

INVESTIGATING THE MORPHOLOGY AND MECHANICAL PROPERTIES OF BIODEGRADABLE NANOCOMPOSITES BASED ON CELLULOSE DIACETATE COMPOSITES AND CELLULOSE ACETATE BUTYRATE

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Abstract

Environmentally benign nanocomposites were synthesized using cellulose acetate (CA) bioplastic and organosilicate nanofillers to eventually substitute the existing petroleum. In order to obtain a nanobiodegradable plastic, SiO₂ nanoparticles have been used as reinforcement to be dispersed in cellulose diacetate (CA) matrix as a biobased polymer for producing a high performance biodegradable nanocomposite. First, kind of silica nanoparticles (modified and non-modified) were physically modified with different percentages of cellulose acetate butyrate (CAB) for improving interfacial adhesion between CA and SiO₂ and then the modified and non-modified SiO₂ nanoparticles were individually incorporated into the polymer through melting process by assistance of a twin-screw extruder. Finally The comparison effects of CAB content and SiO₂ surface modification on mechanical properties and morphology by the aid of scanning electron microscopy (FESEM) were investigated. Morphology studies show that the modified silica nanoparticles could be easily dispersed in CA matrix having particle sizes less than 100 nm. The tensile strength, Young's modulus, and elongation at break were found to decrease with increasing CAB loading.

1. Introduction

In the last few decades, nanocomposite materials have attracted scientists' attractions since they offer multi-functional properties even at low loadings of nano-sized reinforcement. Besides, environmental aspects have been one of the main concerns in this field because long-time bio-recycling process would potentially threaten the human being's life. Many attempts have been therefore made to fabricate nanocomposites based on biodegradable polymers. Cellulose esters such as cellulose diacetate (CA) and cellulose acetate butyrate (CAB), derived from natural plant fibers, are listed in this category. Many attempts have been

therefore made to fabricate nanocomposites based on biodegradable polymers [1-3]. However, the most important question is whether these biodegradable resources can be an alternative for the petrochemical polymers or not. Therefore, many extensive studies concerning the cellulosic plastics have been carried out [4].

Undoubtedly, a good dispersion of nano-sized particles in an organic matrix could beneficially influence the performance of the resultant nanocomposite [5]. To obtain an acceptable dispersion several methods have been considered such as modification of nanoparticles or organic matrices [6]. Silica nanoparticles have been used in the industry to reinforce the elastomers as a rheological solute [7]. Silica nanocomposites have been attracting some scientific interest as well. The advantage of these nanomaterials resides in the lowcost of production and in the high performance features. Studies on nanosilica dispersions in polymer matrices like poly(methyl methacrylate) [8,9], polyethylene [10] and poly(ethylene oxide) 600 [11] have been carried out.

In the study presented below, SiO₂ nanoparticles have been used as reinforcement to be dispersed in CA matrix as a biobased polymer for producing a high performance biodegradable nanocomposite. CAB is also used to modify the surface of SiO₂ nanoparticles and the effect of such modification on morphology of the nanocomposites is investigated

2. Experimental

2.1 Materials

Cellulose acetate (CA, average Mn=30000) and tetraethylcitrate (TEC) were provided from Sigma Aldrich and Merck Chemicals and used as matrix and plasticizer, respectively. Three type of Cellulose acetate butyrate (CAB 381-20, 381-20bp, 381-0.1) without additives in powder form were purchased from Eastman Co. CAB 381-20 (butyryl 37% wt, acetyl 13.5 % wt, hydroxyl 1.8 % wt), CAB 381-20bp (butyryl 36% wt, acetyl 15.5 % wt, hydroxyl 0.8% wt) and CAB 381-0.1 (butyryl 37% wt, acetyl 13% wt, hydroxyl 1.5 % wt)..

Silica nanoparticles (Aerosil 300), (R812) was purchased from Degussa Co (Germany) and kept at 100 °C in a vacuum oven for 1 hr before using.

2.2 Surface Modification of SiO₂ nanoparticles

Three groups of CAB with 10, 100 and 200 % wt based on SiO₂ nanoparticles, means with 1 gr nano SiO₂ (0.1, 1 and 2 gr CAB respectively) were added to butyl acetate while stirring at temperature of 150 °C. Then two modified (R812) and non-modified (A300) that 1 % wt in nanocomposites (1 gr) were added to the solution and stirred at speed of 100 rpm for 8 h. Finally, treated-silica powder was separated from butyl acetate solvent. The total weight of mixture was 60 cc. and dried in an oven at 60 °C so there were 18 samples.

Also there was a SiO₂ (A300) without any CAB content as a reference sample that is obvious the total weight of this mixture (SiO₂/BA) was 60 cc too. Finally 19 samples were produced and then became ready to mix with CA/TEC (matrix of nanocomposite) in twin screw extruder to produce high performance nanocomposite.

2.3 Preparation of nanocomposites

To prepare nanocomposites, first neat CA and tetraethylcitrate (TEC, plasticizer) (CA/TEC= 75/25 wt %) was mixed mechanically with a high-speed mixer for 5 min, and was then fed into a 60cc internal twin extruder (Brabender- PlastiCorder- Germany) at temperature of 200 °C and screw rate of 100 rpm. After 5 min when the torque became constant, 1 % wt modified and non-modified SiO₂ nanoparticles (R812, A300) were filled into the extruder. Eventually,

this procedure lasted 14 min, and afterward the output of extruder was molded in a hot press molding (Mini Test Press- Toyoseiki- Japan) at 210 °C. Also, a sample containing the neat CA and SiO₂ (without any CAB particle) was prepared after extruding as control.

3. Results and discussion

3.1 Morphology studies

1% SILICA	A300			R812		
	381-20	381-20BP	381- 0.1	381-20	381-20BP	381- 0.1
10% SILICA CAB	F 1.a (3)	F 1.b (2)	F1.c (1)	F 1.d (6)	F 1.e (5)	F 1.f (4)
100% SILICA CAB	F2.a (9)	F2.b (8)	F2.c (7)	F2.d (12)	F2.e (11)	F2.f (10)
200% SILICA CAB	F3.a (15)	F3.b (14)	F3.c (13)	F3.a (18)	F3.b (17)	F3.c (16)

Silica	A300 F4 (19)
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Table 1. Base formulation of CAB/silica nanocomposites .

Table 1 combined percentages of cellulose acetate and silica appear to form 1 to 18. Number 1 based on superior morphology. In other words, Figure 1 has top morphology, and Figure 18 has the weakest morphology . It is intended that the superior morphology of silica nanoparticles in thermoplastic matrix CA disperse and have been distributed and weak morphological do not Disperse well and this refers to the silica particles have been Agglomerate.

The same as previously explained we have our two types of nano sio₂ . Sample A300 that any modifications it been done and the R812 to the amount modificate and again it treats with the CAB in different percentages. All of our goals from the use of CAB that CA/ SiO₂ final nanocomposite morphology was improved to acceptable levels.

Owing to the fact that the surface of the silica nanoparticles contains OH functionalities causing inherent hydrophilicity to these particles [12], forming aggregation within a hydrophobe thermoplastic bulk during the process could be possible. In The structural review has been found that the structure of CAB and the group of OH in SiO₂ nanoparticles , Dispersion of SiO₂ is being improved by the reinforcing particles modification(CAB). But it

is also mention the amount of improvement is different. In this paper we improve morphology in the cases of the different percentages of combination of the CAB have been investigated.

We have different moods of morphology . One factor on the morphology can affect and improve it, having the same molecular weight of the CAB and CA . To the other words if the molecular weight of CA and CAB to be close together ,there are more compatibility between the CAB and CA , and we see better morphology.This case for nano SiO₂(A300) and for (R812) exist. We can confirm this Phenomenon in the figures (1.a. / 1.b / 1.c 1.d / 1.e / 1.f)and (2.a. / 2.b / 2.c / 2.d / 2.e / 2.f) and (3.a. / 3.b / 3.c/3.d / 3.e / 3.f) . Now had to explain figures one by one:

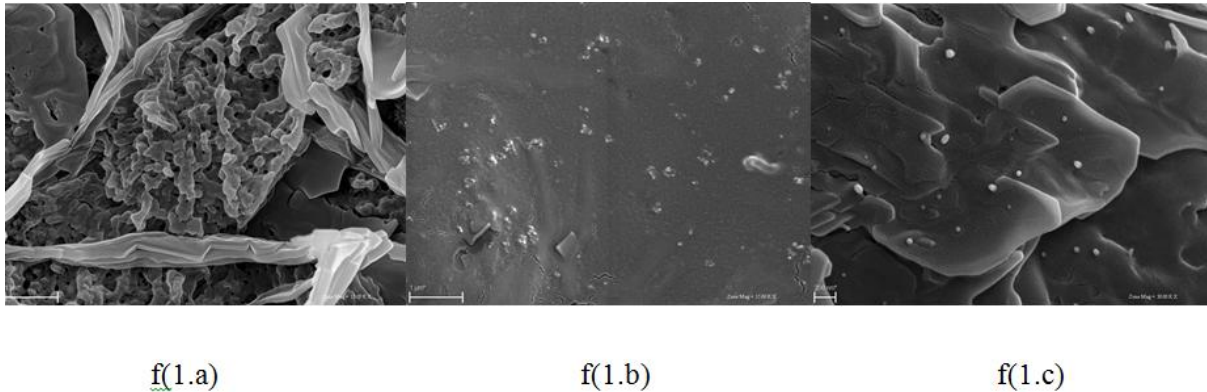


Figure 1.1. FESEM images of CAB/SiO₂ nanocomposites of (f.1a , f.1b , f.1c) samples.

As can be seen in the figure above the figure of “1.c” morphology is best that this due to a molecular weight of modification factor is close to the molecular weight of cellulose acetate. There is also a difference between modifiers CAB 381 20 BP and CAB 381 20 and this mention that although the molecular weight of these two amendments are same, but because of differences in their organic groups ,shown morphology are different, Appropriate morphology of CAB 381 20 BP from the CAB 381 20 shows the superiority and this indicates that treatments have been carried out to better grades.

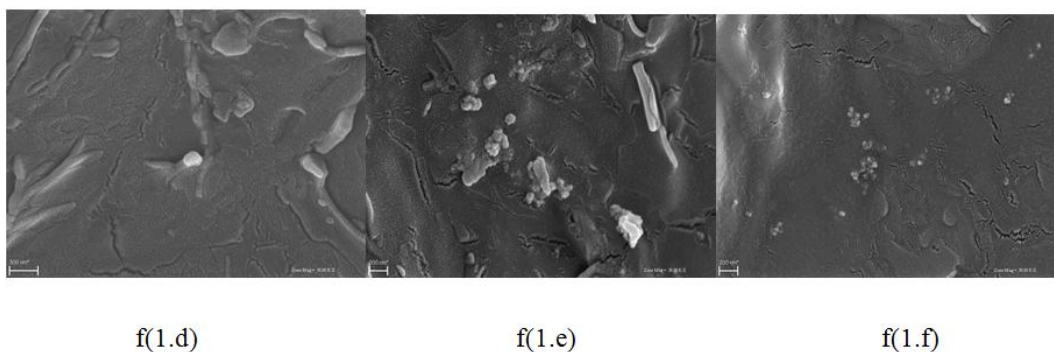
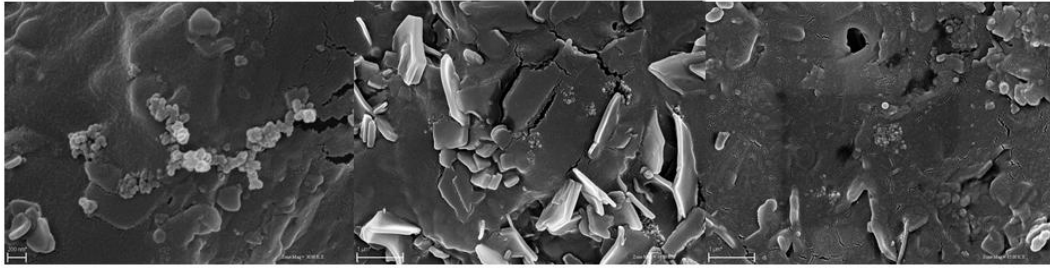


Figure 1.2. FESEM images of CAB/SiO₂ nanocomposites of (f.1d , f.1e , f.1f) samples.

In these Figures of nano-silica that type of R812 is used, we see that the morphology in compare with when silica A300 used, is weaker. Means that this treatments to the previous case, does not show superiority morphology , because the type of silica used is different. It means that statement of basic treatment of the type of silica is R 812 can be prevented from CAB modification.



f(2.a)

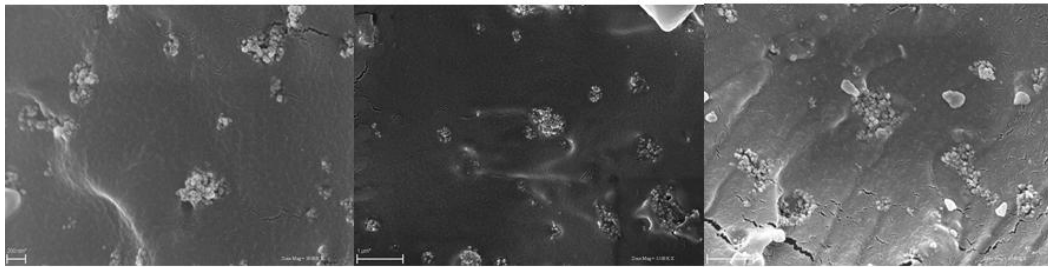
f(2.b)

f(2.c)

Figure

2.1. FESEM images of CAB/SiO₂ nanocomposites of (f.2a , f.2b , f.2c) samples.

It also can be seen in the compatibility between modifier and the matrix phase with a decreasing molecular weight modifier is improved. Modifiers with high molecular mass has also a certain morphology. As we see in the figure above, in two types of modifiers with high molecular weight, we do not see a good morphology. Also due to the increase of CAB to 1 gr in the mixture SiO₂/CAB undermine the dispersion.



f(2.d)

f(2.e)

f(2.f)

Figure 2.2. FESEM images of CAB/SiO₂ nanocomposites of (f.2d,f.2e,f.2f) samples.

Here you can see that the treated nano-silica-type R-812 and modified with CAB, shows no better morphology . To be a re-modification of nano-silica has not better morphology to us. In this figure it is completely clear.

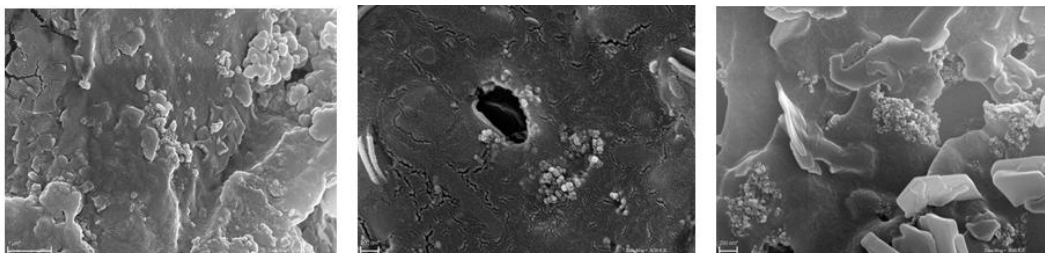


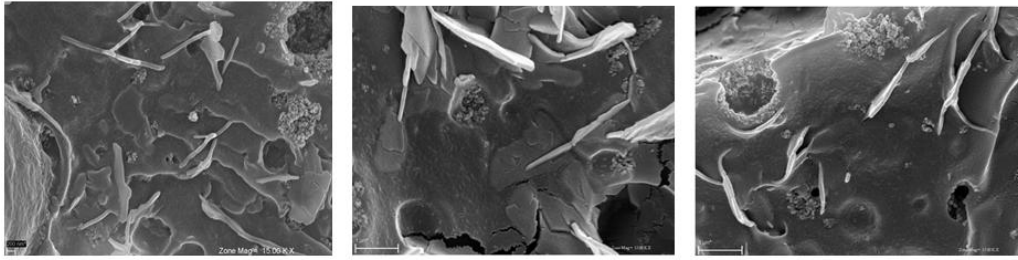
Figure (3.a)

Figure(3.b)

Figure(3.c)

Figure 3.1. FESEM images of CAB/SiO₂ nanocomposites samples.

Such conditions before we see that Modification of nano silica type A 300 with the CAB modifiers, because of no initial treatments in the nano-silica does not exist (unlike R. 812), indicate good morphology . Here the previous analysis as well maintained. With reduced molecular weight of the modifiers we see the better morphology.



Figure(3.d)

Figure(3.e)

Figure(3.f)

Figure 3.2. FESEM images of CAB/SiO₂ nanocomposites samples.

As we see in this figure than previous cases that we used a modified nano-silica R-812 morphology is reduced, in other words the increase cellulose acetate butyrate (CAB) to some extent been able to reduce the morphology and also treatments somewhat reduced.

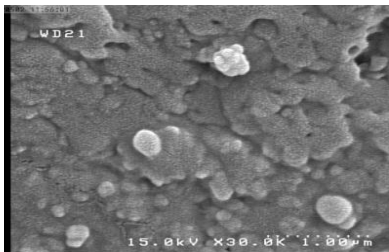


Figure 4. FESEM image of reference sample

Image above as a reference sample, Show the nano-composite cellulose acetate / silica (A300) without modified agents (CAB) (sample 19) is indicated no dispersion of silica particles in the thermoplastic matrix which is cellulose acetate and that is due to the absence of modifiers factor cellulose acetate butyrate(CAB).

3.2.mechanical properties

It was found that the mechanical properties of a sample (1-c) has the best dispersion, is approximately 30% more than other samples. It can be concluded that the degree of dispersion of nanocomposites with enhanced mechanical properties are directly related.

4.conclusion

The comparison effects of CAB content and SiO₂ surface modification on mechanical properties and morphology by the aid of scanning electron microscopy (FESEM) were investigated. Morphology studies show that the modified silica nanoparticles could be easily dispersed in CA matrix having particle sizes less than 100 nm. The tensile strength, Young's modulus, and elongation at break were found to decrease with increasing CAB loading.

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