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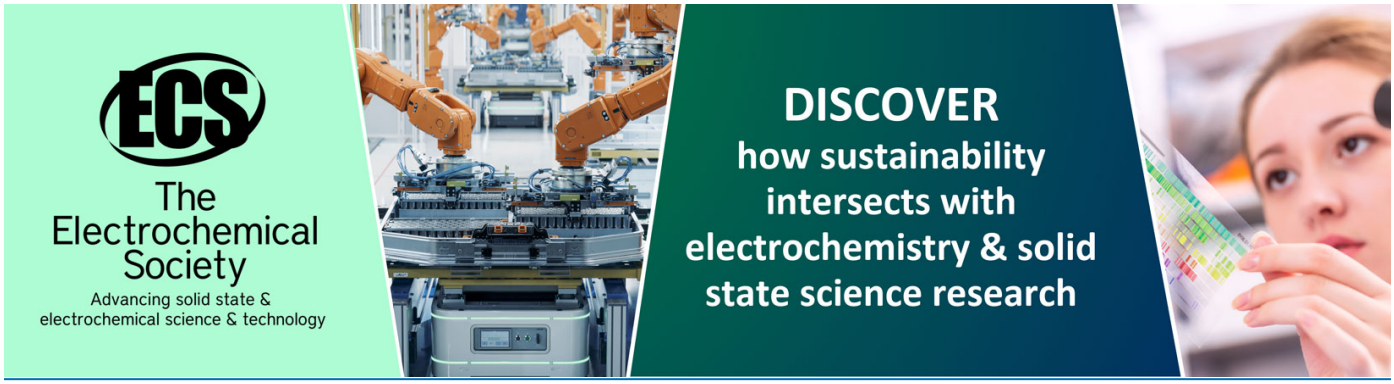

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Silver-Loaded Cellulose Acetate-g-Poly(ε-caprolactone) Composites

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Abstract. Cellulose acetate (CA) was grafted with poly(ε-caprolactone) PCL oligomers via the ring-opening of ε-caprolactone (ε-CL) monomer initiated by the hydroxyl functionality of CA. The incorporation of short PCL oligomers in CA's structure caused the transformation of it crystalline domains into amorphous phases (internal plasticization) as observed by differential scanning calorimetry (DSC). Another evidence of plasticization induced by grafting was the significant reduction of the degradation temperature and stiffness of the copolymers. Proton Nuclear Magnetic Resonance (^{1}H-NMR), Fourier-Transform Infrared (FTIR) Spectroscopies and Gel Permeation Chromatography (GPC) verified success the grafting as suggested by the attachment of PCL on the glucose ring and increase in polymer molecular weights after the reaction. Due to the good films forming ability of the synthesized CA grafted with PCL (CA-g-PCL) material, it was loaded with silver nitrate ($AgNO_3$) and the composite was observed to be have bactericidal against a gram negative bacteria, *Escherichia coli*, and a gram positive bacteria, *Bacillus subtilis*.

1.Introduction

Biodegradable polymers propose an appealing remedy to the environmental problem of plastic waste accumulation and disposal; however, their properties such as poor mechanical properties, high permeability to gases and poor processibility have limited their use to a narrow variety of applications. [1]. The natural polysaccharides cellulose and starch are excellent candidate for making of low-cost materials for high technology applications and to improve their physical, chemical and processing properties of these materials, low molecular weight additives is required (external plasticization) [2], [3]. On the other hand, covalently linking lactones and carboxylic acids to these polysaccharide chain is one method of improving their processing properties (internal plasticization). This technique introduces defects in the crystalline domains and disrupts inter and intrachain hydrogen bonding within the polysaccharide structure [2]. One of the most commonly explored polysaccharide derivative for a myriad of applications is cellulose acetate (CA), synthesized by the reaction of cellulose with acetic anhydride [4]. While the acylation process improves the processibility of cellulose (ie. solubility in many organic solvents), the resulting material has high stiffness and brittleness, agin limiting its application [3]. And so, the rigidity of CA can be tuned by grafting aliphatic polyesters to the hydroxyl group of CA by chemical means. The biodegradable polyester poly(ε-caprolactone) (PCL) has been used as a plasticizer to CA producing a material with characteristics better than their individual polymers. Nevertheless, the high price of PCL has prevented its widespread industrial use. The development of polymer graft is an alternative to reduce costs and tune material properties [3].

Polymers have been modified with other types of materials for them to have multifunctional properties, including the development of antimicrobial polymer composites. There is an effort, nowadays, for the use of inorganic nanoparticles as a potent antimicrobial compounds to relieve the issue of drug resistance. Among the various inorganic metal nanoparticles, silver nanoparticles have received considerable interest for two reasons: (1) silver is a successful antimicrobial agent; and (2) it demonstrates excellent biocompatibility human cells [5]. To the knowledge of the researchers, this is the first study that exhaustively monitored the occurrence of grafting of PCL to CA and the effect of grafting to the thermal and mechanical properties of the CA-g-PCL. The present study also demonstrated a facile method of grafting PCL in CA where the chemical reaction is achieved in 15 minutes. Cellulose acetate has also received attention for biotechnological applications due to its ease in forming films, fibers, textiles and nanoparticles. Similar to CA, the developed CA-g-PCL materials can easily be casted into films. The researchers took the opportunity to embed silver, the form of silver nitrate, to develop an antimicrobial composite film that were tested against *Staphylococcus aureus* and *Escherichia coli.* .

2.Methodology

2.1. CA-graft-PCL synthesis

PCL-graft-CA polymers with weight/volume ratios of 12.5%, 25%, 37.5%, and 50% CA:ε-CL were carried out in polymerization set up equipped with a magnetic stirring bar. The polymer products were designated with sample codes based in the ration between CA and PCL. For example, the polymer product with the code CA_{50}-g-PCL, means that the CA charged in the reactor is 2.5grams with 5mL of ε-caprolactone (ε-CL) in the present of 0.1 wt% catalyst, stannous (II) octoate. Then, this mixture was reacted at 180 ℃ using a thermostatic oil bath for 15 mins under reduced pressure and continuous nitrogen gas purging. Then composites were then further purified by dissolving the polymer products with a small amount of toluene and then precipitating them in hot methanol to remove the unreacted CL and short chain PCL; that may have possibly formed during the reaction. The extracted sample was dried in a vacuum at 60 ℃ for 24 hours. 10 wt/vol% polymer solutions were prepared using THF as solvent. The solutions were casted into petri dishes and the solvent was allowed to evaporate for 24 hours. Polymer/silver composite was prepared by mixing 10 wt% of $AgNO_3$ to 10 % wt/vol of graft copolymers (in THF). The CA-graft-PCL/Ag solution was stirred for 2 hours. The composite solution was then casted on a Petri dishes, and the solvent was allowed to vaporize for 24 hours. Then, the copolymer film was vacuum dried for another 4 hours at 80 ℃. The film was cut into circular discs using a paper puncher. The discs were UV-sterilized for 1 hour before antimicrobial evaluation. The sample was in a desiccator until use.

2.2. Characterization of Cellulose Graft Copolymers

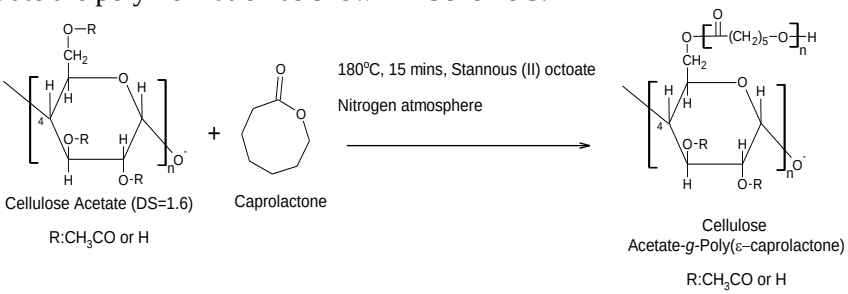
The molecular weight of the samples was determined by a Simadzu HPLC chromatograph apparatus equipped with a Shimadzu refractive index (RI) detector. The samples were eluted with tetrahydrofuran (THF) through a TSK-GEL G3000HHR at a flow rate of 1 mL/min. The molecular weights were determined based on polystyrene standard and the calibration was made using polystyrene standards. NMR spectra of the products were obtained using a JEOL Lambda FT-NMR spectrometer. Samples (10 to 20 mg) were dissolved in deuterated chloroform (CDCl3). The functional groups present in the polymer product were determined using an IR Prestige 21 Fourier Transform Infrared Spectrophotometer. Diamond attenuated total reflection was used for the samples in powder form. The sample was scanned 10 times from 4000 to 600 cm^{-1}. DSC thermograms were acquired using a differential scanning calorimeter (TA Q10 series). The analysis was performed by heating the samples at 10 ℃/min in N_2 The mechanical properties of the composites were evaluated using an Instron Single Column Universal Testing Machine (UTM). The samples were cut into 40mm x 10mm strips and their Young's modulus and %tensile strength at break were measured in triplicate. CA-g-PCL & CA-g-PCL/Ag composite films were tested for their antimicrobial activity by the Kirby–Bauer disk diffusion method against *Bacillus subtilis* and *Escherichia coli*. The bacteria were cultured in Mueller Hinton agar plates for 24 hours. Then, a bacterial colony was introduced to

Mueller-Hinton (MH) broth and was allowed to multiply. The disc samples were placed on each quadrant of the plate that was streaked, previously, with the bacteria. Culture plates with bacteria were then incubated at 35 ℃ for 24 hours.

3.Results and Discussion

3.1. Synthesis of CA grafted with PCL

Cellulose acetate grafted with poly(ε-caprolactone) oligomers was successfully synthesized by ring opening polymerization of ε-CL initiated by the free hydroxyl terminal of the CA. The of the grafted CA was prepared by solvent free ring-opening polymerization of CL. Residual hydroxyl groups of CA was used to initiate the polymerization as shown in Scheme 3.1



Scheme 3.1. Plasticization of cellulose acetate via ring opening polymerization of PCL.

3.2. Molecular weight determination after grafting

Table 3.1. Molecular weight pristine CA and CA-g-PCLs.

Sample Code	M_n	M_w	PDI
CA	45,520	109,900	2.41431
CA_{50}-g-PCL	51,093	113,547	2.22233
$CA_{37.5}$-g-PCL	85,291	139,637	1.63719
CA_{25}-g-PCL	61,163	121,554	1.98739
$CA_{12.5}$-g-PCL	97,631	148,520	1.52124

GPC was employed to measure the resulting increase in the polymers' number average (M_n) and weight average molecular weights (M_w). After grafting, the polymer products exhibited increase in M_n and M_w that suggests that PCL chain are grafted on the CA backbone. Molecular weights of the pristine and modified CA are listed in Table 3.1. The molecular weights of CA-g-PCL were found to be in the range 110,000 to 150,000 g/mol. In addition, it is observed that the molecular weight of the polymer grafts increased with the decreasing CA content. It should be considered that CA contains the hydroxyl initiation sites for ROP and lower CA during the reaction allows the PCL chains to elongated only on few actives sites. Also, fewer initiations sites of polymerization promoted monodispersity (lower PDI) of the polymer molecular weight.

3.3. Analysis Molecular Structure of the ε-CL grafted CA

The chemical structures of CA and the copolymer is quite similar; however, the occurrence of grafting could be verified by FTIR analysis. The IR spectra of the grafted and pristine CA samples can be depicted in figure 3.1. It can be seen that the carbonyl group's vibration can be intensively seen at 1735 cm^{-1}. It is important to see the vibration of the increasing $–CH_3$ moiety of the acetyl groupw in the chain. The presence of this aliphatic carbon chains could indicate the success of the ring opening polymerization reaction from the CL, which could be found at 2943 and 2870 cm-1. The decrease in the OH vibration at 3468.01 cm^{-1} between the neat and modified cellulose acetate is almost unnoticeable. The reason for this could be that the vibration from the free hydroxyl

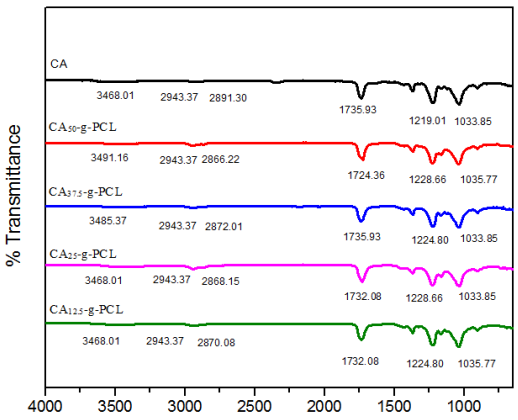


Figure 3.1. IR Spectra of pristine CA and its grafted forms.

groups of unmodified cellulose acetate would not change on esterification because each PCL chain contains also one –OH group at its end.

The structure of the grafted polymer was analyzed in detail by NMR spectroscopy. The ^{1}H-NMR spectra of the CA grafted with PCL is shown in Figure 3.2. The methyl groups of the substituent acetyl groups appear at the region of 2.2–1.7 ppm, and pyran ring protons resonances arising from the seven ring protons of H_1–H_6 in each anhydrous glucose unit appear in the region of 5.5–3.2 ppm. Furthermore, the signals from the ring protons overlap with each other, and the accurate assignment of these resonances has never been performed. In addition, the characteristic peaks of the PCL chain were also observed in the spectra with the chemical shifts at 1.30, 1.54-1.60 and 2.30 ppm which are attributed γ-, overlapping β- and δ-, and α-methylenes, respectively. Again, the peaks from the PCL units are clearly present in the range of δ 1.2–4 ppm and imply that there is an occurrence of ring-opening polymerization reaction of CL. Resonances from the cellulose peaks are evident as small, broad peaks in the region δ 3.4–3.8 and 5.0–5.4 ppm. The results agree well with a previous report [3] that the signal of the hydrogen attached to the aliphatic –CH_2– group appear at 1.7 ppm, those related to the ester group at 2.3 and 4.0 ppm, and the hydrogens of the –CH_2– group neighboring the chain end –OH group are detected at 3.4 ppm.

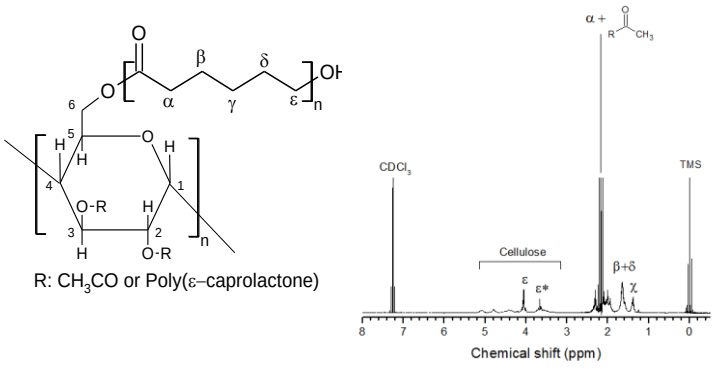


Figure 3.2. (a) Molecular structure of CA-*g*-PCL with its corresponding hydrogen positions, and (b) ^{1}H-NMR spectra of representative modified cellulose acetate.

3.4. Thermal properties of the PCL grafted CA

The melting temperature (T_m) of the grafted polymer composite ranged from 45 ℃ to 50 ℃ with enthalpy of melting (ΔH_m) at 2-3J/g. Interestingly, CA is a semi-crystalline polymer but, with the presence of PCL, CA becomes an amorphous polymer. This may be attributed to the added intermolecular interaction and repeating unit stereo irregularity of the monomer.

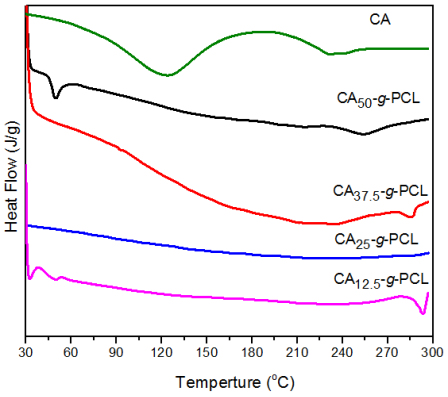


Figure 3.3. DSC thermograms of pristine CA and grafted CA

3.5. Tensile properties of the CA-based materials

Plasticization is assumed to increase the flexibility of chains and lead to a decrease in polymer stiffness. The load-extension curves of the modified CA are presented in Figure 3.4. Pristine CA exhibited the highest modulus of elasticity (876 MPa), derived from the load-extension curve. Significant decrease in moduli observed for the CA-g-PCL products. For example, $CA_{12.5}$-g-PCL exhibited a reduction in Young's modulus to 492 MPa, indicating that pristine CA exhibits high stiffness while CA-g-PCL products is less stiff. This is might be due to the introduction of imperfection on the lattice of CA by the bulkiness of PCL chain, creating void spaces and leading to the decrease in the modulus.

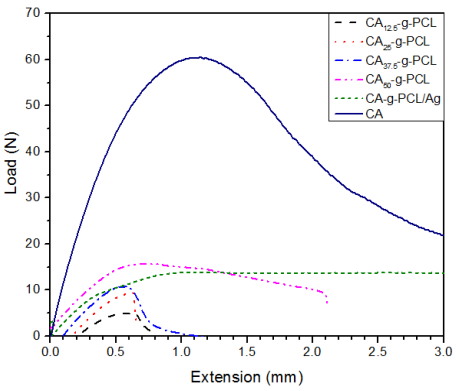


Figure 3.4. Load-extension curves of pristine and grafted CA.

3.6. Evaluation of Bactericidal Property of CA-g-PCL loaded with Ag

Silver particles is a potent antimicrobial material and when incorporated in a polymeric matrix may offer its property to the latter. The Kirby-Bauer disc diffusion assay was conducted to observe the broad antimicrobial activity of silver that is loaded on CA-based polymers. The antibacterial activity of the materials was tested against *Escherichia coli*, a gram negative bacterium and *Bacillus subtilis*, a Gram-positive, rod-shaped bacterium. Figure 3.6 presents the growth of the microorganism on the surface of the agar. Unloaded polymer films Figure 3.6, b, d and e did not inhibit the growth of bacteria where they are placed however, silver-loaded CA-g-PCL exhibited little zone of no growth within its periphery for both microorganisms even if the silver loaded is 10% of the polymer's weight.

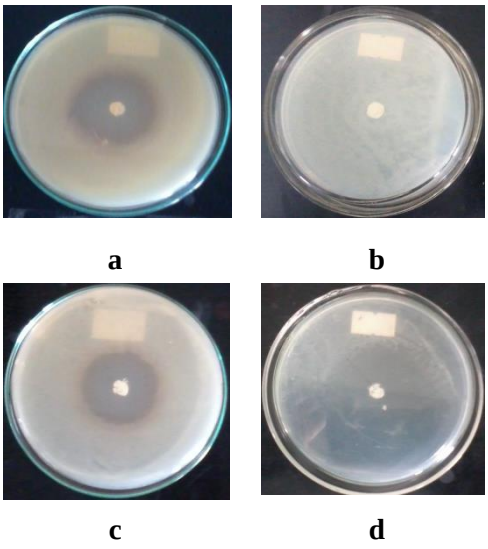


Figure 3.5. Photographs of bacterial cultures after incubation with the composite materials. (a) silver-loaded $CA_{37.5}$-g-PCL and (b) negative control against *E. coli.* (c) silver-loaded $CA_{37.5}$-g-PCL and (f) negative control against *B. subtilis*.

4.Conclusion

The present study demonstrated a facile way of synthesizing a graft copolymer of cellulose acetate (CA) and poly(ε-caprolactone) (PCL). The ring opening of the e-CL monomer is believed to be initiated by the hydroxyl of CA chain and their subsequent polymerization was initiated by the hydroxyl terminal of the growing PCL chain. The grafting of PCL chains to cellulose acetate resulted in internal plasticization. The potential application of the CA-g-PCL as a matrix for antimicrobials was observed by embedding silver in the graft copolymer and antimicrobial efficacy against both gram-negative and gram-positive bacteria. The overall grafting procedure may find many applications as antimicrobial packaging, wound dressing textile, or drug carrier.

5.References

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