of 2.0 mm and exposed to an alkali treatment (a-JFs) to remove impurities existing in the raw jute. MWCNTs were treated under mild acidic conditions to generate carboxylic acid moieties. Afterward, MWCNTs were dispersed in an aqueous media and short a-JFs were allowed to react with them. Raman spectroscopy confirmed the chemical interaction between CNTs and JFs. The JF–CNT exposed quite hydrophobic behavior as revealed by the water contact angle measurements, improving the wettability of the non-polar NR. Consequently, the composite interfacial adhesion strength was significantly enhanced while a micro-scale "mechanical interlocking" mechanism was observed from the interphase-section transmission electron microscopy (TEM) images. SEM analysis of the composite fracture surfaces demonstrated the interfacial strength of NR/a-JF and NR/JF–CNT composites, at different fiber loadings. It can be presumed that the CNT-coating effectively compatibillized the composite structure acting as a macromolecular coupling agent. A detailed analysis of stress-strain and dynamic mechanical spectra confirmed the high mechanical performance of the hierarchical composites, consisting mainly of materials arising from natural resources.

1. Introduction

Natural fiber reinforced polymer composites have been introduced since 1908 when for the first time cellulose fibers were incorporated in phenolic resins [2]. Nowadays, natural fibers such as jute, flax or hemp have attracted considerable scientific interest in the field of polymer composites due to their intrinsic low density as well as the high specific mechanical properties at a very low price. Therefore, it can be easily realized that natural fibers possess great potential to replace synthetic ones, like glass, carbon or aramid for specific applications, since they are recyclable, biodegradable and non-polluting. Accordingly, environment-friendly biodegradable composites can be achieved exposing comparable mechanical properties with that of glass fiber composites [3], but with lower weight and significantly reduced carbon footprint [4].

Recently, natural fibers have been used as alternative reinforcements of conventional glass fibers for petroleum-based polymer composites in the automotive and building product industry [5]. However, the use of natural fibers has to face some specific drawbacks, e.g. the relatively poor thermal stability and especially the poor compatibility and interfacial bond strength with the hydrophobic polymer matrices, due to their basically hydrophilic nature [6,7]. This can result further in weak fiber/matrix interfaces and poor mechanical properties of the final composites. Nevertheless, it has been reported in several studies that most of these drawbacks can be overcome utilizing specific surface modifications [8–11]. In composite materials, it is a well-known fact that the strength and modulus are both dominated by the reinforcement phase which is considered to be the main load bearing constituent. The interphase between fibers and matrix acts as an intermediate bridge which transfers the load from the matrix to the reinforcing

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fibers through the shear stress. Therefore, it is considered as a critical parameter in controlling the overall composite's performance [12,13]. Optimized engineered interfaces can guarantee a "good adhesion" between the composite constituents resulting in enhanced interfacial strength; a key parameter for the effective stress transfer upon mechanical loading. Indeed, the high quality of the interphase is a precondition for the optimal composite's mechanical performance as concluded in various studies [14–16].

The reinforcement of rubbers by particulate and fibrous fillers is quite common method to enhance their mechanical properties, however, useful products and their commercial viability have been found only when these two parameters, viz., lowest dimension of the dispersed phase and strong interaction between the filler/matrix are achieved [17]. Much investigation has been focused on the reinforcement of rubbers by using both synthetic as well as natural fibers. Especially, the incorporation of short fibers in a rubber matrix has become an attractive field of research due to the versatile processing which lowers the production costs compared to unidirectional fiber composites. Short fiber rubber composites can be used in a wide range of applications such as belts, hoses, seals, complex-shaped mechanical goods and tire industries [18]. Several studies are available on the use of short synthetic fibers like glass, carbon, rayon, nylon, aramid and asbestos in various natural and synthetic rubbers [19–22]. Sreeja and Kutty [23] investigated the mechanical properties of rubber composites reinforced with short nylon fibers. In another work, Senapati [24] embedded short polyester fibers in a natural rubber matrix. Generally, the mechanical properties of short fiber reinforced composites are largely governed by the fiber/matrix adhesion strength as well as the state of fiber dispersion, concentration, aspect ratio and orientation which may directly be affected by the processing method and processing parameters [25]. Hintze et al. [22] described that the reinforcement of an EPDM rubber matrix was significantly influenced by the process induced orientation and the residual length of aramid type short fibers. Due to the fact that natural fibers are renewable in nature, a lot of attention is given to achieve rigid rubber-based composites. Many researchers have reported the use of natural fibers, viz., pineapple leaf fiber [26], short jute fiber [27], short coir fiber [28], bamboo [29], sisal/oil palm [30] in elastomer compounds. Murthy and De [31] and Chakraborty [27] investigated the reinforcing effect of short jute fibers in natural and carboxylated nitrile rubber composites. Recently, Götze et al. [22] reported that short cellulose type fibers offered much reinforcement at lower filler content compared to conventional synthetic fillers in a solution processed styrene butadiene rubber.

The fabrication of natural rubber/jute fiber composites is in general a quite new research field and the effective reinforcement could be a challenging topic. Obviously, the dispersion of jute fibers (JFs) in natural rubber (NR), and the formation of a strong interphase between them is a difficult task which requires extensive investigation. It is reported that partial modification of either the fiber surface or the polymer matrix can develop an improved bonding leading to satisfying reinforcing effects [32]. The JFs in the as grown state consist of a cellulose rich core and their outside surface is dominated by cementing which includes waxes, fats, lignin, pectin and hemicellulose. This cementing prevents from the formation of a good interface and normally it is removed by an alkali treatment. However, the hydrophilic and polar nature of JFs after alkali treatment still remains not suitable for direct incorporation with the apolar NR. A lot of different approaches have been utilized to rendering the JFs more compatible with polymer matrices [9,11,33]. A first step usually contains as mentioned above an alkali treatment so that the fibers will expose their cellulosic nature [33]. Silane coupling agents and/or other chemical substances [34] have been further used to promote the fiber/matrix adhesion and endow the desired interfacial strength. Garcia-Hernandez et al. [35] reported an apparent influence of the natural fiber surface modifications on the interfacial shear strength of polystyrene composites. Another method to improve the compatibility between natural fibers and polymeric matrices is to use modified polymers, e.g. the addition of a small amount of maleic anhydride grafted PP to a polypropylene matrix [11]. Recently, carbon nanotubes (CNTs) have been regarded as excellent candidates to modify the fiber surfaces and improve the interfacial strength as well as to introduce interphase functionality due to their unique electrical, mechanical and thermal properties [36,37]. In particular, deposition of CNTs onto glass or carbon fibers using chemical vapour deposition, simple solution dip-coating methods or spray coating techniques has been found to increase the interfacial interaction via increased chemical bonding, mechanical interlocking and local stiffening of the polymer chains at the interphase region, all of which may improve the stress transfer from the matrix to the reinforcement [38]. Subsequently, high loadings of CNTs in the final composites can be achieved while alleviating the critical problems encountered during the composite fabrication related to the high viscosity of the polymer melts and the CNT agglomeration [15]. A review could be found where carbon nanotube-based hierarchical composites and the advantages for the formation of a multi-scale reinforcement were elaborately discussed [39]. The influence of CNT-modified fibers, e.g., on static tensile and dynamic mechanical properties of elastomer composite materials with the aim to be applied finally in products under dynamic loading, are not established yet. Meanwhile, the chemical vapour deposition (CVD) process which is already reported for CNT deposition [40–42] onto fibrous reinforcements cannot be employed in the case of JFs and/or other kind of natural fibers, because they are not stable at high temperatures required for the CVD CNT-growth.

The main objective of the current study is to develop an engineered interface in short jute fiber reinforced NR composites, using CNTs as a novel interphase coupling agent. JFs were coated with CNTs (JF–CNT) via non covalent interactions and hierarchical structures were created. The resulting JF–CNT hybrid fillers were embedded in a NR matrix, and exposed a significant reinforcing effect as revealed by the static tensile tests and dynamic mechanical analysis (DMA). This was mainly attributed to the NR improved wettability towards the CNT-coated JFs at 10, 20 and 30 phr (parts per hundred gram of rubber) loadings, compared to the respective a-JF composites. JF–CNT exposed less polar and less hydrophilic behaviour as shown by the water contact angle measurements explaining more precisely the improved wetting of the NR resin. SEM fractographic analysis exhibited limited JF–CNT pull-out from the NR matrix, and also no significant interfacial debonding. The CNT-networks introduced a mechanical interlocking mechanism illustrated by the TEM interphase-section images. In addition, the JFs were endowed with nano-scale roughness which is responsible for the local stiffening of the NR chains at the fiber/matrix interphase region. Overall, it can be envisaged that the CNT surface layer played an important role on the enhanced interfacial adhesion strength reflecting to the mechanical properties of the final composites. The different micro-scale toughening mechanisms correlated with the improved mechanical performance of the hierarchical natural-based rubber composites will be discussed further more in detail.

2. Experimental details

2.1. Materials

The natural rubber used in our study is Standard Malaysian Rubber (SMR-10). Jute yarn was obtained from Gloster Jute Mills, (TD 4 grade, Howrah, India). Stearic acid was purchased from Acros Organics (Geel Belgium, 97% purity) and N-cyclohexyl-2-mercapto