

Surface-initiated catalytic polymerization of hemp fibers

Désiré Yomeni Chimeni, Charles Dubois, and Denis Rodrigue

A novel surface treatment is experimentally tested as a way to improve the mechanical properties of polymer composites.

Increasing environmental awareness means that the field of material science and engineering is being steered towards the production of high-performance composites that are reinforced by renewable materials. Furthermore, such renewable resources—especially lignocellulosic fibers—are associated with some advantages over conventional reinforcing materials (i.e., inorganic fibers). In addition to biodegradability and renewability, the advantages of the renewable materials include good availability, low cost, low density, and high specific strength and stiffness.^{1–6} However, the materials also have some drawbacks, such as poor fiber–matrix interactions in most polymer matrices, difficult fiber dispersion, and low fiber wetting by the matrix.^{1–3} These problems have therefore prevented high performances (particularly in terms of mechanical properties) being achieved with the renewable-resource-reinforced composites.

To solve these ongoing problems, a number of approaches have previously been presented (e.g., acetylation, silanization, and coupling agent addition).^{7–9} However, few of these proposed methods can be used to modify particles and achieve superior composite properties. It is therefore necessary to find alternative ways to overcome the problems associated with using renewable resources in composite materials.

As one possibility, we have investigated¹⁰ the use of surface-initiated catalytic polymerization to perform fiber modification. In the surface-initiated catalytic polymerization technique, a polymer is forced to grow from the surface of a solid particle in the presence of a Ziegler–Natta catalyst system.^{1,11} However, there is a limited amount of available information on the possibility of using this advanced approach for organic fibers. The objectives of our work were therefore to evaluate the feasibility of modifying hemp fibers with this technique and—if found to be feasible—determine the effect on the properties of linear medium-density polyethylene (LMDPE)-based composites (i.e., as an example of a typical system).

In the first part of our experiments, we mercerized⁵ (with sodium hydroxide) the hemp fibers to increase their surface-active sites (both in number and availability). We then dried the mercerized fibers and

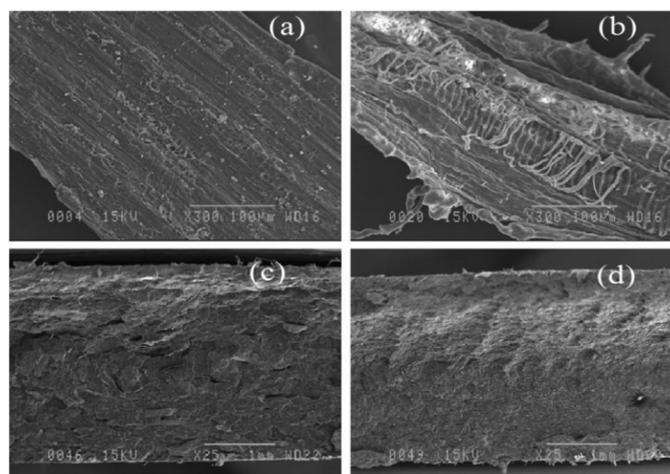


Figure 1. Scanning electron microscope (SEM) images of (a) untreated and (b) polymerized hemp fibers. SEM images of composites containing the untreated and polymerized fibers are also shown in (c) and (d), respectively.

modified them via in situ polymerization. In this process, the catalyst (titanium tetrachloride) is chemically anchored to the reinforcing agent active sites, i.e., hydroxyl groups.¹¹ The polymerization of the monomer (ethylene) then proceeds—in the presence of the co-catalyst (i.e., triethylaluminum)—from the fiber surfaces. In the last step, we prepared the composites by compounding the LMDPE pellets and the hemp fibers (modified or unmodified) in a twin-screw extruder and used injection molding to form the final samples with 30wt% (modified or unmodified) hemp fibers. We have previously provided a full description of our experimental procedures.^{5,6}

Example scanning electron microscopy (SEM) images of our untreated and modified hemp fibers are shown in Figure 1. We find that the untreated hemp—see Figure 1(a)—exhibits a rough surface that is caused by the presence of non-cellulosic materials (impurities).^{5,6} The polymerized hemp—see Figure 1(b)—however, has a different surface texture that we associate with the formation of chemical bonds between the hydroxyl groups of hemp and polyethylene during the

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polymerization of ethylene. The image of the composite containing 30wt% untreated hemp (LNH)—see Figure 1(c)—shows large holes that result from fiber pullout and debonding. These phenomena arise because of the poor wettability and adhesion properties of the matrix, i.e., the fibers cannot support a high level of applied load and they can be easily extracted. In contrast, the polymerized hemp composite (LPH) sample—see Figure 1(d)—has a more homogeneous surface with fewer holes, thus indicating that interfacial improvement was achieved.

We have also measured the tensile mechanical properties of our composite samples (see Figure 2). Our results indicate that the LNH sample has a Young's modulus that is significantly higher (by about 117%) than that of LMDPE. This arises because of the stiffness that is imparted by the hemp fibers, i.e., because their Young's modulus (70GPa) is much higher than that of LMDPE (0.24GPa).^{5,6} Moreover, the Young's modulus of the LPH sample is higher than that of the LNH and LMDPE samples (by 8 and 125%, respectively). We thus find that the catalytic polymerization has a significant contribution to the material's stiffness, which is probably caused by the polyethylene coating on the fibers shown in Figure 1(b). In terms of strength, we observe that the LNH sample is only slightly better (by 10%) than LMDPE. We ascribe this result to the lack of fiber wettability and to poor compatibility, i.e., based on our observations of fiber pullout in Figure 1(c). On the other hand, the tensile strength of the LPH samples is substantially higher than the LNH and the neat LMDPE (by 43 and 53%, respectively). This is because the LMDPE imparts better wettability to the modified

hemp, which in turn causes reduced fiber–fiber interaction (and thus better dispersion). In other words, the polyethylene coating layer of the fibers improves the compatibility because it has the same nature (polyethylene) as the matrix.

In summary, we have investigated the use of surface-initiated catalytic polymerization to modify hemp fibers and to thus improve the mechanical properties of hemp-reinforced composite materials. Our results show that our catalytic polymerization technique can be used to successfully modify the hemp fibers. In addition, we find that the presence of a thin polyethylene layer on the surface of the fibers leads to a significant improvement of the composites' interfacial properties. These improvements are manifest at the macroscale as significant increases in the tensile modulus and strength of the composites compared with samples that included untreated fibers. Our modifications thus improve the rigidity and strength of the composites. In the next stages of our work, we need to determine if our results so far can be applied to other matrices and fibers. We also plan to investigate how the grafted polymer content affects other properties (e.g., impact strength).

Author Information

Désiré Yomeni Chimeni and Denis Rodrigue

Department of Chemical Engineering
and
Research Centre for Advanced Materials (CERMA)
Université Laval
Quebec City, Canada

Désiré Yomeni Chimeni is a PhD student. His main research interests involve natural fiber composites and the improvement of their mechanical properties.

Denis Rodrigue is a professor of chemical engineering. In his work he is mainly interested in polymer processing and characterization, rheology of complex systems, and recycling.

Charles Dubois

Department of Chemical Engineering
Polytechnique Montréal
Montreal, Canada

Charles Dubois is a professor whose main research interests include reactive polymer processing, nanocomposites, and energetic materials.

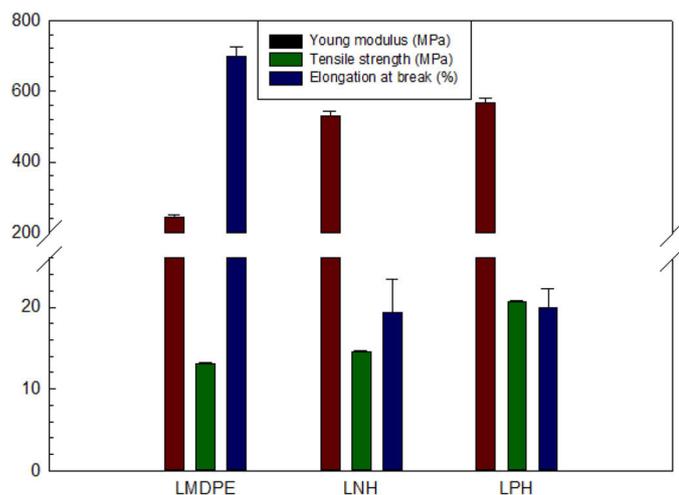


Figure 2. Experimentally measured tensile mechanical properties of the produced samples. LMDPE: Linear medium-density polyethylene. LNH and LPH: Composites containing 30wt% untreated and polymerized hemp, respectively.

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