Preparation and characterization of plasticized cellulose acetate biocomposite with natural fiber

J. S. CHOI, S. T. LIM, H. J. CHOI*
Department of Polymer Science and Engineering, Inha University, Incheon, 402-751, Korea
E-mail: hjchoi@inha.ac.kr

A. K. MOHANTY, L. T. DRZAL, M. MISRA, A. WIBOWO
Composite Materials and Structures Center, Department of Chemical Engineering and Materials Science, Michigan State University, MI 48824, USA

Biodegradable polymers such as poly (hydroxybutyrate) [1, 2], poly(ε-caprolactone), polylactide [3], biodegradable aliphatic polyesters [4–6], and bio-based composite materials have been investigated to reduce environmental problems caused by plastic wastes, since they have low manufacturing costs and easy processibility in large-scale production. Among these biodegradable polymers or bio-based polymer products, cellulose from trees are found to be the most attractive substitute for petroleum feedstock in making plastics for the consumer market [7]. Cellulose plastics, such as cellulose acetate (CA), cellulose acetate propionate, and cellulose acetate butyrate, are thermoplastic materials produced through the esterification of cellulose. A variety of raw materials such as cotton, recycled paper, wood cellulose, and sugarcane are used in making cellulose ester biopolymers in powder form. In processing polymer composites, biofibers such as henequen, hemp (HP), and kenaf can be successful candidates for reinforcing the strength and stiffness in the final composite [8–11].

In the current study, we melt-processed the plasticized CA (CAP) with a biofiber, hemp, and then investigated its characteristics of thermal stabilities, fractured surface morphologies, and rheological properties. Most commercial cellulose acetate products are clear, strong, and stiff. Some applications of cellulose ester biopolymers are film substrates for photography, toothbrush handles, selective filtration membranes in medicine, and automotive coatings [12]. The main drawback of cellulose acetate is that its melt processing temperature is very close to its decomposition temperature, as determined by the structure of its parent cellulose. This means that cellulose acetates should be plasticized if they are to be used in thermoplastic processing applications [13]. In this study, we used CAP containing 30 wt% of plasticizer i.e., plasticized cellulose acetate, as dispersing medium for biofiber.

The major constituents of biofibers (lignocelluloses) are cellulose, hemicellulose and lignin. Cellulose is a hydrophilic glucan polymer consisting of a linear chain, containing hydroxyl groups. Therefore, all the natural fibers are hydrophilic in nature. The details on these biofibers were well summarized in the previous study [14] and partly in Table I. The prepared biocomposite is designated as HPCAP in this study. Fiber content was fixed as 30 wt% in all cases, and was compression-molded into disc type sample in a hot press (HP-200L, Kee-Pae, Seoul, Korea) at 210 °C under the pressure of 1000 psi.

The fractured morphologies were investigated using scanning electron microscope (SEM, Hitachi S-4300, Japan) with various magnifications at 15 kV. The thermal stability was examined using a TGA (TA instrument Q50, USA) from 30 to 650 °C, under a nitrogen atmosphere at a heating rate of 20 °C/min. We also measured their rheological properties via rotational rheometer with a parallel-plate geometry (Physica, MCR 300, Germany) of 1.1 mm thickness and 25 mm diameter at 210 °C. In oscillatory shear mode, storage modulus (G') and loss modulus (G'') were measured as a function of frequency with the deformation of 0.01% for biocomposite.

Fig. 1a shows the relatively smooth surface of pristine matrix polymer (CAP) at the magnification of 100. This surface character was abruptly altered by the addition of biofibers (Fig. 1b). When compared with that of bare fiber, it is not difficult to conclude that the final morphologies are decided by the fiber. As described above, the fiber content (30 wt%) was too high to accomplish homogeneous internal state. In addition, the original structure and morphology of the fiber is maintained in the biocomposite without any deterioration. It means that other final characteristics would be mainly governed by the fiber itself, not by the matrix polymer.

Fig. 2 shows TGA curves of pure CAP and its biocomposite. As indicated in the previous study, CAP exhibited the characteristic of a two-step decomposition behavior caused by the addition of plasticizer [13]. In the case of HPCAP, three major transitions from those of CAP can be addressed. First, the two-step process in HPCAP changed into a single step process, as suggested indirectly in the SEM investigation. As described above, the biofiber, which governed the surface morphologies, also determined the decomposition process. It can be conjectured that wetted matrix resin in

---

*Author to whom all correspondence should be addressed.

0022–2461

TABLE I Chemical composition and structural parameters of hemp

	Type	Cellulose (wt%)	Lignin (wt%)	Hemicelulose (wt%)
Hemp	Bast	70.2–74.4	37–5.7	17.9–22.4

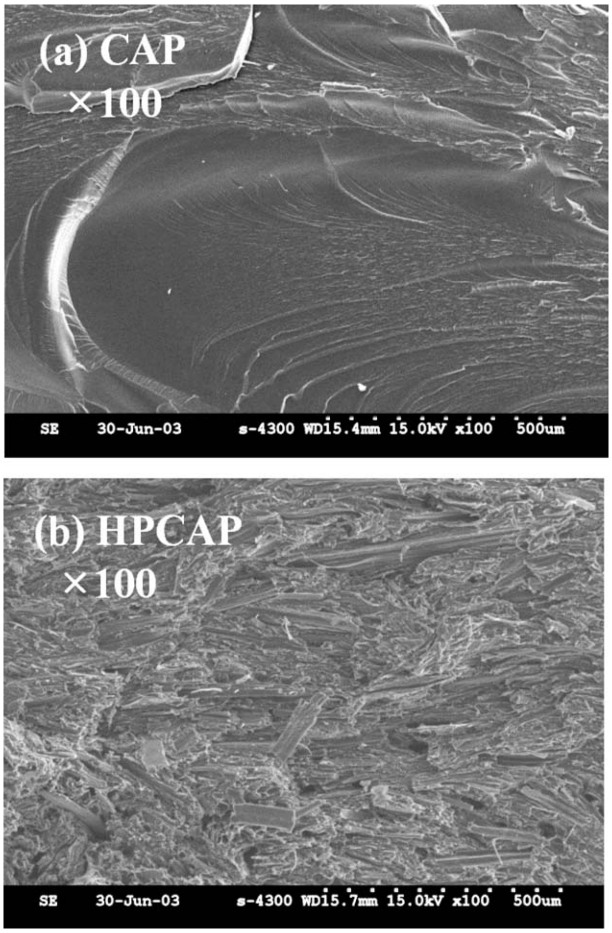

Figure 1 Scanning electron micrographs (SEM) of (a) CAP and (b) HPCAP30 at the magnification of 100.

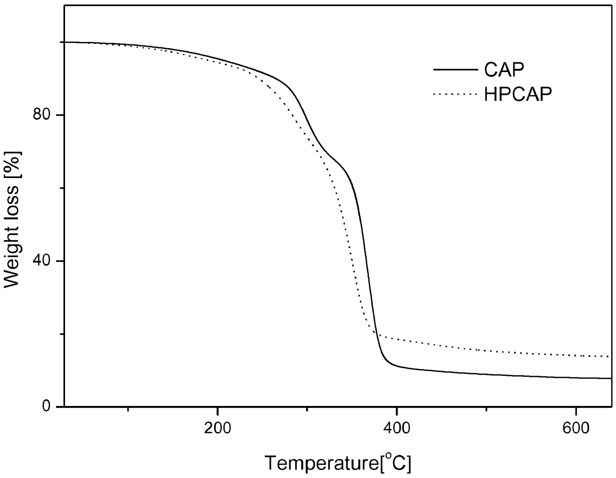

Figure 2 Thermogravimetric analysis of CAP and HPCAP. Temperature scanning speed was set as 20 °C/min under N_2.

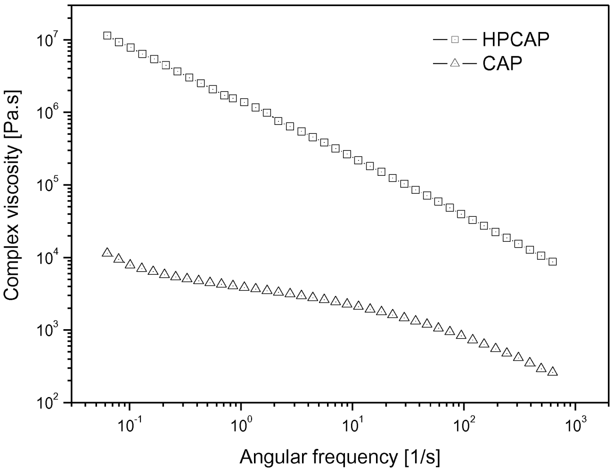

Figure 3 Complex viscosities of CAP and HPCAP as a function of frequency at 210 °C.

the fiber could not show its characteristic of the two step process. Second, inferior thermal stability of biofiber (not shown here) triggered the early stage decomposition. Finally, the residual weight of the biocomposite was somewhat higher than that of CAP. About 10% of char formation increased with the addition of biofiber. The residual weight of biofiber itself was observed as ∼20%, indicating that the increase of residual weight of biocomposite might be generated by the fiber.

In Figs 3 and 4, the measured rheological properties at 210 °C were plotted as a function of angular frequency for CAP and its biocomposite. From these oscillatory measurements, we can investigate visco-elastic responses of the materials without any destruction of internal structure. Except CAP, the pre-set amplitude for oscillatory measurement was chosen as 0.01%, which was abnormally smaller than that of conventional polymer melts, meaning that fluidity of the composite was very different from that of CAP. In the case of CAP, amplitude was fixed at 1%.

Fig. 3 represents that complex viscosities of the biocomposite are much higher than that of CAP by three orders of magnitude. Moreover, the degree of shear thinning for biocomposites is more enhanced by the addition of fiber. It can be explained by the alignment of added fiber in the matrix polymer, such that the induced shear flow makes each fibril component align

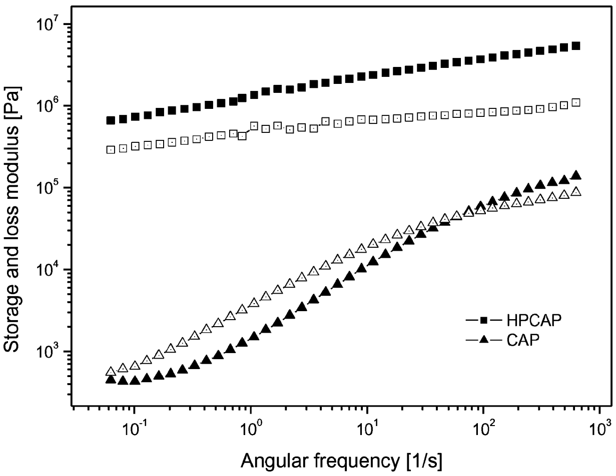

Figure 4 Storage (filled symbols) and loss (open symbols) modulus of CAP and HPCAP at 210 °C.

along the direction of flow. This alignment reduced the flow resistance, resulting in the gradual decrease of viscosities.

In oscillatory test mode, we also measured both storage (G') and loss (G'') moduli as a function of angular frequency. Compared to CAP, the addition of biofibers showed the remarkable increase in both G' and G''. Furthermore, a transition of the slopes to a flattened behavior with biofibers, i.e., non-terminal behavior, is observed at low frequencies. Thus, the low frequency response is indicative of solid-like behavior caused by fibril components. Melt behavior of the CAP is liquid-like ($G' < G''$) at low frequencies while solid-like behavior ($G' > G''$) is found at high frequencies [15]. The cross-over frequency ω_c is defined as $G'(\omega_c) = G''(\omega_c)$. However, ω_c cannot be found or is indistinguishable for HPCAP. With the decreased frequency dependency and higher storage modulus in all frequency ranges, we can conclude that the overall visco-elastic behavior exhibited solid-like characteristics, and was mainly governed by the addition of biofiber.

In summary, we investigated thermal, morphological and rheological characteristics of plasticized cellulose acetate (CAP) processed with biofiber. Via SEM investigation, we found discernable fibril morphologies in the composite. Such morphological characteristics were further analyzed with the results of TGA and rheometry. In the TGA diagram, we explained the two-step decomposition process of plasticized CAP, which was apparently affected by the addition of biofibers. Finally, the obtained rheological properties were also interpreted in conjunction with the formation and destruction of the internal structure in biocomposites.

Acknowledgment

This study was partially supported by research grants from the Industrial Waste Recycling R&D Center, Korea.

References

1. H. J. CHOI, S. H. PARK, J. S. YOON, H. S. LEE and S. J. CHOI, *Polym. Eng. Sci.* **35** (1995) 1636.
2. S. H. PARK, H. J. CHOI, S. T. LIM, T. K. SHIN and M. S. JHON, *Polymer* **42** (2001) 5737.
3. J. J. COOPER-WHITE and M. E. MACKAY, *J. Polym. Sci. Polym. Phys.* **37** (1999) 1803.
4. J. KIM, T. K. SHIN, H. J. CHOI and M. S. JHON, *Polymer* **40** (1999) 6873.
5. J. KIM, S. T. LIM, H. J. CHOI and M. S. JHON, *Macromol. Chem. Phys.* **202** (2001) 2634.
6. T. FUJIMAKI, *Polym. Degrad. Stab.* **59** (1998) 209.
7. W. LIU, A. K. MOHANTY, L. T. DRZAL, P. ASKEL and M. MISRA, *J. Mater. Sci.* **39** (2004) 1051.
8. A. K. BLEDZKI, S. REIHMANE and J. GASSAN, *J. Appl. Polym. Sci.* **59** (1996) 1329.
9. M. H. ALMA, M. A. BASTURK and M. DIGRAK, *J. Mater. Sci. Lett.* **22** (2003) 1225.
10. H. D. ROZMAN, K. W. TAN, R. N. KUMAR and A. ABUBAKAR, *J. Appl. Polym. Sci.* **81** (2001) 1333.
11. S. U. A. REDONDO, M. C. GONCALVES and I. V. P. YOSHIDA, *ibid.* **89** (2003) 3739.
12. K. J. EDGAR, C. M. BUCHANAN, J. S. DEBENHAM, P. A. RUNDQUIST, B. D. SELLER, M. S. SHELTON and D. TINDAL, *Prog. Polym. Sci.* **26** (2001) 1607.
13. A. K. MOHANTY, A. WIBOWO, M. MISRA and L. T. DRZAL, *Polym. Eng. Sci.* **43** (2003) 1151.
14. A. K. MOHANTY, M. MISRA and G. HINRICHSEN, *Macromol. Mater. Eng.* **276/277** (2000) 1.
15. H. J. CHOI, S. G. KIM, Y. H. HYUN and M. S. JHON, *Macromol. Rapid Commun.* **22** (2001) 320.

Received 5 April
and accepted 6 May 2004