VISCOELASTIC PROPERTIES OF BIODEGRADABLE CELLULOSE DIACETATE NANOCOMPOSITES CONTAINING SILICA NANOPARTICLE SURFACE-MODIFIED WITH CELLULOSE ACETATE BUTYRATE

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Abstract

In this study, SiO_2 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, silica nanoparticles were physically modified with cellulose acetate butyrate (CAB) for improving interfacial adhesion between CA and SiO_2 and then the modified and non-modified SiO_2 nanoparticles were individually incorporated into the polymer through melting process by assistance of a twin-screw extruder. The effects of silica content and surface modification on morphology and physical-mechanical properties of the nanocomposites were investigated by the aid of scanning electron microscopy (SEM) and dynamic mechanical thermal analysis (DMTA), respectively. Morphology studies show that the modified silica nanoparticles could be easily dispersed in CA matrix having particle sizes less than 100 nm. The results reveal that silica nanoparticle content and surface modification influence the mechanical properties of the produced nanocomposites while the former has more impact.

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 biodegreadable 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 nancomposite [5]. To obtain an acceptable dispersion several methods have been considered such as modification of nanoparticles or organic matrices [6].

In the study presented below, SiO_2 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 SiO_2 nanoparticles and the effect of such modification on morphology and dynamic mechanical properties of the nanocomposites is investigated. Further, we demonstrate that the content of silica nanoparticles has a significant impact on the performance of biodegradable nanocomposites.

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. Cellulose acetate butyrate (CAB 381-20) was purchased from Eastman chemical Co. (USA), having a butyryl content of 37%, acetyl content of 13.5%, hydroxyl content of 1.8% as well as melting and glass transition temperatures of 195 and 141^0C respectively.
Silica nanoparticles (Aerosil 300) was purchased from Degussa Co (Germany) and kept at 100 ^0C in a vacuum oven for 1 hr before using.

2.2. Surface modification

10 wt% CAB based on SiO_2 nanoparticles was added to butyl acetate while stirring at temperature of 150 °C. Then silica nanoparticles 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 and dried in an oven at 60°C.

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 ^0C and screw rate of 100 rpm. After 5 min when the torque became constant, 1 and 2 wt% modified and non-modified SiO_2 nanoparticles 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 only the neat CA (without any silica particle) was prepared after extruding as control.

2.4 Methods

Morphology of nanocomposite coatings was studied by field emission scanning electron microscope (FESEM, Hitachi S4160).

Dynamic mechanical thermal properties of the samples were examined through a DMTA apparatus (DMTA-Triton, Tritec2000 DMA, England). The measurements were carried out at a

constant frequency of 10 Hz, a heating rate of 5°C/min in tension mode. The samples were prepared by cutting strips from the films with a width of 5 mm.

3 Results and discussion

3.1 Morphology studies

Fig. 1 shows FESEM images provided from the nanocomposites containing different levels (i.e. 1 and 2 wt%) of the modified and non-modified silica nanoparticles. From Fig. 1a and b showing the bulk morphology of the nanocomposites, it is found that a much better dispersion can be achieved when the the silica nanoparticles are modified with CAB.
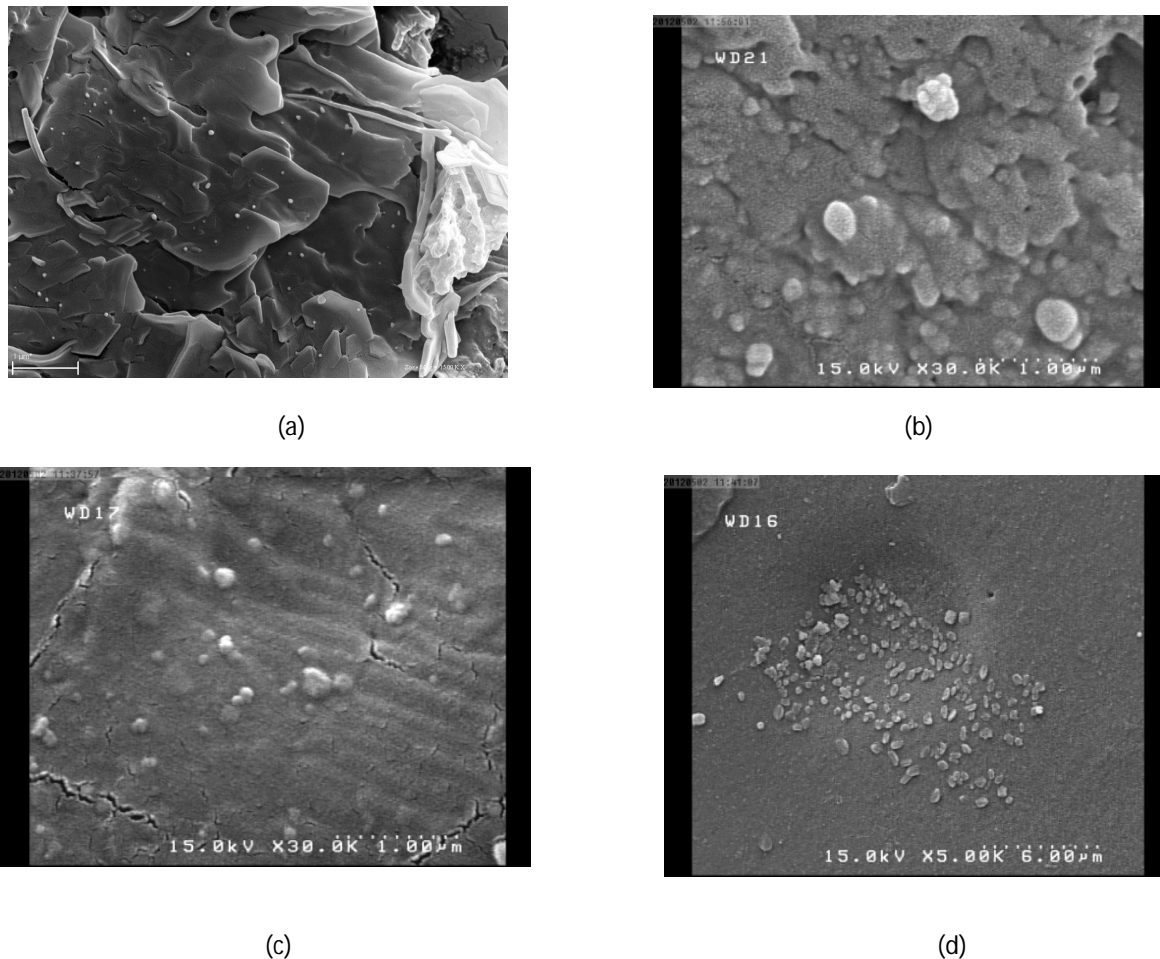

(a)

(b)

(c)

(d)

Figure 1. FESEM images of the nanocomposites containing 1 wt% a) modified, and b) non-modified SiO$_2$ nanoparticles together with images of the nanocomposites containing 2 wt% c) modified, and d) non-modified SiO$_2$ nanoparticles

It seems that modification of nanoparticles by CAB by increases the degree of dispersion of silica nanoparticles within the bulk of such nanocomposite. This behaviour can be argued by

increasing the hydrophobicity of silica particles resulting in a better compatibility of the CAB modified nanoparticles with CA matrix. The cellulose chains surrounding silica nanoparticles could surely help dispersing in a cellulose matrix. This behavior can be also seen in the the pictures taken from the nanocomposites containing 2 wt% modified and non-modified silica nanoparticles (Fig. 1 c and d) indicating this fact that CAB modification has a great influence on the degree of dispersion of silica nanoparticles within CA matrix.

Owing to the fact that the surface of the silica nanoparticles contains OH functionalities causing inherent hydrophilicity to these particles [7], forming aggregation within a hydrophobe thermoplastic bulk during the process could be possible.

3.2 DMTA Studies

Storage modulus (E') is the measure of stiffness or the range where the elastic property is higher. At higher ranges, the stiffness and the load bearing capability of nanocomposites are higher. Also, damping coefficient (tan δ) is an indicator of how a material loses energy to molecular rearrangement and internal friction [8]. The storage modulus of the nanocomposites is depicted in Fig. 2, respectively.
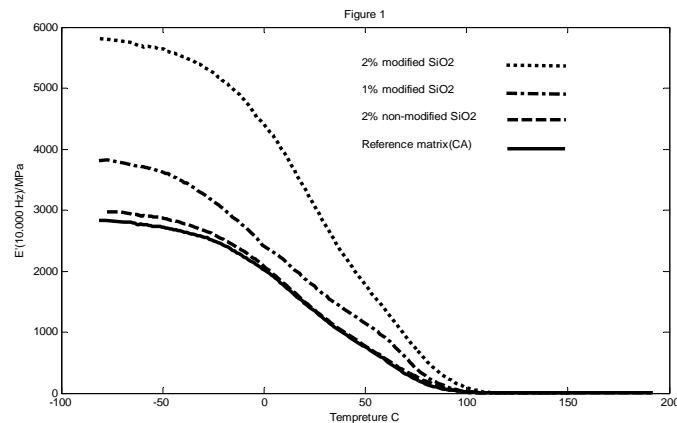

Figure 2. Storage modulus versus temperature of the neat CA and the composites filled with various levels of modified and non-modified SiO$_2$ nanoparticle

As shown in Fig. 2, addition of CAB modified SiO$_2$ nanoparticles into the CA matrix strongly enhances the storage modulus of the resultant nanocomposites. For example, the value of E' (at 0°C) increases from 2.0×10^9 for neat CA to 2.7×10^9 and 5.0×10^9 Pa for the composites loaded with 1wt% and 2wt% silica nanoparticles, This considerable increase is due to the filling effect of high modulus nanoparticles parallel with an increase in contact surfaces of nanoparticles with matrix [9]. However, the nanocomposite sample containg 2 wt% non-modified silica particles a somewhat increase in E' in comparison with neat CA is observed. This is due to CAB modification role that causes better compatibility between nanoparticles and CA matrix. Damping coefficient (tan δ) of the nanocomposites is shown in Fig. 3. As seen in Fig. 3, tan δ of the nanocomposites in compared with neat matrix enhances when the level of the modified silica

nanoparticles increases. In fact, in the presence of the modified fully dispersed nanoparticles, the crystallinity of the matrix decreases leading to the ability of chains movement at T_g increases. It is interesting to note that the glass transition temperature of the nanocomposite containing 2 wt% modified silica nanoparticles enhances in compared with neat CA. This can be argued by the CAB modification leading to a good interfacial interaction between silica nanoparticles and CA matrix.
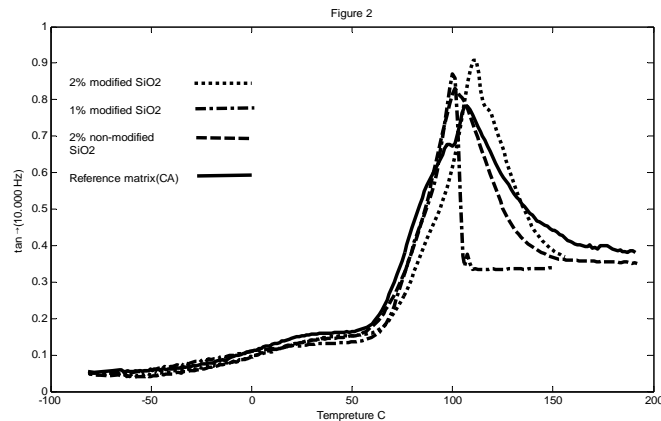

Figure 3. Storage modulus versus temperature of the neat CA and the composites filled with various levels of modified and non-modified SiO$_2$ nanoparticle

4 Conclusions

Hydrophilic silica (SiO$_2$) nanoparticles have been modified with cellulose acetate butyrate (CAB) and then modified and non-modified silica nanoparticles dispersed within cellulose acetate (CA) via melt blending using a twin-screw extruder. Morphology of the nanocomposites has been investigated utilizing FESEM. The obtained results show that an excellent dispersion of the SiO$_2$ nanoparticles is achieved when the CAB modified ones are used. Morphological studies show that the modified nanoparticles could be easily dispersed in CA matrix having particles sizes less than 100 nm. It is found that the modification of silica nanoparticles with CAB has a great impact on the morphology behavior of the nanocomposites.

Dynamic mechanical properties of the SiO$_2$/CA nanocomposites have been also investigated. The results reveal that incorporation of silica nanoparticles into the cellulose diacetate matrix increasingly improves the storage modulus of the nanocomposites. The results also show that the presence of modified SiO$_2$ nanoparticles affects damping coefficient and T_g of the nanocomposites.

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