Introduction

There has recently been a dramatic increase of interest in using biomass such as wood fibers, oil palm fibers and coir as replacements for glass fibers to reinforce thermoplastic composites (for examples dealing with morphological work, see Stark & Berger 1997, Oksman & Clemons 1998, Takatani et al. 2000, Hill & Khalil 2000, Wu et al. 2000), because the woody material offers several advantages over inorganic fillers, such as its low price, biodegradability, recycle-ability, low density, and high modulus. Reviews of wood and plastic polymer composites have shown that they have good potential to improve the water resistance of woody composites, because thermoplastic polymers are highly hydrophobic (Takatani et al. 2000). As has been often pointed out (e.g. Oksman & Lindberg 1995), one of the serious disadvantages of using wood fibers as extenders and reinforcement for polyolefins is that the resulting composites usually have a significantly reduced impact and tensile strength due to poor adhesion between the hydrophilic filler material and hydrophobic thermoplastic.

Some researchers believe that if the interaction can be improved, the composites could be given better mechanical properties and better particle dispersion. Based on this hypothesis, many approaches have been carried out, such as the use of several kinds of compatibilizers and modifications with maleic anhydride (Felix & Gatenholm 1991, Oksman 1996, Oksman & Clemonth1998, Wu et al. 2000). The results showed some mechanical properties of the composites had been improved, but not so much as anticipated. This means that improvements in the interface between wood and polypropylene (PP) by chemical methods by themselves were not enough to explain the fact that the Stark 1997; Stark & Berger 1997). Steam-exploded beech flour has been reported to improve significantly...
mechanical properties and water resistance (Takatani et al. 2000).

Wood as a filler in polymer is different from inorganic materials in its porous nature. Under high temperature and pressure, a melting polymer can penetrate into the macro-cavities of wood such as cell lumina, passing through the pits on cell walls (Fujii and Hatano 2000; Fujii et al. 2001). In this kind of physical way, polymers may act just like a rivet bonding wood and polymer together. Perhaps, this is the real reason why the composites using wood as a reinforcing filler have a better mechanical properties than pure polymer.

Many morphological observations on the composites of wood and thermoplastic polymer have been carried out, but they have focused exclusively on fractured surfaces using a scanning electron microscope (SEM), excepting only one the study by Oksman and Lindberg (1995) who observed a microtome-planed surface. Oksman (1996) investigated the fractured surface from impact test with SEM, and reported that the poor adhesion between wood and polymer caused conspicuous interface between them and created voids around them. However, as Oksman and Clemons (1998) have pointed out, it is generally more difficult to differentiate wood particles from the PP matrix when there is good interaction between them. This suggests that small-size wood fillers may easily be missed in the investigation of fractured surfaces because of the roughness of the surface.

Furthermore, misinterpretation of SEM images in the past studies has led to misunderstanding of the bonding mechanism between woody material and thermoplastic matrix. For example, Felix & Gatenholm (1991) explained poor wetting of wood fiber with the PP matrix by the smooth surface of the fiber in the fractured surface, instead of poor bonding. Furthermore, they reported that fibers of filter paper tended to agglomerate into bundles and became unevenly distributed throughout the matrix due to the hydrogen bonds.

The objective of this study was to investigate the morphology of wood and PP composites in the dispersion of wood fillers within a PP matrix and the interface between them in the injection-molding composites by using wood anatomical techniques such as the thin-sectioning method coupled with optical microscopy and SEM coupled with chemical removal of cell wall material.

Materials and Methods

Materials  
Polypropylene (PP) powder was a commercial preparation. Wood flours were made from dry wood of poplar (Populus sp.) and China fir (Cunninghamia lanceolata) grown in China by a mill machine, and were screened to obtain a narrow particle-size distribution. Fibers for medium density fiberboard (MDF) from poplar were also used as a filling material. Table 1 shows the composition ratio, species and size of the wood fillers in the composites.

Processing  
Wood flours was oven-dried at 105 °C until the moisture content became less than 0.5%. PP and wood flour (and additives as stabilizers in case of MDF/PP) were pre-blended in a high speed mixer and then compounded in a co-rotating intermeshing twin-screw extruder. The barrel temperature was 190 °C. The extruded strands were cooled in a water bath, pelletized, and dried at 105 °C. The compounded pellets were injection-molded into standard tensile-test specimens at a temperature of 200 °C and pressure of 800 kN.

Optical microscopy  
Six small sample blocks (ca. 5 mm cubed) were dissected out of one of the test specimens from each sample (Fig. 1). Sections of 4 mm thickness were cut from every two sample blocks in three different planes using a rotary microtome equipped with a glass knife (Microm HM 340E). Specifically, the first plane was perpendicular to the longitudinal axis of the test specimen (cross section), the second was parallel to the axis and perpendicular to the original injection-molding surface (longitudinal section), and the third was parallel to the original surface (surface section). They were picked up on a slide glass and stained with an aqueous solution of 1% safranin and 0.3 % gentian

| Table 1. Composition and species of wood and polypropylene composites |
|------------------------|----------------------|------------------|
| Sample No. | Sample characteristic | Percent of wood filler (by weight) % | Wood species and particle size |
| 1 | Pure PP | 0 | Poplar, below 350μm |
| 2 | Wood-Flour/PP | 30 | Poplar, below 150 and 75μm |
| 3 | Wood-Flour/PP | 30 | Poplar, below 75μm |
| 4 | Wood-Flour/PP | 30 | China fir, below 75μm |
| 5 | Wood-Flour/PP | 30 | Poplar, fibers for MDF (additives: urea formaldehyde 12 %) |
violet, rinsed with water, dried in an oven at 60 °C, and then mounted with Canada balsa diluted with xylen.

To observe the shape and size of wood fillers within the composites, small pieces dissected form the test specimens were softened and plasticized on a slide glass heated at 190 °C on a hot plate, and pressed between slide glasses into a thin layer. After staining, they were mounted and pressed again to be spread between a slide glass and a cover glass with Canada balsam diluted with xylen on a hot plate at 150 °C.

The microscopic slides were investigated with biological, polarized-light and phase-contrast microscopes.

**Scanning electron microscopy**

One set of the sample blocks remaining after the sectioning was used to investigate the sectioned surfaces. Another set was treated alternatively with concentrated sulfuric acid and a mixture of hydrogen peroxide and acetic acid to remove cell wall materials completely according to the modified resin-casting method applying a thermo-elastic polymer (Fuji and Hatano 2000). However, the present specimens were treated at room temperature for 10 days, after which they were rinsed well with water and dried at 60 °C.

Both treated and untreated samples were coated with Pt in an ion-sputter coater at 1.5 keV for 7 min. The scanning electron microscope (SEM: Jeol JSM-840) was generally operated under the following conditions: accelerating voltage 5 keV; probe current ca. 1*10^{-9} A; objective diaphragm 50 µm in diameter; working distance 11 mm.

**Results and Discussion**

**Optical microscopic observations of wood flour/PP composites**

Optical microphotographs of Sample 2 are shown in Figs. 2 and 3. Wood fillers in the extended thin layer were not stained at all (Fig. 2a). Only large particles were conspicuously visible under an ordinary optical microscope owing to the accumulative coloration and reflection of cell walls, but small fillers such as fragments of fiber walls were obscure. However, they clearly appeared under a polarized microscope because of the birefringence of the secondary walls (Fig. 2b). Large particles were usually not bright in the polarized light images perhaps because of the high light absorption. It is obvious that wood flour was composed of both large and small particles. In contrast, wood fillers were stained well in sections (Fig. 3). These results suggest that wood particles and fibers within the thin layer were completely covered with the PP matrix and could not accept the dye. This agrees with the results and deductions of Takatani et al. (2000) that the wood fillers would not be susceptible to water outside the composite and to biological degradations because PP is highly hydrophobic or water repellent.

Wood particles and fibers in the sections were stained well with dyestuffs giving clear images in contrast to unstained PP matrix as a background (Fig. 3). Consequently, microscopic images of the sections were apparently clear enough to differentiate wood fillers from this PP matrix. Comparing cross and longitudinal sections, wood particles appeared more or less longer in the longitudinal section (Figs. 3a & b), and they tended to be orientated concentrically. In the surface section (Fig. 3c), wood particles appeared wider than those in the longitudinal
Here, it should be noted that the orientation of the pellets in the manufacturing process as well as the orientation of wood fillers within those pellets may significantly affect their orientation within the composites. Wood fillers may be orientated longitudinally and concentrically within each pellet and also those pellets may probably be orientated in the direction of the injection-molding.

Secondary walls of xylem elements were stained preferably with safranin and compound middle lamellae were stained with gentian violet. In monochrome photos, they appeared light gray and dark gray, respectively. Therefore, the structure of wood fillers was apparently distinguishable as wood particles, isolated fibers and fragments of cell walls (e.g. Fig. 4a). In the cross section of Sample 2 (Fig. 4a), large-size particles were well dispersed together with isolated fibers and small-size fragments. In sample 3 (Fig. 4b), the larger class of particles were apparently smaller than in Sample 2 owing to the screening below 150 μm, but also smaller-size fillers such as fibers and fragments were dispersed together despite the screening of over 75 μm.

In Sample 4 (Fig. 4c), where finer wood flour screened below 75 μm was used, only small-size particles and fragments of cell walls were observed and were well dispersed in PP matrix without any aggregation. In Sample 5 (Fig. 4d), where wood flour of Cunninghamia screened below 75 μm were used, wood fillers were mostly fragments of tracheid walls, and the dispersion and the orientation appeared to be similar to Sample 4 (Fig. 4c) regardless of the differences between softwood and hardwood.

**SEM observations of wood flour/PP composites**

Surfaces obtained by microtome-sectioning sometimes showed clear knife-marks, which were caused by a damaged knife-edge and were parallel to the direction of knife movement on the microtome. Wood fillers finely cut with a fine knife caused fewer knife-marks, but those roughly cut with a damaged knife left irregular surfaces (Figs. 5a & b). It is assumed that wood fillers were not so tightly bonded to the PP matrix that they could be pulled out a little by a moving knife-edge, and the PP behind them were pressed and deformed by such fiber walls. As a result, cavities developed around wood fillers and hollows extended in the direction of knife-marks (from right to left in Figs. 5a & b). Nevertheless, the wood fillers were restrained within the PP matrix against the sectioning force (Fig. 5b).

Large wood fillers such as wood particles were recognized in the microtome-planed surfaces because they were roughly cut in contrast to the fine surface of the PP matrix around them (Fig. 5a). Cell lumina of fibers in wood particles were usually impregnated fully or partly with PP. This result corresponds to the result of Oksman & Lindberg (1995) who observed a microtome-planed surface of a composite of wood flour and low density polyethylene by SEM. Small wood fillers such as fibers and fragments of cell
Fig. 4 Optical microphotographs of cross sections. a: Sample 2, b: Sample 3, c: Sample 4, d: Sample 5.

Fig. 5 SEM micrographs of microtome-planed blocks. a, c & d: Sample 3. b: sample 5. a-c: longitudinal section, d: surface section. a & b: untreated, c & d: treated for complete removal of cell wall materials.
walls were also often obvious as they were surrounded by voids or hollows, but occasionally not well defined from the PP matrix (Fig. 5b) despite their certain presence among wood particles as investigated in stained sections under an optical microscopes.

The distribution of wood fillers became conspicuous with the treatment of cell wall digestion (Fig. 5c). Small-size wood fillers such as fragments of cell walls left simple holes because they did not have any macro cavities inside to be impregnated with PP. Wood particles left complex cavities which maintained the cell arrangement. The cavities derived from each wood particle were partly disconnected from each other even though the cell walls in cross section usually appeared to be honeycombed. On the other hand, PP in the molds of wood particles were usually membranous and occasionally columnar in shape.

In the surface section, ray parenchyma cells appeared to be well impregnated with PP and showed clearly the shape of cells and pit cavities projecting from PP molding cell lumina (Fig. 5d). In contrast, PP filling fiber lumina were not as smooth as resin-casts of intact fibers (compare with figures by Fujii and Hatano 2000) but were complex with flat to wavy plates of PP filling cracks running along the fiber walls. These results suggest that PP penetrated very well into lumen cavities of cell inside particles through cracks of inter- and intra-walls. PP occasionally filled the lumina and in some other cases developed a lumen-lining layer forming a tube. Consequently, PP filling cracks extended to neighboring PP impregnated into cell lumina, comprising a three-dimensional network within a wood particle and also connecting to the PP matrix outside.

Observations of Sample 6

Fibers in Sample 6 (poplar MDF/PP) were mainly long wood fibers and partly fragments of wood fibers (Fig. 6a). Parenchyma cells and fragments of vessel walls were occasionally observed. In the cross section (Fig. 6b), there were roughly transverse sections of thin to thick-walled wood fibers. There were also incidentally contaminations of thick-walled latewood tracheids from coniferous wood, showing a secondary wall outlined by compound middle lamella. Flattened fibers were also often distributed among oblique to partly longitudinal sections of wood fiber walls. Fibers were well dispersed in the PP matrix and rarely aggregated with each other. They appeared to be overlapping in the section image, but they were practically separated in the depth of section. In the longitudinal section (Fig. 6c), fibers appeared more or less longer suggesting their longitudinal orientation within the composite.

In the cross section treated to remove cell wall material, fibers were separated from each other by the PP between them even when they were close together (Fig. 7a). Major part of fibers left simple holes without any contents, but some part of fibers had a thin to thick membranous layers of PP (Fig. 7b). Such membranous PP is presumed to be a lumen-lining layer which penetrates into fiber lumina through cuts, cracks and/or pit cavities on the lateral walls.
Conclusion

The thin sectioning method effectively visualized both the distribution and the structure of wood fillers within the PP matrix. The wood fillers were disperse very well inconsistent with the summary of Oksman and Lindberg (1995) citing earlier works that the cellulose fillers tend to form aggregates during the mixing due to the high degree of intermolecular hydrogen bonding. As a result of investigating of the sections in three different directions, wood fillers may probably be orientated longitudinally and concentrically during the processing to pellets and injection-molding. By the screening of the wood flour, large particles were removed, but numerous fragments of cell walls still remained. This result corresponds to the result of Stark and Berger (1997) that particle size distributions in wood flours screened with different meshes overlapped each other despite the narrower distributions in each sample. This may be caused by the aggregation of fibers and fragments each other and/or their adhesion to a large particle, and the dispersion during the blending with PP and the extrusion.

The interface between the wood and PP can be well illustrated by the chemical treatment to remove cell wall material. PP can penetrate into macro-cavities such as fiber lumina inside particles through cracks of inter- and intra-walls and comprises a three-dimensional network within a wood particle and also connecting to the PP matrix outside.

The high wetability of PP to wood cell wall was well illustrated with very thin lumen-lining layers and absence of bubbles in the interface. It is likely that wood fillers can be completely isolated and covered by PP owing to their high wetability to wood cell wall and high permeability into narrow macro-cavities. However, high wetability does not directly result in chemical bonding. It is obvious in the results that wood fillers in the sectioned surface were partly peeled off from the PP matrix but not completely pulled out. Cell wall sculptures such as pit cavities were often revealed with the chemical removal of cell wall material. There may be a mechanical rivet or anchor effect of PP. This suggests that the chemical bonding of wood fillers and PP matrix is more important for the improvement of the adhesion properties than the surface compatibility.

References

木材とポリプロピレン複合材料の微細構造

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要 旨
木材とポリプロピレン（PP）の複合材料における界面の構造および木粉の分布状態を、薄切片法による光学顕微鏡観察および細胞壁除去処理による走査電子顕微鏡観察により調べた。
木粉はPP中によく分散し、軸方向および同心円状に配列する傾向が見られた。木材とPPの界面は化学処理によって明らかとなり、PPが木材構成細胞の内腔や細胞壁の亀裂に浸透し、複合材料の全体に広がる三次元的な網状構造を形成していると考えられる。木粉はPPと強固に化学結合している訳ではないが、PP中で完全に隔離されていると考えられる。複合材料の性能向上のためには、木材とPPの相和性を改善するよりも、相互の化学結合を強化することが重要である。

キーワード：複合材料、木材、ポリプロピレン、形態学、構造学、走査電子顕微鏡、光学顕微鏡

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