

EFFECT OF SURFACE POLARITY OF CELLULOSE NANOFIBERS ON THE MECHANICAL PERFORMANCE OF STARCH BASED COMPOSITE

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1. Introduction

Nano-reinforcement of polymer is gaining a deliberate interest not only due to tremendous alteration of mechanical properties but also due to probability of reduction in weight of resulting composites in order to enhance fuel efficiency by producing light weight automobile parts [1]. Therefore, several nano-fillers and their effect on different properties of polymers have been studied in order to optimize the cost performance ratio [2]. Recently, a renaissance in the use of nano filler from natural resources is taking place mainly to introduce eco-friendly character in resulting composites [3]. Cellulose has traditionally been used to develop biodegradable polymer composites and recently it was observed that the composites, prepared by reinforcement of polymers through nano-crystalline cellulose can exhibit remarkable improvement in many polymer matrixes at very low filler concentrations in comparison of their neat host matrix. [4].

Plant cell wall is a complex structure, comprises of different macromolecules such as cellulose, lignin, hemi-cellulose, pectin etc. During the biosynthesis of cellulose in plant a continuous and controlled deposition of microfibrils occur that finally dictate the mechanical properties of plants by adjusting hierarchy and orientation [5]. It has been found that these microfibrils are highly crystalline in nature and have modulus around 157 GPa which is similar to engineering polymer like Kevlar [6].

Cellulose nano-crystals can be created by mechanical analysis and chemical treatments or both together. The cellulose micro-fibrils are constituted by crystalline and amorphous regions. The amorphous regions are randomly oriented in spaghetti like arrangement leading to a lower density in these non-crystalline regions [3,7, 8]. The hydronium ions can penetrate the cellulose chains in the amorphous domains promoting the hydrolytic cleavage of the glycosidic bonds and finally releasing individual crystallites.[4,9,]. The different treatments of these hydrolysed crystallites, such as mechanical dispersion or ultrasonification, permit the dispersion of the aggregates and finally produce colloidal suspensions. Cellulose nano-crystals have been used as fillers in many polymer matrixes, such as silk fibroin, cellulose acetate butyrate, starch, polylactic acid, polyvinyl alcohol, and other plastics [7]. However, the extraction of nano-fibers required to balance the drawbacks, such as time-consuming preparation, low yield, and hydrophilicity, prior to industrial applications [4, 8].

Surface charges on the nano-fillers are highly significant in term of adhesion with matrix and therefore, interest is increasing [8] to evaluate the interactions of cellulose nano-fibers with matrix as these interaction profiles determine the final properties of the products. In the present work we aimed to evaluate the effect of surface charges of cellulose nano filler on the

mechanical properties of biodegradable resin. The biodegradable resin was a blend of poly caprolactone) and corn starch. Chemical structures of biodegradable resin components are depicted in Figure 1. Two types of cellulose nanofibers were employed to reinforce the biopolymer, i) with charged surface, prepared by acid hydrolysis of crystalline cellulose and ii) with neutral surfaces, those were extracted merely by mechanical processes without using any chemical treatment. The comparison of tensile strength and elongation with measurement of stiffness was conducted thoroughly to evaluate the effect of surface polarity of cellulose nano-fibers on mechanical performance.

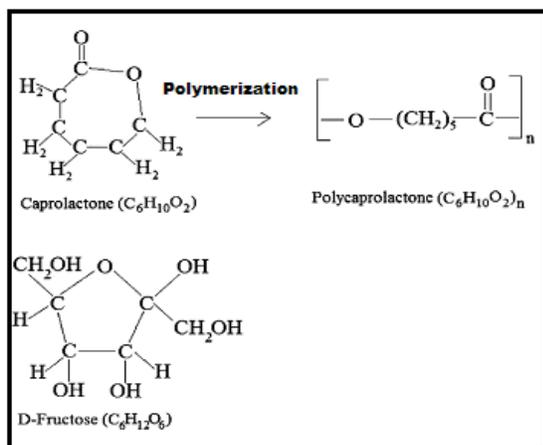


Figure 1. Components of biodegradable resin.

2. Experimental Procedure.

2.1 Preparation of cellulose nano-fibers and Composites

Crystalline cellulose was obtained from Daicel Chemical Industries Ltd. Japan having brand name KY-100G. This product has 10 % solid content in water and the fiber thickness is refined to between 0.1 and 0.01 μm . The material was further sonicated for 35 minutes at 45 % output at 5 minute intervals causing further individualization of fibers. This sample was named as Neutral Nano Fiber (NNF). In another attempt the cellulosic material was

allowed to digest in 64% H_2SO_4 for 25 minute at 45 $^{\circ}C$. The product was washed several time with deionized water and subjected to sonication for 20 minutes and sample was designated as Charged Nano Fiber (CNF). The biodegradable aliphatic polyester (Randy CP-300) was obtained from Miyoshi Oil & Fat Co., Ltd (Nagoya, Japan) which is hydrophilic polyester and a blend of polycaprolactone and cornstarch. The biodegradable polymer has density 1.17 g/cm^3 , Tensile strength 10.1 MPa, Young's modulus 0.4 GPa and particle diameter was around 4.9 micrometer. The composites of these cellulose nano-fibers were prepared through the methods described in our earlier work [9] by keeping 3 and 5 % (w/w) filler loads. The results of composites loaded with 5 % filler were discussed in detail in order to reduce the volume of manuscript.

The mixing of composite components was performed in a mechanical stirrer for 10 hrs. followed by 5 minute sonication [10]. TEM analysis was performed by putting drops of cellulose nano-fiber suspension on carbon grid, followed by 24 drying. SEM microscopy was carried out directly in JEOL microscope. Specimens for tensile testing were molded in a specially designed mold and average value of 5 samples was taken into account. Universal tensile testing machine Instron Corp. Model 5567 was used to evaluate the mechanical performance of resulting composites.

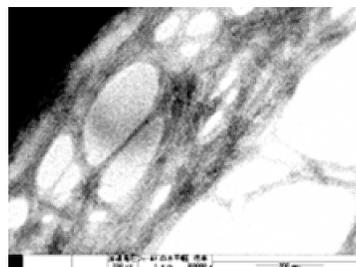


Figure 2a. TEM of Cellulose nanofibers extracted through acid hydrolysis

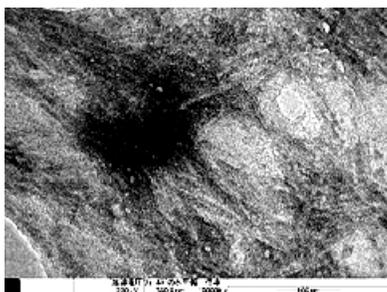


Figure 2b. TEM of Cellulose nano-fibers extracted through acid hydrolysis at higher magnification.

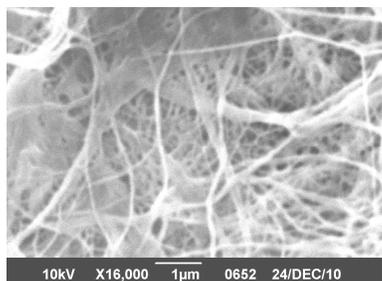


Figure 2c. Cellulose nano-fibers through mechanical analysis.

3. Results and Discussions

Morphology of cellulose nano-fibers were observed through TEM as presented in Figure 2a, b and c for acid and mechanically treated samples. During treatment with sulphuric acid, the hydrolysis usually could cleave the amorphous region transversely, resulting diameter reduction from macro to nano level [7,13] as could be seen in figure 2 a and b. The whiskers like structures were highly populated with many aggregated cluster. The formation of aggregated cluster is obvious in such type of specimens due to water evaporation during drying process. On the other hand, mechanically extracted fibers by homogenization process (from Daicel Chem.Ind.) exhibited highly fibrillated web like network, those are entangled with each other randomly. The entangled network was supposed to be destroyed during sonication treatment before employing as filler [14]. Table 1 present

the tensile strength, modulus and elongation of the prepared composites. Comparison with neat polymer showed a little improvement in tensile strength and modulus at 5 % filler load in case of NNF reinforced composites which may be attributed to smoother energy transfer from matrix to filler at the interface resulting in a delay failure of composites. This behavior may also be explained on the basis of slippage mechanism in micro-fibrils which can take place at interface probably by creating a flexible region, after removal of surrounding cementing material from fibers such as hemicellulose and lignin [11]. The composites of CNF showed a decrease in the properties and values were lower than both neat and NNF in the present system. Such types of observations were strongly suggesting that surface charges of cellulose nano-fiber may play a decisive role during mechanical performance of PCL-Starch composites. There may be few possibilities to explain the higher strength and modulus of NNFs than CNFs. i) micro-fibrillation of cellulose may influence the bulk properties by enhancing the matrix interactions and depend on the parameter that how fine is the reinforcing fiber [15]. ii) CNF was extracted through acid treatment (sulphuric acid) and carrying negative charges that repelled each other and form colloidal suspension in the water [12]. As soon as water evaporates during drying, CNF must have higher tendency to agglomerate inside matrix. These agglomerated clusters may act as stress concentration points during load, generating catastrophic failure of matrix. There should be higher possibility of brittle, heterogeneous and active interface in these specimens [16] due to higher charge density than NNF. iii) Since the resin constitutes starch as one of its phase, the degree of electrostatic attraction in the form of hydrogen bonding with NNF should be better than CNF due to more number of unbalanced and exposed hydroxyl groups. A non-linear stress-strain behavior of both the composites may be attributed to the

permanent deformation of corn starch (mainly composed of d-fructose which is a carbohydrate isomer to glucose with chemical structure $C_6H_{12}O_6$.) phase in the blend [17]. While the analysis of elongation of specimens, NNF showed competitively better performance (lower than neat) than CNF that may be attested to the more agglomeration tendency in CNF.

Table 1. Mechanical properties of composites 5% filled composites (standard deviation).

Sample	Tensile strength (MPa)	Modulus (MPa)	Elongation (%)
Neat	11.4 (1.2)	627 (78)	11 (0.9)
CNF	7.1 (0.8)	570 (41)	4.8 (1.0)
NNF	12.9 (1.0)	697 (35)	6 (0.8)

An attempt was made to ascertain the initial effect of sonication by preparing a separate batch of samples with and without sonication of NNF at 5 % filler concentration. During the morphological analysis, a better dispersion was appeared in SEM for sonicated samples however bulk mechanical properties were not significantly influenced. The studies are in progress to have conclusive results whether, small particulate type of cellulose nano-fibers are beneficial or highly micro-fibrillated one, for the mechanical properties polymeric matrix. Surface observation through SEM was performed to obtain the information about distribution of fillers and correlate with results of mechanical properties. SEM was carried out at very small portion of sample and relevant information of surface could be extracted. The SEM of stretched portion of 5 % filled specimen shows the uneven surface with lots of small whole on it as can be seen from Figure 3. Some kind of accumulation, appeared like clumps, could be found on the surface of samples. There are two probable explanation of this type of failure mechanism. Firstly, resin itself is an

emulsion of micro-order particles consisting polycaprolactone and corn starch. All micro-order particles did not melt mixed entirely and may remain in the original form inside the host matrix. This explanation was supported by micrographs where some scattered particle like structures were visible on the surface. When samples were put under tensile , these particles may stretch out of matrix, generating hole as can be seen from Figure 3 where small patches of embedded micro-particle were found. Secondly, cellulose nano-fibers tend to establish higher degree of electrostatic bonding or hydrogen bonding with starch chains [7] and such type of bonding may inhibit the cellulose nanoparticles from homogenous dispersion in the matrix and aggregated heterogeneously which can propagate the initiation of matrix fracture. The SEM images support this interpretation where large clumps were detected. This explanation was further reinforced by the gradual decrease in the elongation of composites with the increasing filler load. A detailed analysis is still under progress and the initial results confirmed that other than the surface charges of filler, the micro-particles of resin should be completely destroyed before the mixing of cellulose; it may not only enhance the dispersion of filler but also improve the reinforcing potential of nano-fibers for this biodegradable resin.

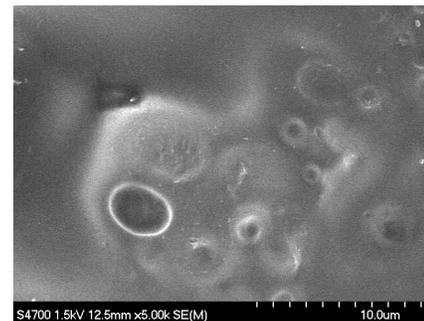


Figure 3. SEM micrograph of specimen 5 % filled composites,

4. Conclusions

Future development for a cellulose nanofiber reinforced biodegradable polymer composites are predicted by varying the surface characteristics of nano fibers. The lowering in mechanical properties of sulphuric acid treated nanofibers was attributed to the higher agglomeration of nanofibers during drying process of composites preparation which results in the heterogeneous dispersion of filler inside the host polymer and finally catastrophic failure of matrix due to stress concentration under load. In general it was proposed that merely mechanically extracted cellulose nanofibers may be comparatively better option as reinforcement of polycaprolactone-starch composites than nanofibers extracted through acid treatments. Further, detailed studies are under progress to obtain a quantitative comparison by analyzing the effect of shape and size on the mechanical properties, crystallization behavior and thermal analysis of resulting hybrid.

Acknowledgement

Authors are gratefully acknowledging the Japan Society for Promotion of Sciences (JSPS).

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