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Melting Processing of Biodegradable Cellulose Diacetate/Starch Composites

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Summary: Natural polymers and their derivatives are attracting increasing interest as promising biodegradable materials that can meet the environmental and recycling demands from society. This study prepared biodegradable composites of cellulose diacetate and starch, and examined their physical and thermal properties. In addition, the morphology of the composites was examined by scanning electron microscopy. For melt processing, epoxidized soybean oil, as a lubricant, and triacetine, as a plasticizer, were added to the composites. The optimal conditions for the preparation of the biodegradable composites were determined. Increasing the amount of starch in the composites resulted in further enhancement of the processability of cellulose diacetate. The tensile strength and Young's modulus decreased, and the amount of elongation and T_g value increased with increasing amount of starch.

Keywords: cellulose diacetate; biodegradable; bio-composites; starch; triacetine

Introduction

Cellulose diacetate (CDA) is the most commercially important cellulose derivative that was recently demonstrated to be a biodegradable plastic. [1–5] However, this material has a high glass transition temperature (T_g) resulting in limited processibility compared with typical commodity plastics. In addition, it has low solubility in common solvents and is not melt processible because it decomposes before undergoing melt flow. Therefore, reducing the T_g and the flow temperature of CDA are important. The material needs to be plasticized in order to improve its thermal behavior and tensile properties.[6–8]

There has been significant interest in the utilization of starch as a biodegradable plastic material.[9,10] Next to cellulose, starch is the second most abundant renewable polysaccharide in nature.[9] Starch is not a true thermoplastic. However, it readily melts and flows in the presence of plasticizers, at high temperature (90–180 °C) and under shear, which can allow for its use as an injection or extrusion material in a similar manner to most conventional synthetic thermoplastic polymers.[11] Native starch suffers from a lack of moisture and abrasion resistance,[12] and it is normally used in combination with polar synthetic polymers.[13,14]

The preparation and characterization of a melt processable plasticized cellulose diacetate (CDA) using triacetin (TA) as a plasticizer has previously been reported.[15,16] The processability of the plasticized CDA was further enhanced using a small amount of epoxidized soybean oil as a secondary plasticizer. The T_g of the plasticized CDA was observed at 50 °C lower than that of the pure CDA, and the incorporation of 5 % of ESO also resulted in an additional 20 °C decrease in the T_g. In this study, various levels of cornstarch were added to the plasticized CDA containing TA and ESO. The processability and mechanical properties of the CDA/starch composites were examined as function of the starch content.

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Experimental Section

Material

Cellulose diacetate (Mw ca. 202, 332 g/mol, 54.5 wt.% acetyl content, degree of substitution 1.83) was supplied by Eastman. Corn-starch was supplied by Daesang Chemical co. and consisted of 25% amylase and 75% amlylopectine. The particle size was 15 μm. The triacetine (TA) used as a plasticizer was purchased from Aldrich Chemicals, and the epoxidized soybean oil (ESO, Mw. 1000, Shindongbang Chemical Co) was used as a secondly plasticizer. All the materials were used without further purification. The CDA powder and starch were dried overnight in a vacuum oven at 70 °C before processing.

Processing

The plasticized compound was prepared by mixing the appropriate amounts of cellulose diacetate (CDA), starch, triacetine (TA) and epoxidized soybean oil (ESO) in a high speed mechanical mixer for 2 min. The mixture was then dried overnight in a vacuum oven at 70 °C. The plasticized mixture was fed into a twin-screw extruder (BAUTECH, in Korea) to yield a pellet form. The temperature profile of the extruder from Zone 1 through to Zone 6 was kept between 130 °C and 190 °C, and the exit temperature was 200 °C.The extruder was operated at a screw speed of 100 rpm. The resulting plasticized pellets were injection molded to yield a dog-bone shaped product that could be used for the mechanical tests based on ASTM 1708. The resulting plasticized pellets were compression molded for DMA-analysis. The specimens were 0.5 × 40 × 0.3 mm in size.

Characterization

The tensile test was performed using a universal testing machine, a LLOYD LR 30K. The maximum load was 1 kN and the strain rate was 10 mm/min. Dynamic mechanical analysis was carried out using a thermal analysis system, an Exstar 6000 (Seiko Instruments Japan). The experiments were carried out at a frequency of 1 Hz. under a pre-tension of 200 mN and at temperatures ranging from 25 to 250 °C at a heating rate of 2 /min. This set up allowed measurements of the storage and loss modulus (E' and E'') and the damping parameter or loss factor (tan δ), which is defined by the following formula: $\tan\delta = E''/E'$.

Results and Discussion

The plasticized cellulose diacetate (CDA) and starch were prepared using melt processing methods with triacetine (TA) as a plasticizer. In addition, the processability of CDA was further enhanced using a small amount of epoxidized soybean oil (ESO), as a secondary plasticizer. A starch free composite was also fabricated for comparison. The tensile test of the plasticized CDA and starch composites was performed. Table 1 gives a summary of the results, and shows the mechanical properties of the plasticized CDA/starch as a function of their composition. In the processing of the plasticized CDA/starch, at least 35 wt.% of starch is needed to allow melt processing to be carried out. Table 1 shows the tensile strength, elongation and the Yong's modulus of the composite prepared with TA and ESO and the CDA with TA. At 7 wt.% starch in a blend, the tensile strength decreased from 62 MPa to 49 MPa for pure CDA, and the elongation increased from 4 to 6 wt.%. The tensile strength was 16 MPa with 18% elongation at a 35 wt.% starch content. These mechanical properties correspond to those of low-density polypropylene.

Figure 1 shows the DMA results of CDA and the composites with various starch levels. These results, which show that the presence of TA and ESO decreases the T_g of the composites, are in agreement with the tensile test. A single T_g between the T_g values of CDA/starch composites was detected for each film. This feature suggests that CDA/starch with TA and ESO are

Table 1.
Properties of the CDA/st/TA/ESO composites

Sample	CDA [wt.%]	Starch [wt.%]	CDA-starch ratio	Tensile strength [MPa]	Elongation [%]	Young's modulus [MPa]	T_g [°C]
CDA	70	0		62	4	2254	114.3
CS 91	63	7	9:1	49	6	1727	111.9
CS 82	56	14	8:2	44	10	1551	101.7
CS 73	49	21	7:3	26	12	1064	98.8
CS 64	42	28	6:4	23	15	953	95.2
CS 55	35	35	5:5	16	18	858	91.5
*polypropylene	—	—	—	38	9	1795	—

At constant of 30 wt.% TA and 5 phr ESO.
* Polypropylene: Hyundai Petrochemical Co., Ltd (H1500).

compatibilized and dispersible at all compositions examined. Table 1 shows the dependence of T_g on the compositions. The glass transition temperature of the plasticized CDA was 80.7 °C lower than that of the pure CDA (195 °C)[17]. Moreover, the incorporation of TA and ESO resulted in a further decrease in the T_g value. Pure CDA is not suitable for melt processing because it undergoes thermal degradation before reaching the melting transition temperature. However, the plasticized CDA showed feasible melt processability.

Generally, the tensile properties of a blend are dependent on its microstructure.[18] Figure 2 shows SEM micrographs of the fragile fractured surface of CDA and various CDA/starch composites at 500 × magnifications. The figure shows that the starch is very well dispersed in the CDA matrix. The fractured surface of CDA was relatively smooth [Fig. 2 (a)], where the surface of CS91, CS73 and CS55 were rough, which are typical of a compatible structure. For the 7 wt.% starch composite, only a few starch granules could be

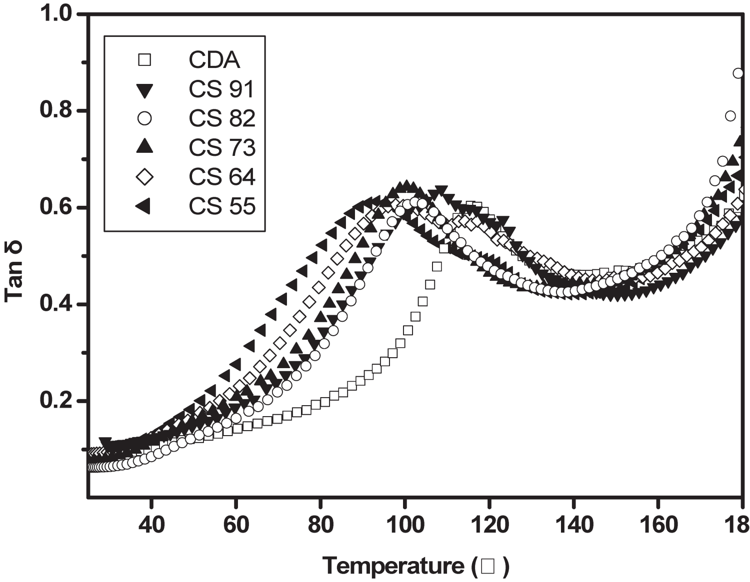
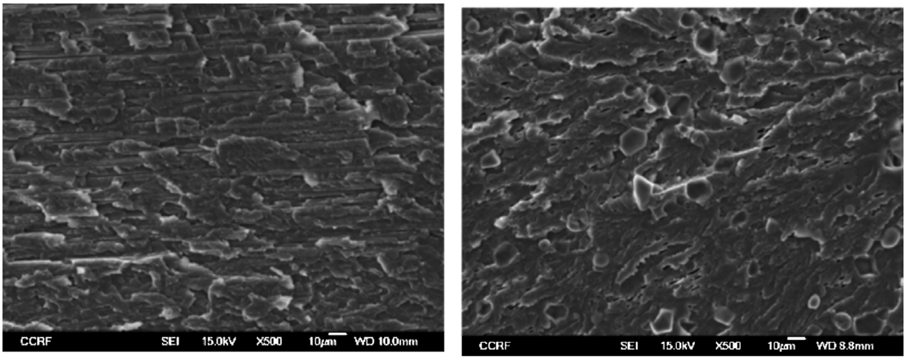
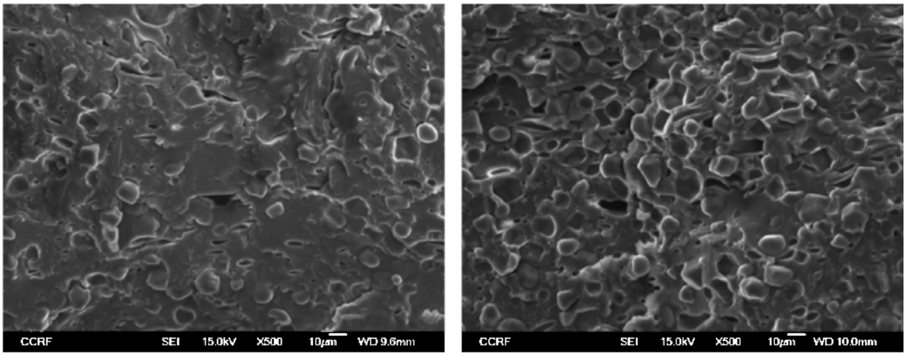


Figure 1.
Dynamical mechanical properties of the composites (tan δ vs. temperature).



(a) CDA (b) **CS 91**



(c) **CS 73** (d) **CS 55**

Figure 2.
SEM micrographs at of the fragile fractured surface of CDA/TA/ESO and various CDA/st/TA/ESO composites (500 × magnification).

observed in the matrix. At starch levels >7 wt.%, most of the starch granules were well enveloped by the CDA matrix. At 35 wt.%, the starch granules aggregated due to the high starch concentration.

Conclusion

Composites of CDA with various levels of cornstarch were prepared by melt processing. For melt processing, epoxidized soybean oil (ESO), as a lubricant, and triacetine (TA), as a plasticizer, were added to the composites. The CDA, starch, TA, and ESO were charged directly into an extruder at 130–190 °C at a screw speed of 100 rpm and were molded under hot-pressure to form the test specimens. The mechanical properties, fracture microstructure, and thermal properties were examined. Pure CDA had a tensile strength of 62 MPa and an elongation of 4%. The tensile strength and Young's modulus decreased and the level of elongation increased with increasing starch content in the CDA matrix. Dynamic mechanical analysis showed that storage modulus increased and tan δ decreased with increasing starch level. SEM of the fractured surfaces revealed very good adhesion between the starch and the CDA matrix. The results obtained clearly show the advantages of using thermoplastic starch compatibilized with CDA, which is a natural, cheap and abundant material.

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