

Crystallization Behavior and Viscoelasticity of Bamboo-Fiber Composites

Yasuyuki Kori,¹ Kazuo Kitagawa,² Hiroyuki Hamada³

¹Kyoto R&D Laboratories, Sekisui Chemical Company, Limited, 2-2, Kamichoshi-cho, Kamitoba, Minami-ku, Kyoto 601-8105, Japan

²Industrial Technology Center, Kyoto Municipal Industrial Research Institute, Chudoji, Shimogyo-ku, Kyoto 600-8813, Japan

³Advanced Fibro-Science, Kyoto Institute of Technology, Matsugasaki Sakyō-Ku, Kyoto 606-8585, Japan

Received 17 June 2004; accepted 11 January 2005

DOI 10.1002/app.22062

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article deals with the effect of the kneading temperature on the crystallization of a matrix polymer and the viscoelasticity of a bamboo-fiber-reinforced biodegradable polymer composite. Upon the investigation of poly(butylene succinate) after melt mixing, spherulite generation was observed with polarized light microscopy and differential scanning calorimetry measurements. An increase in the spherulite dimensions was observed at high kneading temperatures (>150°C) in both the neat polymer and the bamboo-fiber composite. Spherulite growth was

initiated from the bulk matrix polymer and not from the surface of the bamboo fibers. The kneading temperature influenced the melt viscoelasticity above the melting point of poly(butylene succinate) but did not influence the viscoelasticity below the melting point. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 603–612, 2005

Key words: biodegradable; crystallization; polyesters; spherulites; thermal properties

INTRODUCTION

Recently, composites from natural fibers and biodegradable plastics (so-called biocomposites) have been studied as environmentally friendly materials. In particular, biodegradable plastics from biomass such as poly(lactic acid) (PLA) are called *carbon-neutral materials*, and they have the potential to reduce the consumption of petroleum and reduce the concentration of carbon dioxide. The mechanical properties of PLA are close to those of polypropylene, so the replacement of polypropylene by PLA has been studied. However, in some cases, PLA cannot be used independently for the adjustment of toughness. A material compatible with PLA is needed. On the other hand, poly(butylene succinate) (PBS) will be made from biomass commercially in the near future. It has good flexibility and better biodegradability than PLA, so it is thought that PBS can also be used as films, injection moldings, PLA modifiers, and many other applica-

tions. However, there has not been enough observation of the thermal characteristics and crystallinity of PBS to clearly establish the relationships between the processing conditions, product performance, and structure. This is more so for composites of natural fibers and PBS. There are no reports referring to the crystallization behavior. In general, crystallinity can affect the mechanical characteristics and biodegradability. Some reports on biodegradable plastics refer to the effect of crystallinity on their characteristics.^{1–4} However, there are no publications that evaluate the growth of polymer crystals on biocomposites and relate this to the molding conditions.

So far, most studies on composites from natural materials have focused on vegetable fibers, which have good mechanical performance, good renewability, and good economical efficiency. Many workers have studied bamboo fibers as naturally organic fillers of polymer composites. The reason that many studies focus on bamboo is that bamboo is an abundant natural resource in Asia, and its overall mechanical properties are comparable to or surpass those of wood.⁵ Furthermore, bamboo can be renewed much more rapidly than wood. However, because of bamboo's rapid growth, it has gradually invaded wood forests and reduced the wood supply. Therefore, researchers are anxious to find effective uses for bamboo.

For the study of bamboo-fiber composites, Mi et al.⁶ reported that transcrystals of polypropylene were

Correspondence to: Y. Kori (kori@sekisui.jp).

Contract grant sponsor: Advanced Software Technology & Mechatronics Research Institute of Kyoto (through the program "The Development of Natural Fiber/Biodegradable Polymer Composites with Designable Interphase", which is subsidized by the Kansai Bureau of Economy, Trade, and Industry).

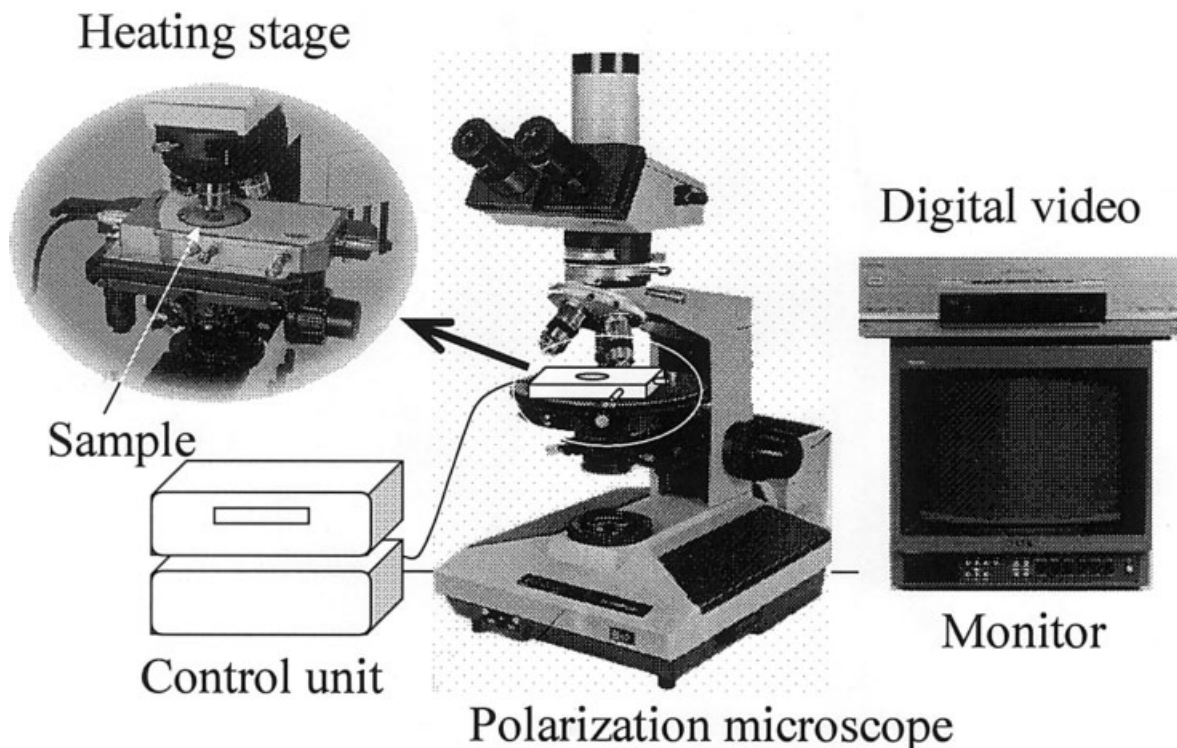


Figure 1 Polarization microscope with heating stage.

generated on the surface of bamboo fibers in a composite of polypropylene and bamboo fibers. The addition of maleic polypropylene made the transcrystals on the fibers much more than neat polypropylene. However, they did not discuss the influence of the molding conditions on the crystallinity, especially for biodegradable plastics.

In this study, we evaluated the influence of the molding conditions (especially the kneading temperature) on the spherulite growth of the matrix polymer in a composite of PBS and bamboo fiber with a polarization microscope with a heating stage and differential scanning calorimetry (DSC) measurements. Moreover, for the improvement of the interface between the fibers and matrix polymer, Kitagawa et al.⁷ applied a glyoxal treatment to the fibers and obtained improved mechanical characteristics. Here the effect of such a treatment on the crystallization behavior at the interface between the matrix polymer and bamboo fiber was studied.

As for the mechanical characteristics, we studied the influence of the molding conditions on the dynamic viscoelasticity of the composites by tensile and melt shearing.

EXPERIMENTAL

Polymer and bamboo fiber

PBS (Enpol #5300, Ire Chemical, Seoul, Korea) was used as a matrix polymer. The melt flow index (D1238)

of PBS was 2.6. The glass-transition temperature of PBS was about -20°C , and its melting temperature was $110\text{--}120^{\circ}\text{C}$ (D2117). Bamboo fibers were obtained by a special crushing technique (diameter $\sim 70\ \mu\text{m}$, length $\sim 500\ \mu\text{m}$). The volatile content was 7.4% (130°C , 10 min). A composite pellet of bamboo fiber, which was treated with 10 wt % glyoxal was prepared with a coextruder (Nihon Seikosyo, Kyoto, Japan) at 135°C .

Preparation of the samples

PBS and the fiber were kneaded with a laboratory plastomill with a segmented mixer (KF70, Toyo Seiki Seisakusyo, Hyogo, Japan) for the evaluation of the molding conditions. The composites (10 g) were kneaded at a rotating speed of 30 rpm for 10 min at temperatures ranging from 130 to 200°C . Sheet molding for 10 min at 130°C for each compound followed.

Polarization microscopy

The changes in the spherulites with the temperature were observed with a polarization microscope (BH-2, Olympus, Olympus America, Inc., Melville, NY) with a heating stage (LK-600PM, Japan Hitech, Japan Hitech, Tokyo, Japan; Fig. 1). The continuous image data were stocked by digital video via a video scope. To minimize the influence of deviation in the crystallization after kneading, the samples were first heated

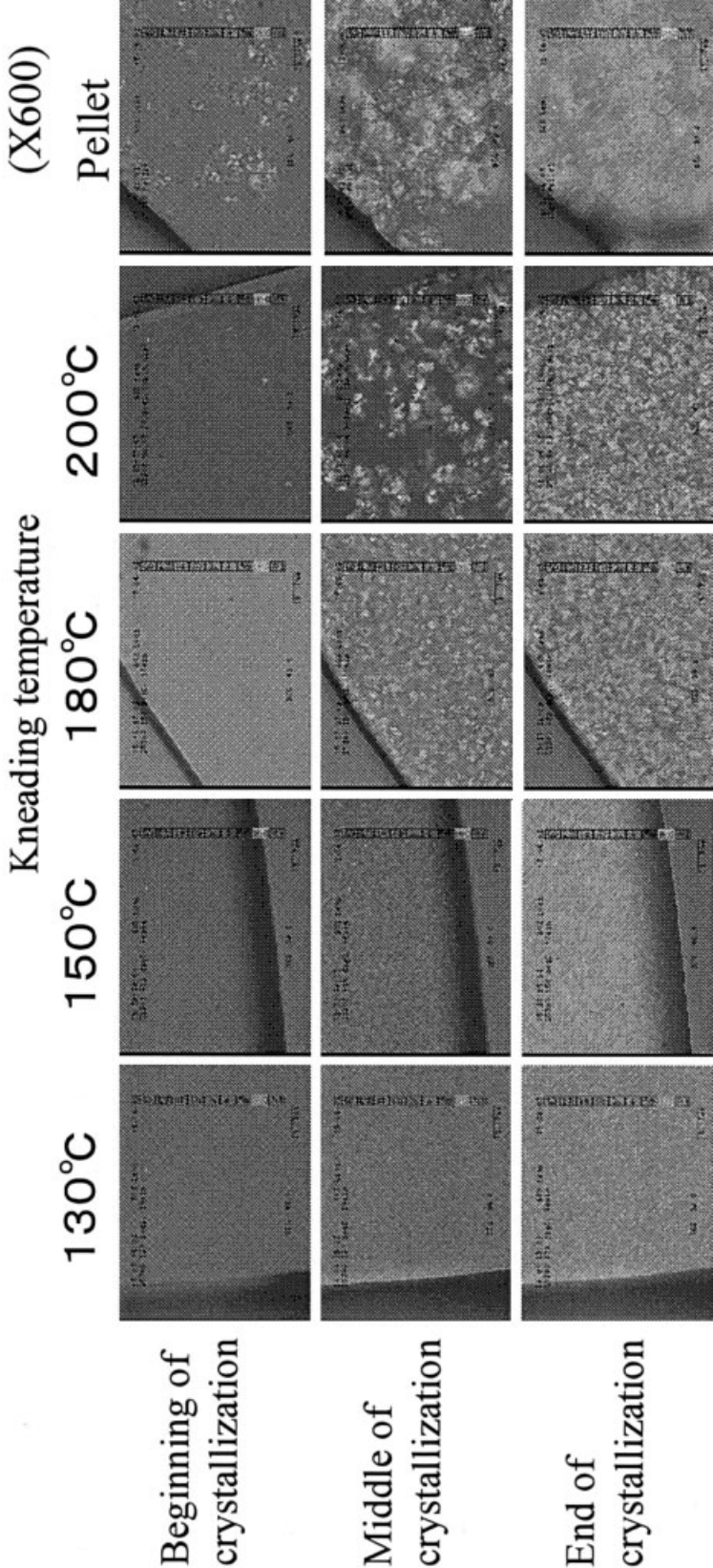


Figure 2 Images of spherulite growth of neat PBS polymer at different kneading temperatures.

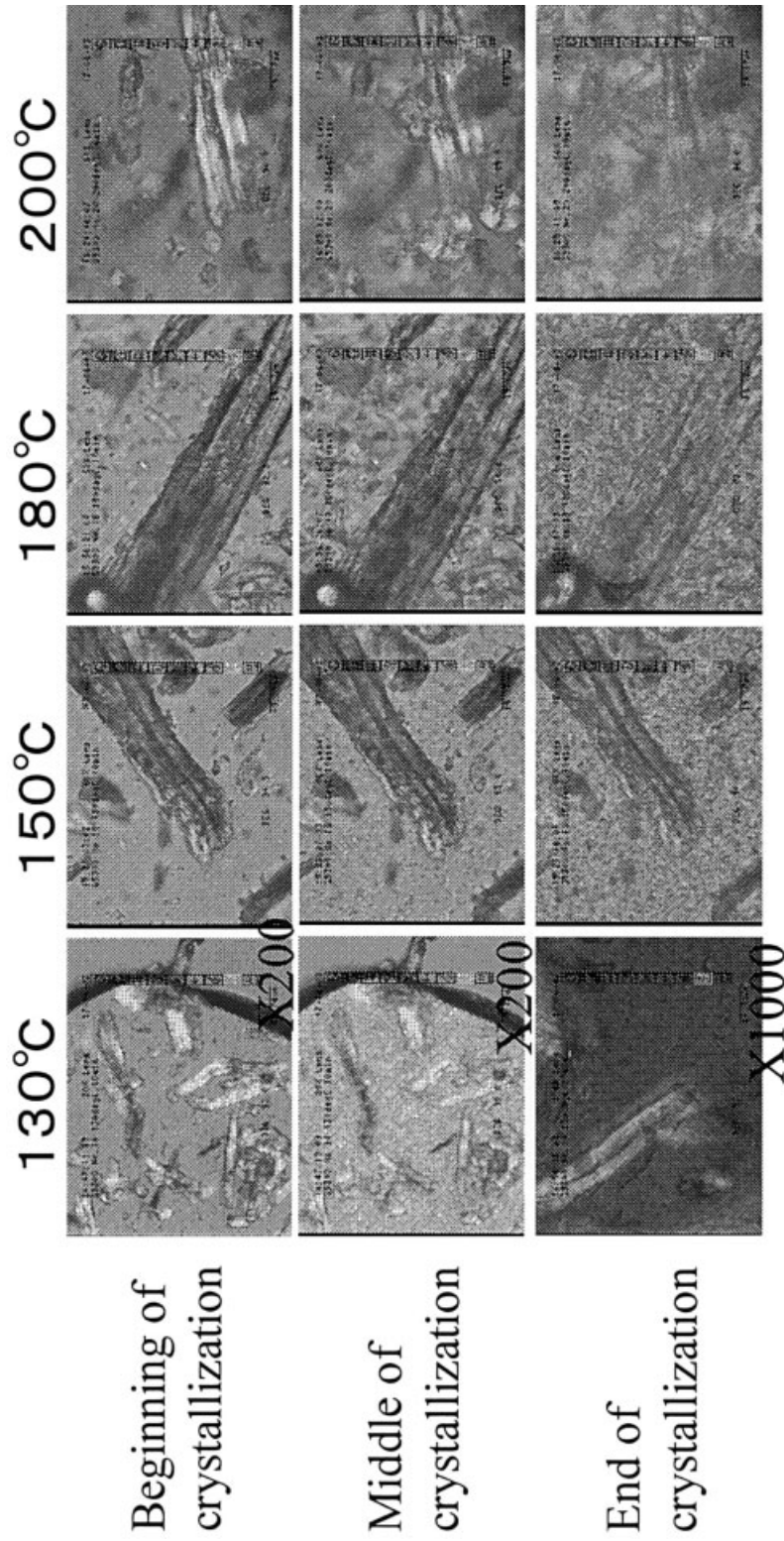


Figure 3 Images of spherulite growth of the bamboo composite at different kneading temperatures.

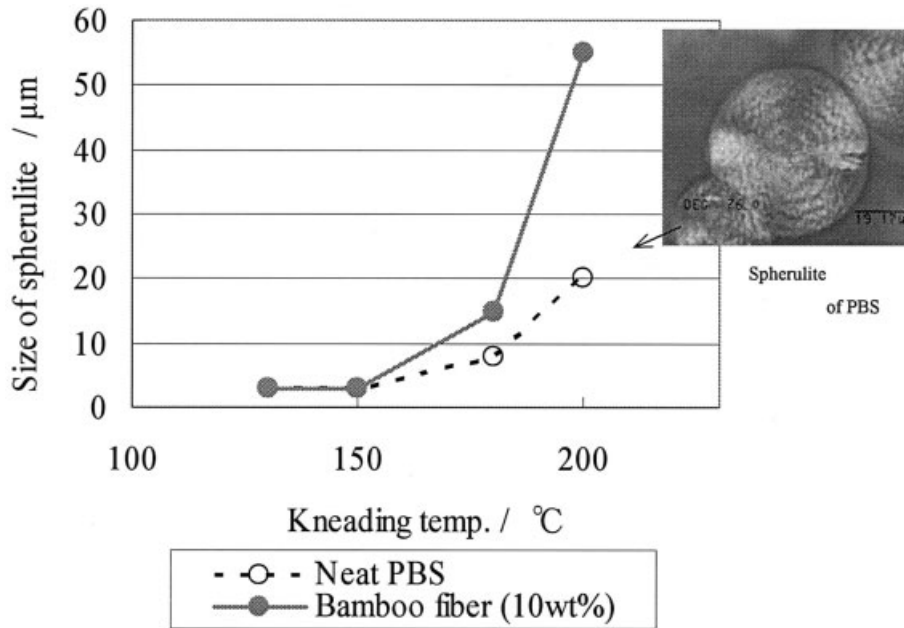


Figure 4 Sizes of the spherulites at different kneading temperatures.

to 150°C at a heating rate of 100°C/min. After the initial heating, the samples were cooled at a rate of 20°C/min, and we observed the starting temperature of recrystallization, the spherulite size, and the melting temperature by watching the growth and disappearance of the spherulites.

DSC measurements

The crystallization and melting behavior of the matrix polymer was observed via DSC measurements with a DSC220C calorimeter (Seiko Instruments, Inc., Chiba, Japan). The measurements were taken in an N₂ atmo-

sphere, with the temperature ranging from room temperature to 150°C, at a rate of 10°C/min.

Molecular weight distribution

For the evaluation of the polymer decomposition, the molecular weight distribution of the neat polymer was observed with a high-temperature gel permeation chromatography (GPC) system (GPCV2003, Waters, Milford, MA) with a Styragel+HT6E column, *o*-dichlorobenzene as a carrier, and a column temperature of 150°C.

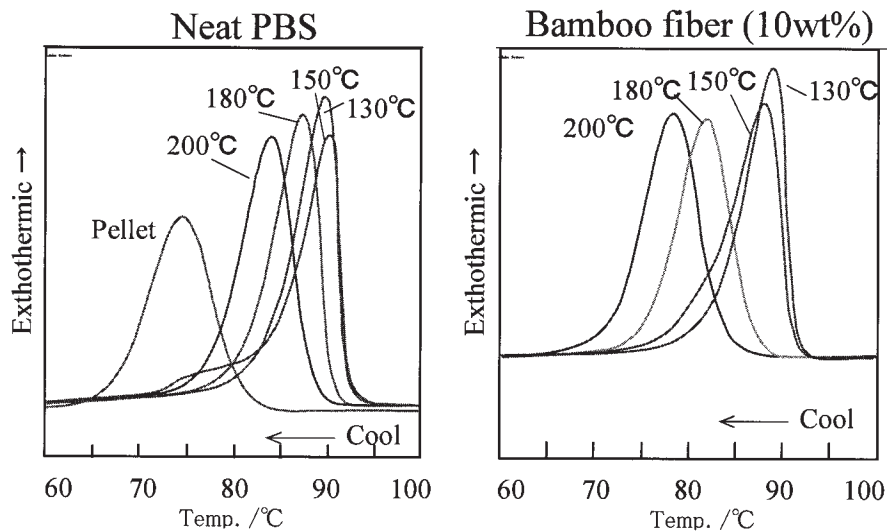


Figure 5 DSC cooling curves of the neat polymer and bamboo fiber (10 wt %) at each kneading temperature.

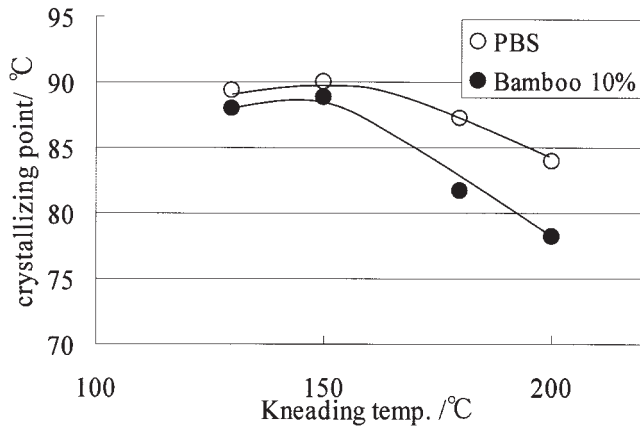


Figure 6 Effect of the kneading temperature on the crystallizing point.

Viscoelasticity

The melt dynamic viscoelasticity of the composites at different kneading temperatures was observed with a rheometer (RDA-II, Rheometrics, Inc., Piscataway, NJ). The temperature variance was measured from 120 to 200°C at a frequency of 1.0 rad/s and a strain of 10% with a 25-mm ϕ parallel plate. The tensile dynamic viscoelasticity of the composites, from -50 to 150°C, was

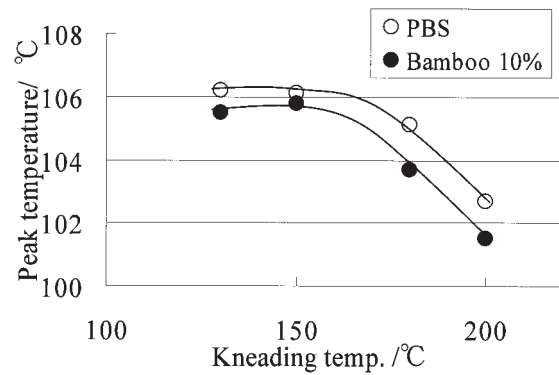


Figure 8 Effect of the kneading temperature on the second endothermic point temperature.

also evaluated with a dynamic viscoelastic analyzer (DVA-200, IT-Seigy Co., Japan) at a frequency of 10 Hz, a strain of 0.1% and a heating rate of 6°C/min.

RESULTS AND DISCUSSION

Polarization microscopy observations

Figure 2 shows the images of the neat PBS spherulites for each kneading temperature just after crystallization

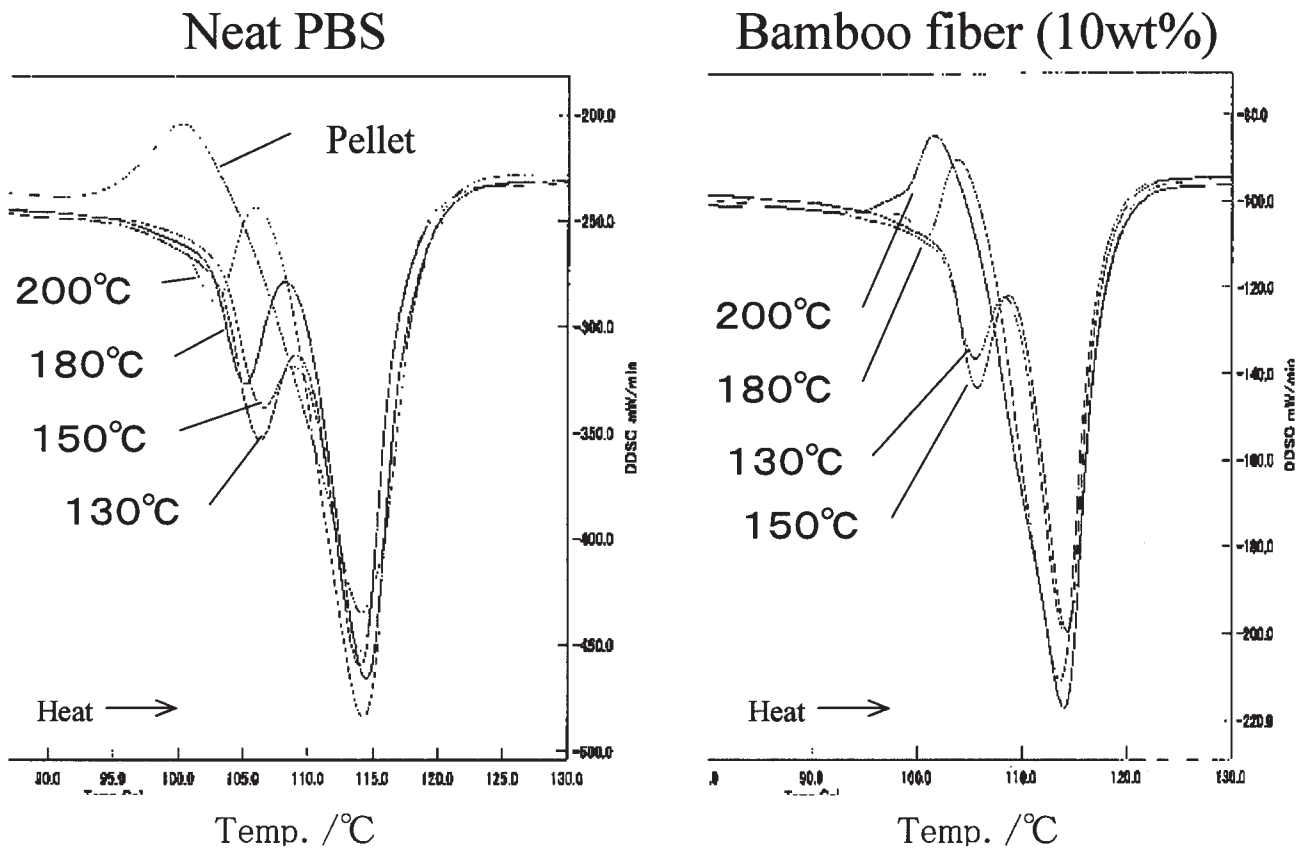


Figure 7 DSC heating thermograms for the neat polymer and bamboo fiber (10 wt %) at each kneading temperature.

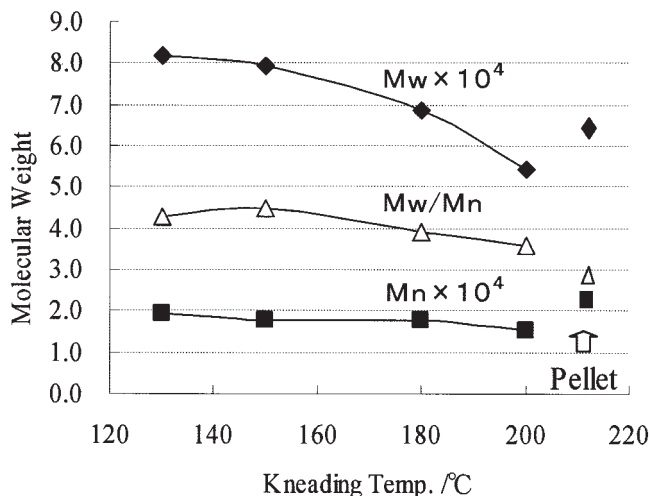


Figure 9 Molecular weight at different kneading temperatures (M_n = number-average molecular weight; M_w = weight-average molecular weight).

started and just before it finished. Below 150°C, heterogeneous nucleation (which indicated that the activating energy for nuclei generation was heterogeneous or unstable in the area) could be observed; small spherulites appeared at the same time and grew rapidly. Above 150°C, heterogeneous nucleation could be observed; spherulites grew gradually with dimensions larger than those of the previous spherulites. Figure 3 shows the images of spherulites of the 10% bamboo composite for each kneading temperature. The growth of the spherulites could be heterogeneous, similar to that of neat PBS, and the spherulites grew gradually above 150°C. Each spherulite appeared in the bulk of the matrix, not from the interface of the bamboo fibers and matrix polymer. Figure 4 shows the dimensions of the PBS spherulites at each kneading temperature. Above 150°C, the dimensions of the spherulites of the bamboo-fiber composite

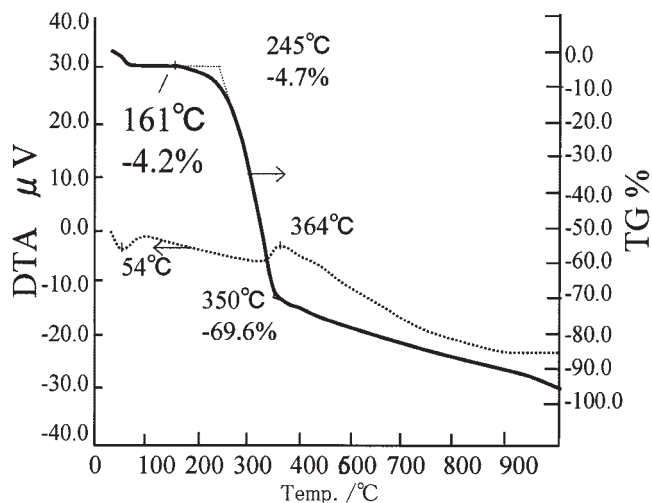


Figure 11 TG-DTA curve of the bamboo fiber.

were bigger than those of neat PBS. The bamboo fibers slowed the growth of the spherulites.

On the other hand, the spherulite growth of the neat pellet before kneading could be homogeneous nucleation, in which nuclei of crystals appeared gradually with time at random in the bulk of the polymer and spherulites grew slowly to become large. As for the surface of the bamboo fibers, no transcrystals formed. The results were the same at each kneading temperature. It can be suggested that no chemical or strong interfacial bonding between the bamboo fibers and polymer existed. The bamboo fibers did not act as nuclei for crystal formation.

DSC measurements

The DSC thermograms of the neat PBS and 10% bamboo-fiber composites at each kneading temperature were studied. Figure 5 shows the cooling thermograms. Below

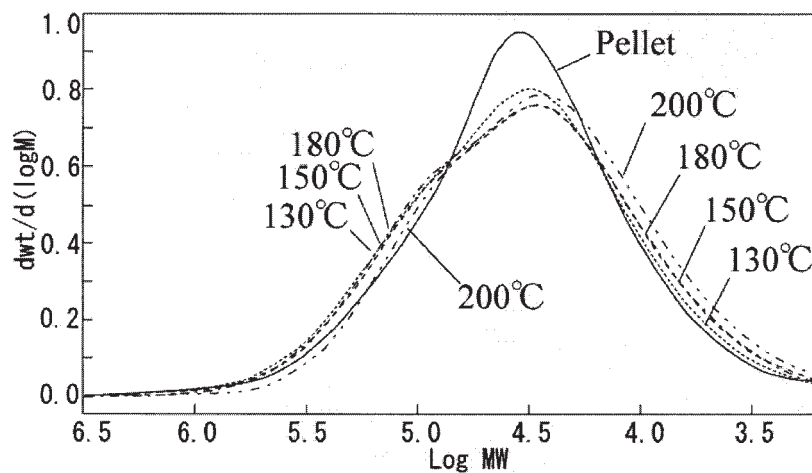


Figure 10 Molecular weight distribution at different kneading temperatures.

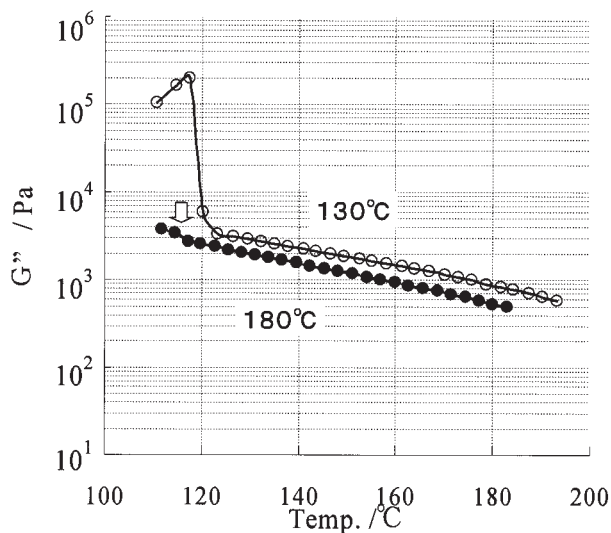


Figure 12 G'' of PBS at different kneading temperatures.

150°C, the crystallization exothermic peaks were sharp, and above 150°C, the peaks shifted to lower temperatures, whereas the peak shape became broader. The result was equivalent to that of the spherulite growth observation by polarization microscopy. Figure 6 shows the effect of the kneading temperature on the crystallization point of the neat PBS and 10% bamboo-fiber composites. In the bamboo-fiber composites, above a kneading temperature of 180°C, the peaks of crystallization were shifted to a lower temperature. Figure 7 shows the heating thermograms of the neat PBS and 10% bamboo-fiber composites. For both materials, two endothermic peaks were observed from 100 to 120°C. The maximum endothermic change at 115°C was for the melting of crystals, and it was not influenced by the kneading temperature and bamboo fiber. Smaller endothermic peaks

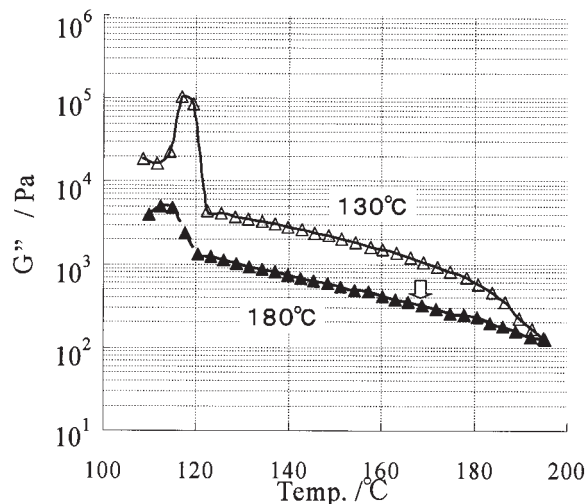


Figure 13 G'' of 10% bamboo fiber at different kneading temperatures.

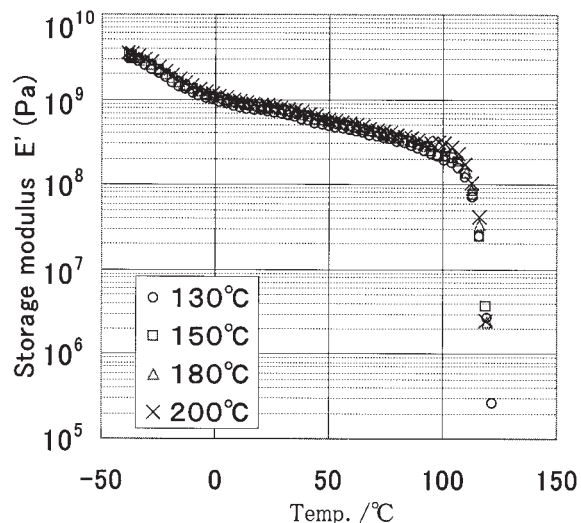


Figure 14 Tensile storage modulus of 10% bamboo fiber at different kneading temperatures.

that appeared at lower temperatures were influenced by the kneading temperature and bamboo-fiber content.

Figure 8 shows the effect of the kneading temperature on the second smaller endothermic peaks. The second smaller peak was shifted to lower temperatures and became smaller as the kneading temperature increased. The bamboo fibers further lowered the temperature of the peaks.

Molecular distribution measurements

For kneading above 180°C, the decomposition of PBS was expected. Then, the molecular distribution of PBS after kneading was observed.

Figure 9 shows the molecular weight distribution results from GPC for all kneaded PBS. The weight-average molecular weight of PBS decreased with an increase in the kneading temperature. Above 200°C, polymer pyrolysis occurred. On the other hand, the molecular weight of PBS kneaded below 150°C was higher than that of the neat pellet.

Figure 10 shows the distribution curves of the molecular weight at each kneading temperature. The molecular weight increased on the higher molecular weight fraction below 150°C kneading. This may be the reason for the polymer entanglement that occurred so much with kneading at a low temperature near the melting point. Some microcrystal might have been generated that made the molecular weight higher because of less solubility in the solvent during the GPC measurements.

On the basis of the DSC measurements, two kinds of crystals were generated, and only one of them was affected by kneading. For kneading above 180°C, shear and heat could make a certain crystal decompose and thus reduce the entanglement between polymer chains, and the conformation could become fixed similarly to

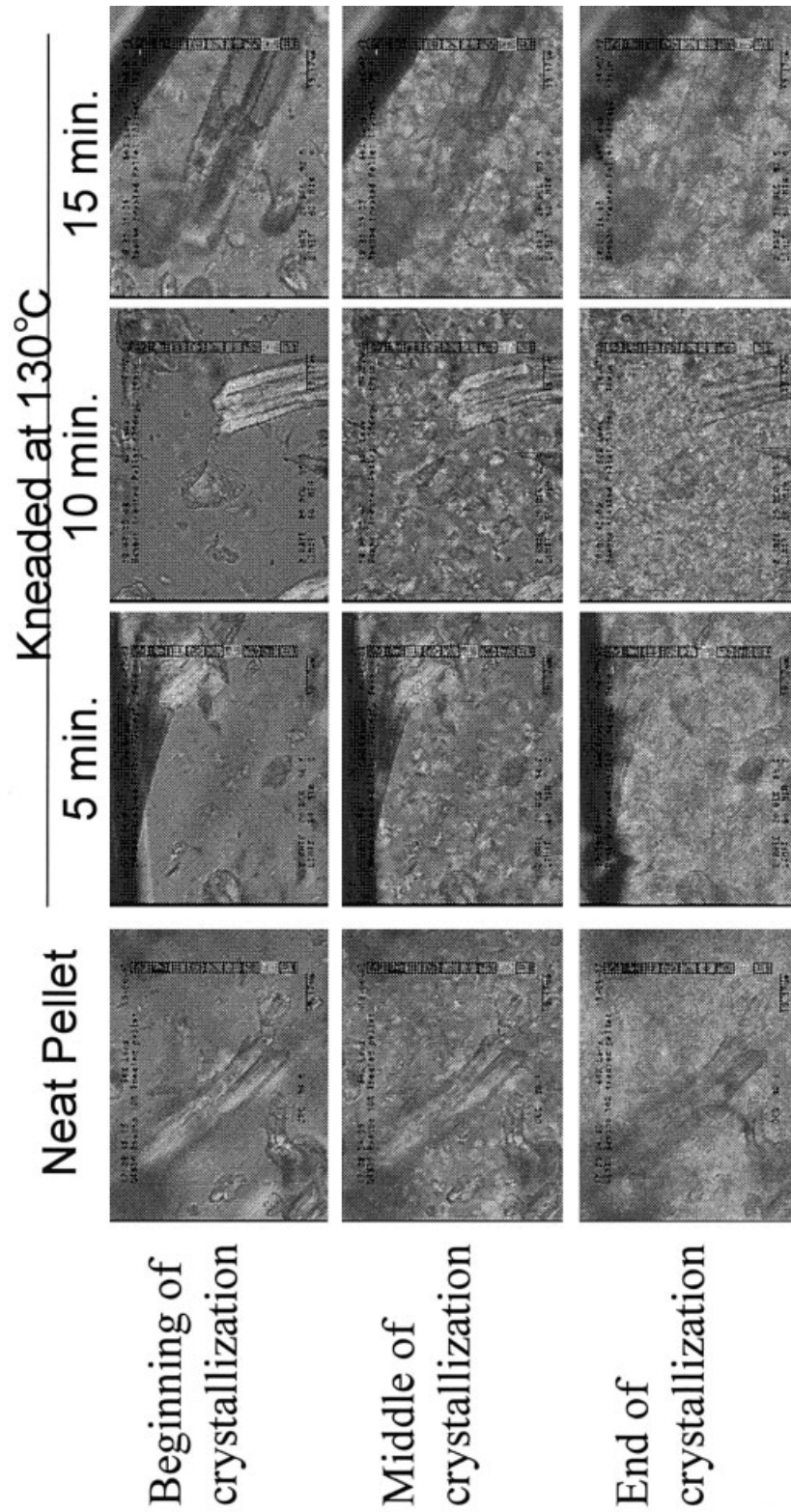


Figure 15 Images of spherulite growth of the bamboo composite with bamboo fibers treated with glyoxal.

the neat pellet. Therefore, recrystallization was very slow, like homogeneous nucleation, but it could be heterogeneous nucleation because of minute impurities.

For kneading below 150°C, the polymer could not be dispersed sufficiently. Some entanglement of the polymer could occur during kneading, or a certain crystal could be generated during pelletizing by the supplier. As a result, some nuclei for crystallization could make spherulites in the bulk of the polymer, and this could be heterogeneous nucleation.

It might be thought that the second exothermal change between 90 and 110°C on heating could come from the melting of different crystal structures (e.g., the β -crystal form of polypropylene).

Bamboo-fiber decomposition affected the spherulite growth and melting. Figure 11 shows the thermogravimetry/differential thermal analysis (TG-DTA) curve of bamboo fiber. The bamboo fiber decomposed gradually from 161°C; thus, the decomposition of the bamboo fiber occurred above the kneading temperature of 150°C. The decomposition products from the bamboo fibers could influence the crystallization behavior.

Dynamic viscoelasticity

Measuring the dynamic viscoelasticity of a material is one of the methods used to assess processability and mechanical performance. Figure 12 shows the loss modulus (G'') obtained by the shearing of kneaded PBS at 130 and 180°C. There was a small drop in G'' of neat PBS due to kneading at 180°C. This could account for the decrease in the matrix molecular weight caused by heat degradation.

Figure 13 shows G'' of the 10% bamboo-fiber composite after kneading at 130 and 180°C. G'' of the sample kneaded at 180°C decreased much more than that of the composites kneaded at 130°C and more than that of neat PBS.

Figure 14 shows the tensile storage modulus of the 10% bamboo-fiber composite after kneading at 130, 150, 180, and 200°C. There was little change between them. If some decomposed product from the bamboo fiber had existed, it would have affected the tensile storage modulus sufficiently below the melting temperature of PBS. However, the results from viscoelasticity did not suggest that the decomposition products of the bamboo fiber above 150°C could make the polymer degradation higher.

However, the influence of the bamboo-fiber decomposition at high temperatures above 140°C has been mentioned with respect to the tensile strength.⁸ After a heat treatment above 140°C of the fiber, a big decrease in the tensile strength was observed. Consequently, in our viscoelasticity measurements, the tensile strain of 0.1% was much less than the strain of 1–10% in a conventional tensile test. Therefore, the decomposition of the fibers or the change in the binding strength between the fibers

and polymer might not be reflected enough by dynamic viscoelasticity measurements.

Surface treatment of bamboo fibers

Figure 15 shows images of spherulite growth of the matrix polymer in the composite of bamboo fibers treated with glyoxal. The growth of the spherulites was similar to that of nontreated bamboo fibers. The spherulite growth was affected by the kneading temperature. There was no transcystal generation on the treated surface of the fibers. This result suggests that glyoxal treatment could not improve the interfacial crystallization of the matrix PBS on the bamboo fibers.

CONCLUSIONS

1. For neat PBS, kneading below 150°C made the crystallization rapid, and the spherulites were smaller. It generated nuclei in the bulk of the matrix. The nuclei could be microcrystals suitable for the nucleation of spherulites and make heterogeneous nucleation of spherulites possible.
2. Kneading neat PBS above 150°C slowed down spherulite growth while increasing the dimensions of the spherulites. This could be homogeneous nucleation of spherulites.
3. For the bamboo-fiber composites, kneading above 150°C could result in homogeneous nucleation of spherulites. It made the crystallization slower and made the spherulites grow larger than those of neat PBS.
4. Kneading above 150°C reduced G'' of the bamboo-fiber composite. The degradation products of the bamboo fibers could have caused this change.
5. The kneading temperature did not influence the tensile storage modulus below the melting point of the matrix polymer.
6. The spherulites were not generated from the surface of bamboo fibers at any kneading temperature.
7. The spherulites were also not generated from the surface of treated bamboo fibers at any kneading temperature.

References

1. Chanprateep, S. *J Chem Eng Jpn* 2003, 36, 639.
2. Todo, M.; Shinohara, N.; Arakawa, K. *J Mater Sci Lett* 2002, 21, 1203.
3. Kim, K.-S.; Chung, S.; Chin, I.-J.; Kim, M.-N.; Yoon, J.-S. *J Appl Polym Sci* 1999, 72, 341.
4. Qiu, Z.; Ikehara, T.; Nishi, T. *Polymer* 2003, 44, 5429.
5. Amata, S. *Nihon Senpaku Kikan Gakkaishi* 1999, 38, 527.
6. Mi, Y.; Chen, X.; Guo, Q. *J Appl Polym Sci* 1997, 64, 1267.
7. Kitagawa, K.; Tsutsui, K.; Watanabe, D.; Mizoguchi, M.; Hamada, H. *Proceedings of the 1st International Conference on Eco-Composites*; Queen Mary University of London: London, England, 2001.
8. Ochi, S.; Takagi, H.; Niki, R. *J Soc Mater Sci Jpn* 2002, 51, 1164.