Structure and Physical Properties of Cellulose Acetate/Poly(butylene succinate) Blends Containing a Transition Metal Alkoxide

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ABSTRACT: Two biodegradable polymers, that is, poly(butylene succinate) (BN) and cellulose acetate (CA), were solvent-cast blended with chloroform. Homogeneous films were obtained from the blend by the addition of tetraisopropyl titanate (TP) as a compatibilizer. We measured the viscosity of the blend solution to investigate the function of TP during the blending process. From the measurement, we conclude that there are interactions among TP, BN, and CA. From optical observation and thermal measurements of the blend films, we found that the structure of blends is in a pseudostable state and that the addition of TP makes the structure units small. From thermogravimetric analyses, we found that the addition of TP decreases the thermal decomposition temperature of the BN/CA blends. From the measurements of mechanical properties of the blends, we found that changing the blend ratio can produce the materials with a wide range of mechanical properties. The hydrolysis of the blends was investigated. The molecular scission of BN/CA blends takes place uniformly not only from the outside but also from the inside of the films. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1750–1758, 2002

Key words: poly(butylene succinate); cellulose acetate; solvent-cast blend; alkoxide; hydrolysis

INTRODUCTION

In recent years, the biosphere has been, and continues to be, in worse condition than in earlier times. A cause of the worsening environment is the increase in plastic waste matter, and thus, the recycling and biodegradability of plastics should be seriously considered. If all disposable plastics were made from biodegradable polymers, environmental problems would be alleviated. It is clear that biodegradable plastics that have various physical properties will be in high demand from now on. Solvent-cast and melt blend methods are convenient for the production of new plastics. The solvent-cast blend method has the following added benefit: because the dispersed phase is so small, the phase could be formed homogeneously in the blends, as the polymer molecules are dispersed individually in a good solvent.

Poly(butylene succinate) [Bionolle (BN)[1]] is a biodegradable aliphatic thermoplastic polyester that is a semicrystalline polymer and that is flexible, as can be seen from the molecular structure. The polymer was designed to have the processibility of polyethylene with physical properties similar to those of polyethylene terephthalate.

Cellulose acetate (CA) is made from natural resources—some of the three OH groups in a glucose unit of cellulose are substituted for $OCOCH_3$

groups. It is known that the biodegradability of CA depends on the degree of the substitution (DS) $(0 \leq DS \leq 3)$. This biodegradation can be observed in samples whose DS is <2.5;[2] the biodegradable CA with a DS of 1.52 is used in this article. CA is usually an amorphous polymer and is rigid, as can be supposed from the molecular structure.[3–5] As there is a large difference in the chemical structure between BN and CA, a new biodegradable composite would be produced by the blend of these polymers.

Cellulose derivatives that include cellulose have been blended with biodegradable polymers, using not only the solvent-cast blend method but also the melt-blend method.[6–12] From these studies, it is clear that biodegradable polymers are partially miscible with CA. In other words, a compatibilizer would be necessary to improve further the blend miscibility of the polymers.

The blending of CA with a transition metal alkoxide has been performed, and it has been reported that there is an interaction between these materials.[13,14] Tetraisopropyl titanate (TP) is a transition metal alkoxide and has relatively high reactivity; its chemical structure is $Ti[OCH(CH_3)_2]_4$. Taking account of these reports, we considered the possibility that TP could be used as a compatibilizer for a BN/CA blend system; to the best of our knowledge, the use of a transition metal alkoxide as a compatibilizer for the polymer blends has been studied little.

In this study, we prepared BN/CA blends by using the solvent-cast method and investigated the effect of the addition of TP during the blending process on the structure and the physical properties of the BN/CA blends.

EXPERIMENTAL

Materials

Bionolle B1001 (BN) was supplied by Showa Highpolymer (Tokyo, Japan). Its molecular weight is $Mw = 60{,}000$, and the chemical structure of the repeat unit is $[O(CH_2)_mOCH(CH_2)_nCO]_l$. The parameters of m and n were determined preliminarily with an ordinary nuclear magnetic resonance (NMR) apparatus (JEOL LA-500, Tokyo, Japan); these values were found to be 4 and 2, respectively. CA was purchased from Wako Pure Chemicals (Tokyo, Japan); its molecular weight was $Mw = 45{,}000$, and its acetyl content was 39.8%. The value of DS was calculated from the acetyl content and found

to be 1.52. Reagent grade chloroform (Nakalai Tesque, Kyoto, Japan) was used as the cosolvent of these polymers without further purification. Reagent grade of ethanol (Nakalai Tesque) was used to solve CA in chloroform. Furthermore, extra-pure reagent grade TP (Nakalai Tesque) was used as a compatibilizer.

Preparation of Blends

Specified amounts of BN and CA were placed in a beaker; the total amount of these materials was 1 g. Further, 20~30 mL of chloroform and 2 mL of ethanol were added to the beaker; the amount of chloroform was usually 30 mL unless otherwise noted. After being stirred vigorously for about 2 h, the mixture became homogeneous solution. As a compatibilizer, 100 μL of TP was added to the solution; the function of TP in the solution will be discussed later. Considering the engineering application of the blends, we should limit the amount of TP as much as possible, as TP is expensive. The viscosity of the solution was markedly increased by the addition. To control this, we changed the amount of chloroform. After being stirred for about 15 min, the solution was cast in a glass Petri dish. After chloroform was vaporized at 30°C, the homogeneous films (ca. 0.1 mm in thickness) were obtained. The physical properties of the films were measured. The blend film containing a given amount of BN will be referred to as $\phi_{BN} = X$, where X represents the weight percentage of BN in the blend. The samples containing no TP were also made. The samples will be referred to as $\phi_{BN} = X$ (TP = 0 μL).

Characterization of Blends

To measure the transparency of the blends' films, a light-transmittance test was performed with a Shimadzu (Kyoto, Japan) UV-2100 spectrometer; a wavelength of 500 nm was used. The viscosity of the blend solution was measured with a Yamaichi (Tokyo, Japan) VM-1G-M viscosity meter. The value does not represent accurate viscosity in a strict sense, as it is evaluated from the induced force on the probe as it vibrates while immersed in the solution.

The thermal behavior of the blends was measured with a Shimadzu DSC-60 differential scanning calorimeter (DSC) at a heating rate of 10°C min^{-1}. The melting point, T_m, and heat of fusion, ΔH_m, were evaluated from the maximum position and the area of the endothermic peak, respec-

tively. The nonisothermal crystallization of the blends was also measured with the DSC. The blends were heated to 150°C at a heating rate of 20°C min^{-1}, held for 10 min at this temperature to destroy all crystallites, and cooled down to room temperature at a cooling rate of 5°C min^{-1}. The thermal behavior was recorded during the cooling process. The crystallization temperature, T_c, and the calorific value during crystallization, ΔH_c, were evaluated from the peak position and its area, respectively.

We performed the thermogravimetric analyses (TGA) of the blends by placing a piece of the material in a platinum dish and heating it from room temperature to 500°C under a nitrogen atmosphere at the heating rate of 5°C min^{-1} in a Shimadzu thermogravimetric analyzer (DTG-60).

Dynamic mechanical analyses (DMA) of the blends were performed with a Rheometric Scientific RSA II Viscoelastic Analyzer. Temperature scans at a frequency of 1 Hz were carried out with a heating rate of 2°C min^{-1}. The glass transition temperature, T_g, was evaluated from the peak position of the loss modulus (E'') versus the temperature curve.

The tensile test for the blends was performed at room temperature with a Tensilon UTM-II tensile tester (Toyo Baldwin, Tokyo, Japan); the cross-head speed was 10 mm min^{-1}, and the initial gauge length was 50 mm.

Hydrolysis of Blends

About 0.1 g of the blend film, 0.1 mm in thickness, was hydrolyzed at 40°C by using 0.3N—NaOH solution (30 mL), which was shaken at a constant speed; the normality of the solution was determined to finish the hydrolysis of the blends within a week. The samples were removed from the solution after a given time, washed by water for about 5 h, and dried at 50°C. The weight of the dried remaining samples was measured. Molecular weights and their distribution of the remaining samples were also evaluated in chloroform at 40°C with a gel permeation chromatography (GPC) system (Tosoh HLC-8220GPC, Tokyo, Japan); three TSK(HM-N) gel columns were used, and the measured molecular weights were calculated by the universal calibration method, using nine polystyrene reference materials. The blend samples (7 mg) were dissolved in 5 mL of chloroform. After the elimination of insoluble matter by filtration, 20 μL of the solution was injected into the GPC system.

RESULTS AND DISCUSSION

Structure of Blends

Figure 1 shows the effects the addition of TP has on the homogeneity of the BN/CA blend films. The addition of TP seems to prevent the macro phase separation and to form homogeneous blend films, which, we made by using a large amount of chloroform. In this case, the viscosity of the solution was relatively low, and a well-developed polygonal pattern was sometimes observed in the localized part of the films; the pattern originated from the formation of spherulities of BN. From these results, we conclude that homogeneous blend films containing no polygonal pattern can be made both by the addition of TP and by using the highly viscous BN/CA solution (see Fig. 1). In other words, these results suggest that the structure of blend is in a pseudostable state. From an engineering point of view, the formation of a homogeneous structure means that fine continuous fibers could be made from BN/CA blend by the addition of TP: inhomogeneous structure prevents the formation of the fine fiber. Figure 2 shows the effects of the BN content (ϕ_{BN}) on the transparency and homogeneity of the blend films. The transparency decreases with an increase in ϕ_{BN} up to about $\phi_{BN} = 40$, above which it remains almost constant, and then decreases with increasing ϕ_{BN}. Samples $\phi_{BN} = 90$ and 100 show the scatter of measured values. This means that the macro phase separation occurs in these samples despite the addition of TP.

To clarify the function of TP during the blend process, we discuss how the addition of TP changes the viscosity of the blend solution. From preliminary tests, we have the following results: (1) the viscosity of chloroform/ethanol solution containing no BN and CA polymers is scarcely increased by the addition of TP, and (2) the viscosity of the solution containing BN and CA increases with the addition of TP; the gelation takes place when the viscosity of the solution before the TP addition is high. These results suggest that there is an interaction between TP and the polymers used.

Figure 3 shows the effect of the addition of TP on the viscosity of the blend solution. The viscosity of the solution containing no TP is scarcely increased with increasing ϕ_{BN}. It is clear that the addition of TP increases the viscosity of the blend solution. The increase in viscosity of the ϕ_{BN} =100 sample caused by the addition of TP is
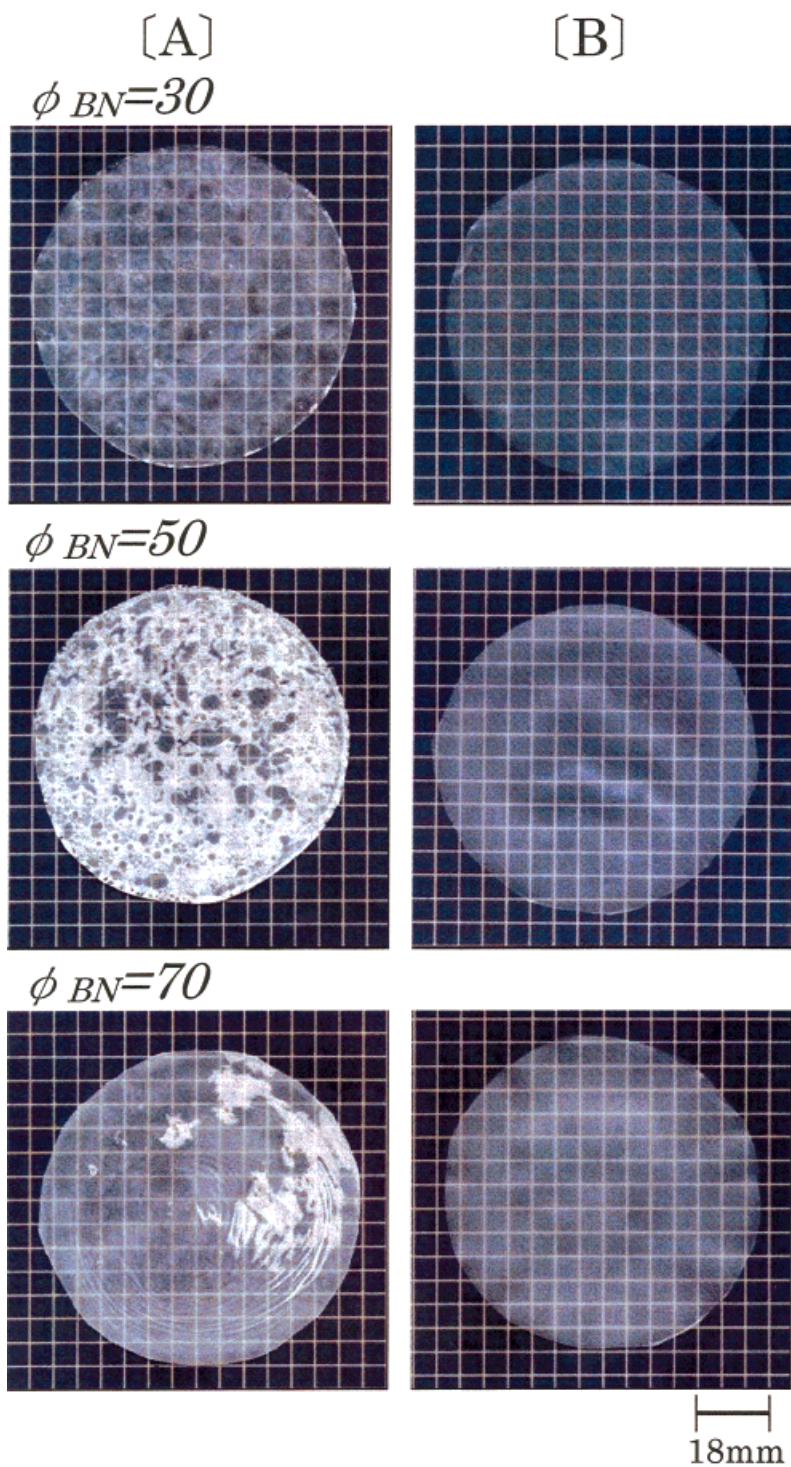
Figure 1 Photographs of poly(butylene succinate)/cellulose acetate blends. (A) TP = 0 μL, (B) TP = 100 μL.

about two times larger than that of the $\phi_{BN} = 0$ sample. A maximum of viscosity of the solution can be seen in the $\phi_{BN} = 50$ sample that contains TP. This means that there is a synergistic effect among TP, BN, and CA. At this time, we cannot explain this result; however, the increase in the viscosity seems to be caused by the formation of the interaction between TP and the polymers
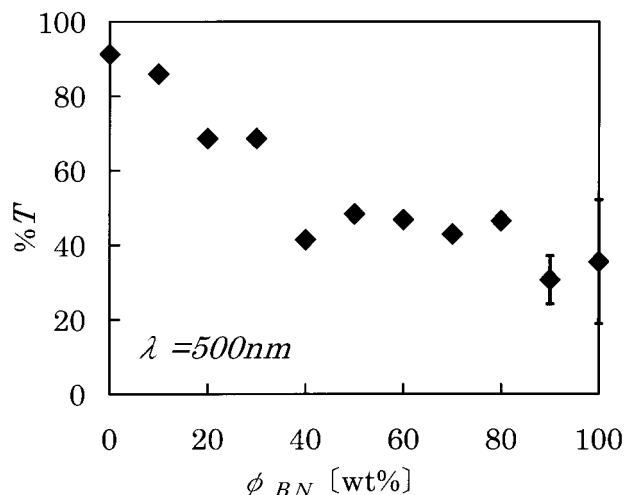
Figure 2 Effect of ϕ_{BN} on the transparency of the blend films.

Figure 4 Differential scanning calorimeter curves of blend films.

such as BN and CA. To clarify the mechanism of the interaction, we performed NMR and FTIR measurements of the blend solutions and the blend films. However, the clear evidence for supporting the existence of the interaction between TP and BN/CA polymers was not obtained. These results may indicate that the interaction is very weak.

Thermal Properties of Blends

Figure 4 shows the DSC curves of the samples. An endothermic peak can be seen at approximately 110°C in each blend sample; this temperature corresponds to the melting point of BN. It can be
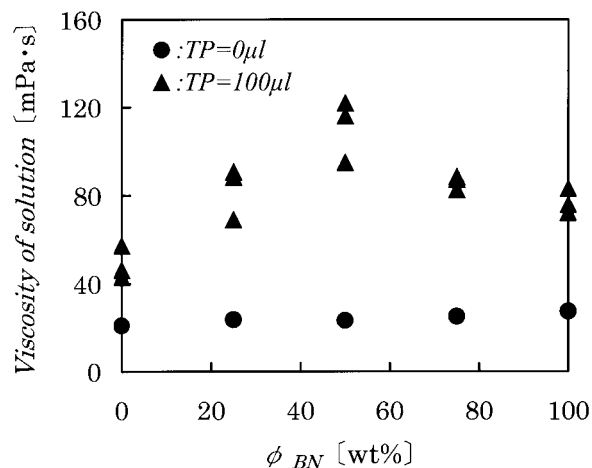
seen that the values of Tm for the blends are lower than that of pure BN (TP = 0 μL). To discuss the effect of the BN content (ϕ_{BN}) on the melting behavior of BN in detail, we evaluated the values of T_m and ΔH_m for each sample. The result is shown in Figure 5. A straight solid line was drawn through the values of ΔH_m at $\phi_{BN} = 0$

Figure 3 Effect of the addition of tetraisopropyl titanate on the viscosity of a solution of poly(butylene succinate)/cellulose acetate blends.
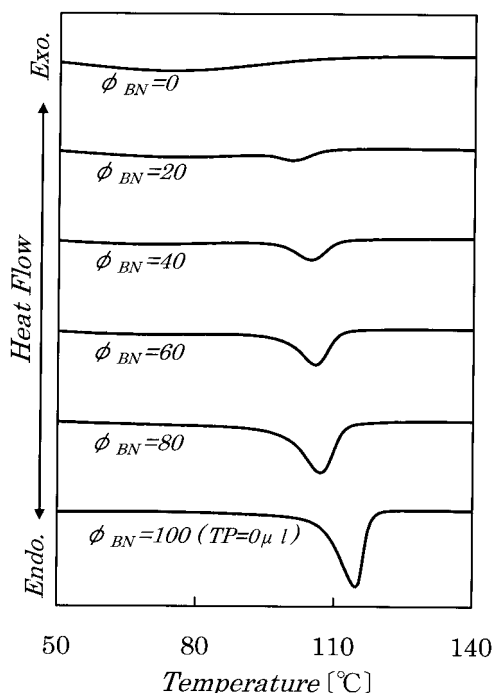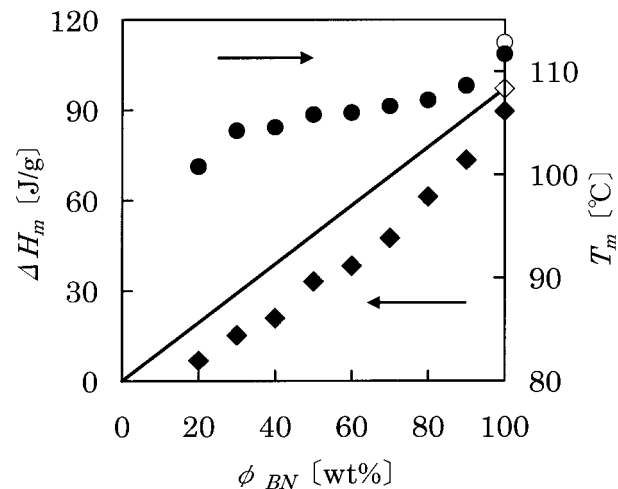

Figure 5 Effect of poly(butylene succinate) content on T_m and ΔH_m. Open symbols: tetraisopropyl titanate = 0 μL samples.

and ϕ_{BN} = 100 (TP = 0 μL), where the value of ΔH_m at ϕ_{BN} = 0 was zero. It can be seen that T_m decreases slightly with decreasing ϕ_{BN}. These results indicate that the addition of CA and TP makes BN crystallites small and that larger BN crystallites are formed with an increase in the BN content. A similar phenomenon has been obtained in our study on TP/BN/CTA blends[15] [CTA stands for cellulose triacetate (DS = 2.99)]. It can be also seen that the experimental ΔH_m values deviate downward from the straight line. These results mean that CA and TP molecules hinder the formation of BN crystallites. On BN/CTA blends, we have reported that the melting behavior of BN cannot be observed at $\phi_{BN} \leq 40$ and BN molecules in the CTA-rich samples ($\phi_{BN} \leq 40$) are amorphous state.[16] The results obtained in this work and in our previous works[15,16] indicate that there is a large difference in structure between BN/CTA and BN/CA blends; that is, that the degree of acetylation of cellulose markedly influences the miscibility of BN with cellulose molecules and that the BN molecules in BN/CA blends are crystallized even at the low value of ϕ_{BN} = 20.

The nonisothermal crystallization behavior of the blends was also studied. Figure 6 shows the effects of ϕBN on the crystallization temperature, T_c, and the calorific value during crystallization, ΔH_c. A straight sold line was also drawn through the values of ΔH_c at ϕ_{BN} = 0 and ϕ_{BN} = 100 (TP = 0 μL), where the value for ΔH_c at ϕ_{BN} = 0 was zero. The value of T_c decreases with an increase in the CA content. It also can be seen that the ex-
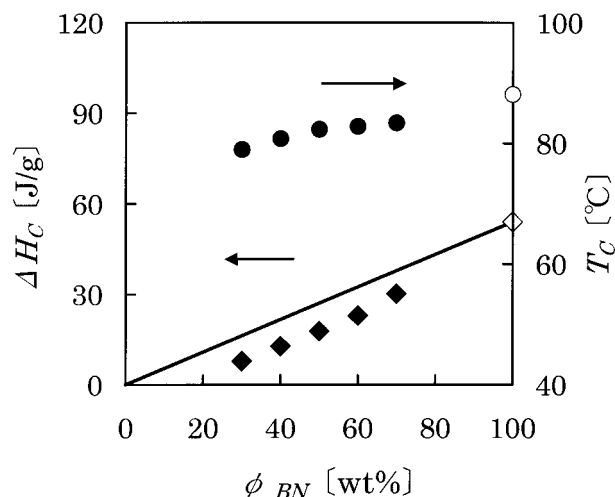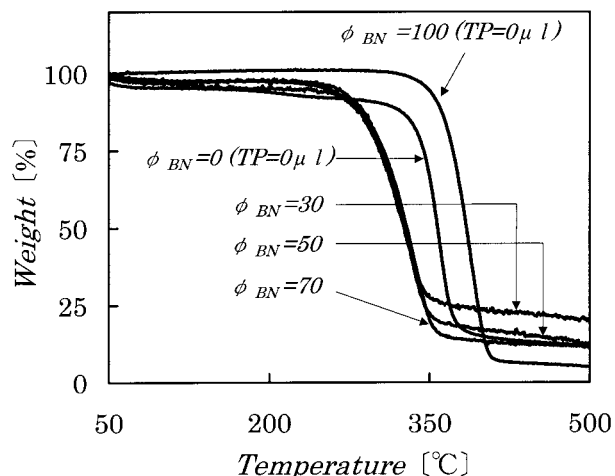

Figure 7 Thermogravimetric analysis curves of blend films.

perimental ΔH_c values deviate downward from the straight line. These results indicate that the existence of the CA molecules does not enhance the crystallization of BN but restricts it. During the crystallization of BN, BN molecules should be aggregated, and this process would be hindered by the geometrical structure of CA molecules being in frozen state and by the weak interactions originated from TP. In a previous study,[15] we reported that the addition of TP makes BN crystallites small in the TP/BN/CTA blends. As discussed, the addition of CA and TP seems to decrease the size of BN crystallites.

We investigate the effect of the addition of TP on the thermal degradation of the blends. Figure 7 shows the TGA curves for the blends. It is found that the addition of TP markedly decreases the temperature at which decomposition starts: a decrease of approximately 50°C can be seen. The incorporation of the oxide of TP into the BN/CA matrix seems to accelerate the separation of the polymer chains. A similar effect on decomposition temperature caused by the addition of alkoxide has been reported in niobium(V) oxide/cellulose acetate blends.[17]

Mechanical Properties of Blends

Figure 8 shows the DMA curves of the BN/CA blends. The value of E' of ϕ_{BN} = 30 decreases gradually with an increase in temperature, changes abruptly at about 120°C and decreases gradually again up to about 200°C, above which it decreases abruptly. Similar changes can be seen in other ϕ_{BN} samples. It is apparent that the
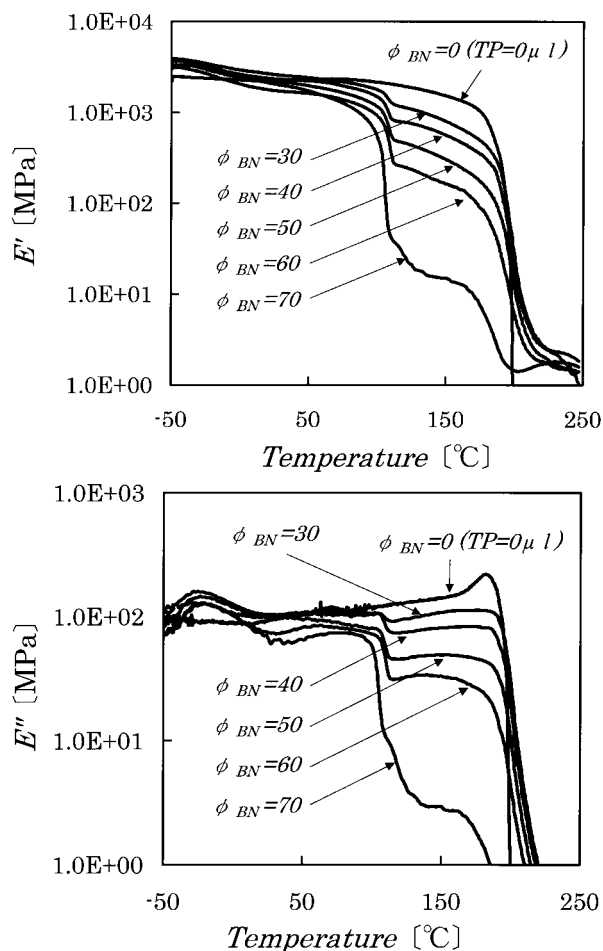

Figure 6 Effect of poly(butylene succinate) content on T_c and ΔH_c. Open symbols: tetraisopropyl titanate = 0 μL samples.

Figure 8 Dynamic mechanical analysis curves of poly(butylene succinate)/cellulose acetate blends.

Figure 9 Effect of poly(butylene succinate) on Young's modulus oonf poly(butylene succinate)/cellulose actetate blends. Open symbols: tetraisopropyl titanate = 0 μL samples.

Hydrolysis of Blends

Figure 10 shows the mass of the residue of blends as a function of hydrolysis time. With an increase in hydrolysis time, the mass of each sample decreases markedly at first and then indicates almost a constant value. The sample with high ϕ_{BN} indicates a marked decrease. The mass of the residue is thought to decrease with an increase in water-soluble oligomers formed by hydrolysis. If only the BN component in the blend was hydrolyzed, the constant value would be determined by the amount of the BN content. However, the ex-

abrupt decrease in E' at about 120°C is caused by the melting of the BN crystallites. The abrupt decrement of E' at about 120°C becomes smaller when the CA content increases. This result implies that CA molecules forming the matrix in the frozen state effectively prevent the thermal deformation of the blends. In the loss modulus, E'', versus the temperature curves, we can see a peak at about −30°C in each blend containing BN; this peak corresponds to the T_g of BN. Although we investigated in detail the effects of ϕ_{BN} on T_g by using three samples for each ϕ_{BN}, a clear dependence of T_g on ϕ_{BN} was not observed.

Figure 9 shows the effect of the BN content on the Young's modulus of the blends. The Young's modulus decreases with an increase in the BN content because the modulus of BN is lower than that of CA. This means that by changing the BN content, we can prepare the samples to have various mechanical properties.
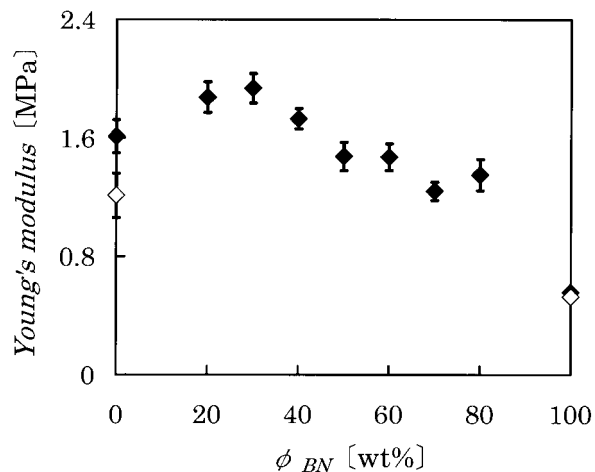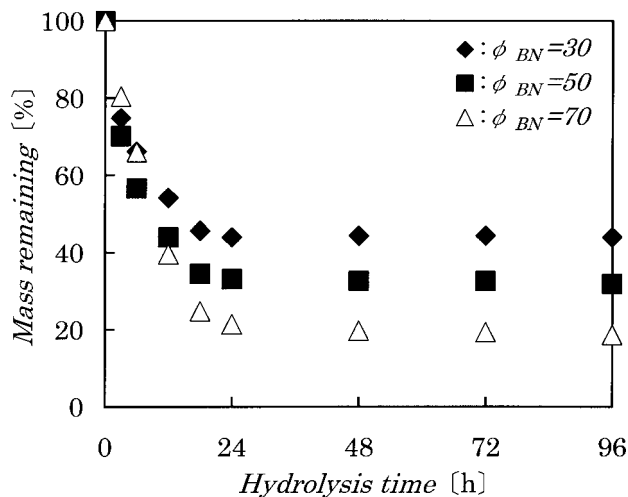

Figure 10 Mass remaining of poly(butylene succinate)/cellulose acetateblends as a function of hydrolysis time.

(a)　　　　　　　　　(b)

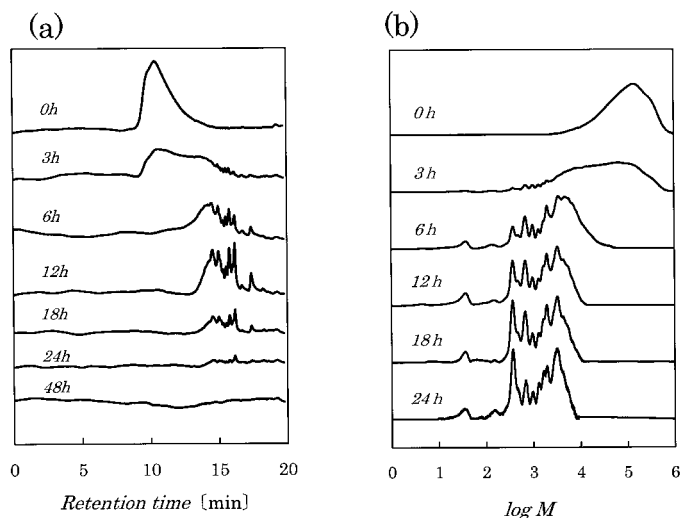**Figure 11** Gel permeation chromatography spectra of $\phi_{BN} = 70$ films before and after hydrolysis for different times.

perimental result demonstrates that the constant value is always lower than that estimated from ϕ_{BN}. This means that the CA component is also hydrolyzed during the hydrolysis of the blends. Figure 11 shows the effect of hydrolysis time on GPC spectra of $\phi_{BN} = 70$ blends. In Figure 11(a), it can be seen that the GPC curve becomes flat with an increase in hydrolysis time. This means that the number of water-soluble oligomers increases with increasing hydrolysis time. Figure 11(b) shows the effect of hydrolysis time on the molecular weight distribution of $\phi_{BN} = 70$ blends; these curves were calculated from Figure 11(a). The high molecular weight component at log $M = 5$ disappears with increasing hydrolysis time, and several peaks appear in the low molecular weight region from log $M = 2$ to 4. This means that high molecular components were degraded and that oligomers with special molecular weights were formed during the hydrolysis; several oligomers remained in the residues. Such peaks are originated from the oligomers of BN, as the peaks were observed in the hydrolyzed $\phi_{BN} = 100$ sample. The appearance of peaks may mean that the molecular scission does not occur along BN molecules at random: the molecular scission mechanism seen in BN/CA blends, presented in this article, has not be observed in the hydrolysis of poly(lactide).[18] Now, we discuss the mechanism of the hydrolysis.

At room temperature, the blends have a large amount of free volume because the T_g of BN is lower. Moreover, because TP is easily hydrolyzed,

the incorporation of the oxide of TP into BN/CA seems to assist the penetration of NaOH into the matrix. The high molecular weight component appearing at log $M = 5$ cannot be seen in the sample hydrolyzed for 6 h, although the mass remaining is 60% (see Fig. 10). Considering the above discussion and this experimental result, the hydrolysis seems to take place uniformly not only from the surface but also inner part of the blends. Such hydrolysis mechanism has been proposed for TP/BN/CTA blends.[15]

CONCLUSION

A new biodegradable polymer composite material was prepared from the blend of poly(butylene succinate), BN, and CA by the addition of TP. The structure and physical properties of the blends have been investigated. The following conclusions are deduced from the above result and discussion: First, the viscosity of the BN/CA blend solution is increased by the addition of TP. Although TP interacts with BN and CA molecules during the solvent blending, the evidence for interactions cannot be observed with NMR and FTIR. Second, the interactions seem to make the sizes of BN crystallites small in the BN/CA blends. Third, there is a possibility that TP would be used as a compatibilizer of the BN/CA blends. Namely, homogeneous films can be obtained from the blend of CA and BN by the addition of TP. Fourth, the addition of TP decreases the thermal decomposi-

tion temperature of the BN/CA blends. Fifth, the Young's modulus of the blend increases with an increase in the CA content. Finally, the molecular scission of BN/CA blends takes place uniformly not only from the outside but also from the inside of the films during hydrolysis of the blends.

REFERENCES

1. Technical data sheet of Showa Highpolymer, Tokyo, Japan.
2. Sawada, H.; Fujimaki, T. In Handbook of Biodegradable Polymer; Doi, Y., Ed.; NTS: Tokyo, 1995; p 130.
3. Reese, E. T. Ind Eng Chem 1957, 49, 89.
4. Williams, G. R. Bio Int Biodetn Bull 1982, 18, 31.
5. Buchanan, C. M.; Gardner, R. M.; Komarek, R. J. J Appl Polym Sci 1993, 47, 1709.
6. Nishio, Y.; Manley, R. St. J Polym Eng Sci 1990, 30, 71.
7. Nishio, Y.; Hirose, N.; Takahashi, T. Polymer J 1989, 21, 347.
8. Nishio, Y.; Hirose, N.; Takahashi, T. Sen'i Gakkaishi 1990, 46, 441.
9. Buchanan, C. M.; Gedon, S. C.; White, A. W.; Wood, M. D. Macromolecules 1992, 25, 7373.
10. Buchanan, C. M.; Gedon, S. C.; White, A. W.; Wood, M. D. Macromolecules 1993, 26, 2963.
11. Saimos, E.; Dart, R. K.; Dawkins, J. V. Polymer 1997, 38, 3045.
12. Nagata, N.; Okana, F.; Sakai, W.; Tsutsumi, T. J Polym Sci Part A Polym Chem 1998, 36, 1861.
13. Ohmori, Y.; Kurokawa, Y. J Biotech 1994, 33, 394.
14. Nakane, K.; Takahashi, K.; Suzuki, F.; Kurokawa, Y. Sen'i Gakkaishi 1999, 55, 563.
15. Uesaka, T.; Ogata, N.; Nakane, K.; Ogihara, T. Sen'i Gakkaishi 2001, 57, 165.
16. Uesaka, T.; Nakane, K.; Maeda, S.; Ogihara, T.; Ogata, N. Polymer 2000, 41, 8449.
17. Campos, E. A.; Gushikem, Y. J Colloid Interf Sci 1997, 193, 121.
18. Tsuji, H.; Mizuno, A.; Ikeda, Y. J Appl Polym Sci 2000, 77, 1452.