

Extrudability of Solid Wood by Acetylation and *In-Situ* Polymerisation of Methyl Methacrylate

Masako Seki,^{a,*} Soichi Tanaka,^b Tsunehisa Miki,^a Ichinori Shigematsu,^a and Kozo Kanayama^b

Recently, a processing technique resembling plastic-type forming has been developed for solid wood. To improve the recyclability of the formed products, thermoplastics were used as a binder. In this study, a hydrophobic monomer of methylmethacrylate (MMA) was used as a thermoplastic binder and was impregnated into wood, then polymerised by heat to form polymethylmethacrylate (PMMA). The effects of wood acetylation, a hydrophobising treatment of wood, on the extrudability of solid wood impregnated with PMMA (wood-PMMA composite) during extrusion were investigated. The acetylated wood was found to swell much more after the PMMA treatment than the untreated wood. The extrusion loads obtained from capillary fluidity tests of the acetylated wood-PMMA composite were lower than those of untreated composite. The fluidity improvement by acetylation can be attributed to a weakening of the cohesive interactions in the wood polymer, and this is primarily caused by the acetylation reaction itself. When the acetylated wood-PMMA composite was repeatedly extruded, the starting load of the extrusion decreased with increasing extrusion repetitions, probably as a result of decreasing wood particle size.

Keywords: Wood; Extrusion; Composites; Thermoplasticity

Contact information: a: Eco-Renewable Materials Group, Structural Materials Research Institute, National Institute of Advanced Industrial Science and Technology, 463-8560, Japan; b: Laboratory of Sustainable Materials, Research Institute for Sustainable Humanosphere, Kyoto University, 611-0011, Japan; *Corresponding author: m-seki@aist.go.jp

INTRODUCTION

Wood forming techniques have been limited because of the poor deformability of wood. However, to obtain more complex products with woods, some techniques used for plastic forming, such as extrusion and injection molding, have been developed. For example, compound-type wood plastic composites (WPCs), which are generally produced by compounding wood flour with thermoplastic resin, are widely used in decks, louvers, and other construction materials (Clemons 2002). The application of such plastic forming techniques to wood primarily depends on the production of wood flour, which requires considerable energy and is expensive to produce.

Recently, an interesting wood flow phenomenon has been observed in solid wood containing water or certain binders (Yamashita *et al.* 2009; Miki *et al.* 2012, 2013, 2014; Seki *et al.* 2014). This phenomenon is caused by wood cell deformation and slippage between adjoining wood cells and occurs in a specific stress state during heating. Using this phenomenon, we have developed plastic forming techniques for use with solid wood, and we call these techniques “wood flow forming”.

Wood flow forming enables wood to be deformed into three-dimensional shapes without undue damage of wood cells in comparison with the wood flour used for WPCs.

In wood flow forming, binder impregnation during material preparation is the most important process, as it determines the fluidity during forming and controls the product characteristics. In this process, a binder is impregnated into the wood cell lumens and penetrates the cell wall. Previously, hydrophilic resins of lower molecular weight, such as phenol formaldehyde resin, melamine formaldehyde resin, and polyethylene glycol, have been used as binders (Miki *et al.* 2013). An earlier study suggested that the penetration of the binder into the cell wall is an important factor in generating the wood flow phenomenon. The wood fluidity during the forming process can vary widely, not only with the binder type but also with the binder content in the cell wall (Miki *et al.* 2013, 2014).

To meet recent requirements for products with more complex shapes and recyclability, we have conducted repetitive flow forming using a thermoplastic binder. For example, a hydrophobic monomer of methylmethacrylate (MMA) was used as a thermoplastic binder, which was impregnated into wood, and then polymerised into polymethylmethacrylate (PMMA). Woods impregnated with this thermoplastic binder can be extruded repeatedly during wood extrusion (Seki *et al.* 2014). However, the relationship between wood extrudability and binder penetration of the cell wall is not well understood. Generally, it is difficult for a hydrophobic liquid to penetrate the cell wall because of its low compatibility with the hydrophilic wood. Improving binder penetration of the cell wall should make it easier to generate wood flow.

Wood acetylation is one of the chemical modifications of wood to improve the dimensional stability (Stamm 1964). Obataya and Shibutani (2005) reported that acetylated wood, a type of hydrophobised wood, enables hydrophobic organic liquids to penetrate the cell wall. The fewer and weaker intermolecular hydrogen bonds present in the acetylated wood polymers enable greater penetration of hydrophobic organic liquids. Shiraishi (1986) reported that acetylation is an effective method for improving the affinity of wood with MMA, which can then be polymerised into PMMA within the cell wall. In this study, we focused on the chemical modification of wood by acetylation to improve the penetration of MMA.

The main objective of this study was to clarify the effects of wood acetylation on the extrudability of solid wood impregnated with a thermoplastic binder during wood extrusion. The experiments were conducted using both acetylated and untreated solid woods containing various amounts of PMMA (wood-PMMA composite) impregnated using MMA-ethanol solutions of various concentrations. To examine the polymer distribution in the composite, the inner structure of the wood and composite were observed. Capillary fluidity tests were performed, and the extrusion loads were investigated to determine the extrudability changes resulting from the acetylation and polymer content. Another purpose of this study was to investigate the possibility of repetitive forming technique using acetylated wood-PMMA composites. Capillary fluidity tests were repetitively conducted using the same wood-PMMA composites to investigate the extrudability changes during repetitive extrusion. Moreover, the wood particles in the extruded material were analysed by microscopic observation to determine the cause of the extrudability change.

EXPERIMENTAL

Wood Materials

Rotary-cut veneers of Japanese cypress (*Chamaecyparis obtusa*) were used in this study. Veneers approximately 3-mm thick (in the radial direction, R) were cut into 25-mm-diameter disks (longitudinal, L × tangential, T), and then completely dried in an oven at 105 °C.

Wood Acetylation

In the acetylation process, the wood materials were soaked in acetic anhydride under vacuum and then heated to 120 °C for 24 h. The acetylated wood materials were washed in water to remove the remaining acids and then completely dried at 105 °C. The weight gain after acetylation was found to be approximately 18%. Figure 1 shows the Fourier transform infrared spectroscopy (FTIR) spectra of the untreated and acetylated woods. The absorbance due to OH stretching in the range 3500 to 3300 cm^{-1} was decreased, and the absorbance peaks, which are assigned to the acetyl groups, at 1738 cm^{-1} (C=O stretching), 1369 cm^{-1} (C–H vibrations of the methoxy group), and 1222 cm^{-1} (C–O stretching) were increased remarkably with acetylation (Mohebbi 2008). These results indicated that the wood sample was acetylated successfully by which OH groups of wood polymers are substituted by acetyl groups.

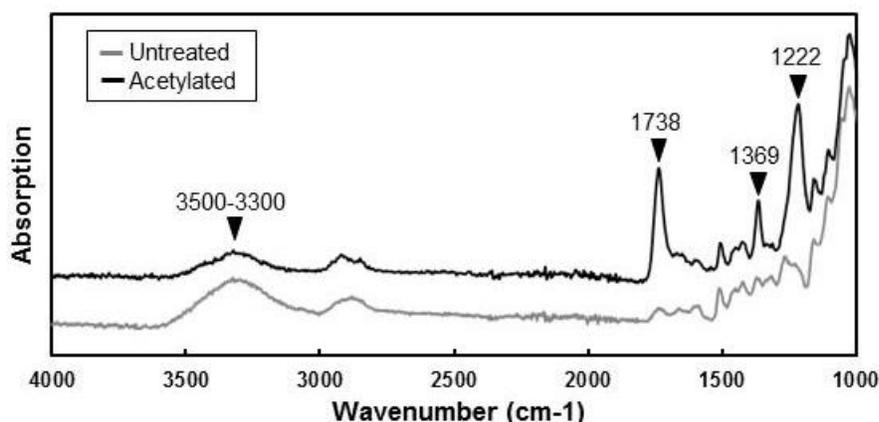


Fig. 1. FTIR spectra of the untreated and acetylated wood

Preparation of Wood-PMMA Composite

Figure 2 shows a schematic flow of the preparation of the wood-PMMA composites. To control the PMMA content of the composites, various concentrations of MMA-ethanol (MMA-EtOH) solutions were impregnated into untreated and acetylated woods under reduced pressure (Furuno and Goto 1978). Then, the impregnated woods were soaked in the solution at 30 °C under atmospheric pressure for 20 h, allowing the MMA-EtOH solution to penetrate the cell wall. A polymeric initiator (V-601, Wako Pure Chemical Industries, Japan, 10-h half-life decomposition temperature: 66 °C) equivalent to 1% of the MMA was added to the solution prior to the impregnation. The soaked wood was then hermetically sealed in aluminium foil to suppress MMA volatilisation and then placed in an oven at 85 °C for 24 h to polymerise the MMA. The polymerised samples were then vacuum dried at 50 °C for 5 h to remove unreacted MMA and ethanol. The grass transition of the wood-PMMA composites, which is attributed to the PMMA, was

confirmed using differential scanning calorimetry (DSC), which indicates that the impregnated MMA was polymerized in the wood samples. The weights of all impregnated samples and the tangential dimensions of five samples were measured to calculate the polymer content of the wood-PMMA composites and the wood-to-composite size change.

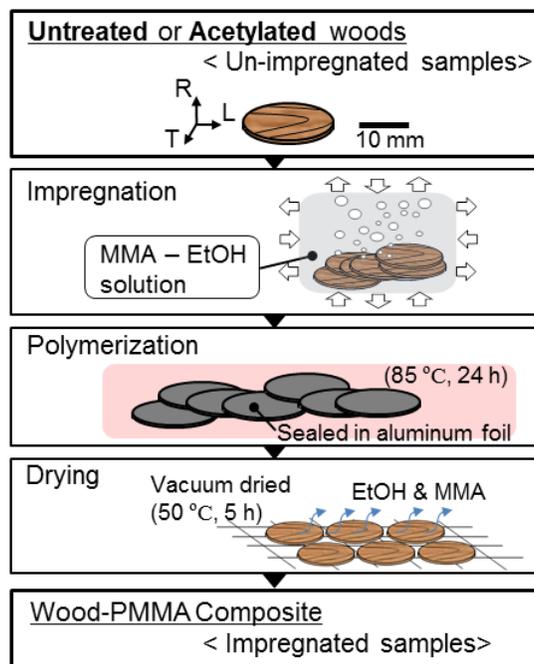


Fig. 2. Schematic flow of the preparation of wood-PMMA composites

Observation of the Inner Structure of Wood-PMMA Composite

The inner structure of the wood-PMMA composite was observed by the scanning electron microscope (SEM, JSM-5600ED, JEOL Ltd., Japan) with Au coating treatment over the cut surface. The cross sections of the wood and composite sample were cut using a rotary microtome (RMS, Nihon Microtome Laboratory, Inc., Japan). Then, thicknesses of the wood cell wall and intercellular layer were measured using the image analysis software (ImageJ, National Institutes of Health, USA) from the SEM micrographs at 1500-fold magnification. The thicknesses at the 50 points were measured for the each wood samples.

Capillary Fluidity Test

Figure 3 shows the experimental procedure employed for the capillary fluidity tests. The diameter of the barrel used was 30 mm, and a die containing a capillary tube 10 mm long and 4.0 mm in diameter was used to study the extrudability (*i.e.*, extrusion ratio: 56.25). As shown in Fig. 3, 25 g of impregnated or unimpregnated wood samples were stacked in the same fiber orientation direction and placed manually into the barrel followed by the punch, and these molds were placed in the servo press machine (V-1815, Saginomiya Seisakusyo, Inc., Japan). Then, the molds were heated to 160 to 170 °C. After 10 min of temperature equilibration, the punch was moved with displacement control (5 mm/min) until the distance from the capillary die was 2.0 mm. Then, the samples were compressed and extruded through the capillary while the force applied to the punch (F) was recorded. The sampling time was 500 ms.

To examine the extrudability changes during repetitive extrusion, approximately 20 g of extruded materials were chopped and reused in the next capillary fluidity test. The chopped materials were placed into the barrel again and supplemented with 5 g of unprocessed material. The materials were pre-compressed with a 10 kN load at room temperature, and then the temperature of the mold was increased to 160 to 170 °C and held for 10 min to equilibrate. Then, a second fluidity test was conducted under the same conditions as the first test. These reprocessing procedures were repeated three times.

Analysis of the Extruded Materials

The extruded materials were observed using a digital microscope (VHX-900, Keyence Corporation, Japan). After that, to investigate the wood particle size and morphological characteristic in the extruded materials, approximately 0.2 g of the extruded material was leached in acetone at room temperature for seven days to remove the PMMA. The separated woods were collected by filtration. Then, the wood parts were examined using scanning electron microscopy (SEM, JSM-5600ED, JEOL Ltd., Japan).

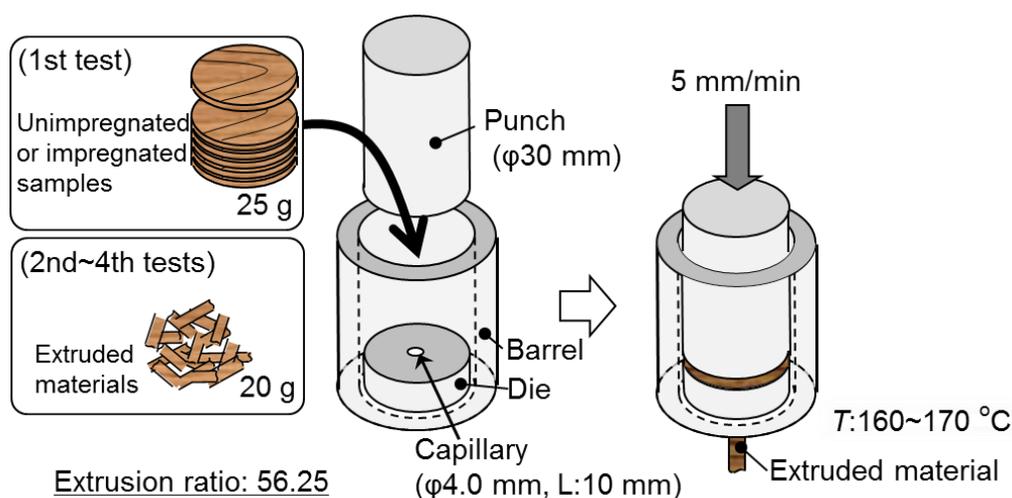


Fig. 3. Schematic illustration of the capillary fluidity test

RESULTS AND DISCUSSION

Polymer Content of the Wood-PMMA Composites and the Wood-to-Composite Size Change

Figures 4(a) and (b) show the polymer contents of wood-PMMA composites and the wood-to-composite size change in the tangential direction, respectively. The polymer content increased with increasing MMA concentration of the impregnated solution. The polymer contents of the untreated and acetylated samples were similar. On the other hand, remarkable differences were observed in the size change results, as shown in Fig. 4(b). In contrast with the untreated sample, which swelled only slightly, the acetylated samples swelled noticeably especially at higher MMA concentrations. These swelling behaviours were similar to those reported in previous studies (Furuno and Goto 1978; Wada and Fushitani 1992).

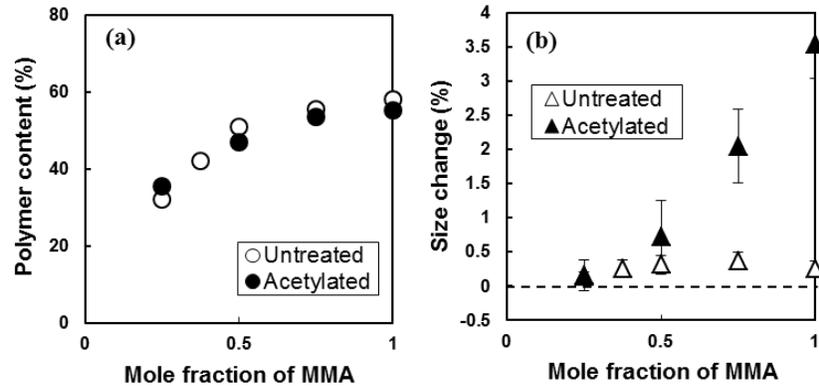


Fig. 4. (a) Polymer contents of wood-PMMA composites and (b) the wood-to-composite size change in the tangential direction

Inner Structure of Wood-PMMA Composite

To consider the distribution of PMMA in the wood-PMMA composite, the inner structure of the wood (un-impregnated) and composite (impregnated) samples were investigated. Figure 5 shows the scanning electron micrographs of transverse sections of the samples. The results show that a large majority of the cell lumens were filled with the PMMA by the impregnation of MMA in both untreated and acetylated woods.

Figure 6 shows the thicknesses of the cell wall and intercellular layer of the wood and composite samples. The micrograph in Fig. 6 shows the example of the thicknesses' measurement. There was no significant difference between the thicknesses of cell wall in untreated and acetylated samples for the un-impregnated samples. For the impregnated samples, the thickness of cell wall in acetylated sample was larger than those of the untreated samples. It is considered that the thickness increase of cell wall by the impregnation contributed to the noticeable swelling of the acetylated woods in Fig. 4(b).

The results from Figs. 4 to 6 suggested that the PMMA in the acetylated sample was present not only in the cell lumens but also in the cell walls, while most of the PMMA in the untreated sample was present in the cell lumen. Therefore, it is assumed that MMA is unable to penetrate the hydrophilic untreated wood polymers in which strong intermolecular hydrogen bonds are present. On the other hand, the acetylated wood polymers, where fewer and weaker intermolecular hydrogen bonds are present, showed an increased affinity with hydrophobic MMA.

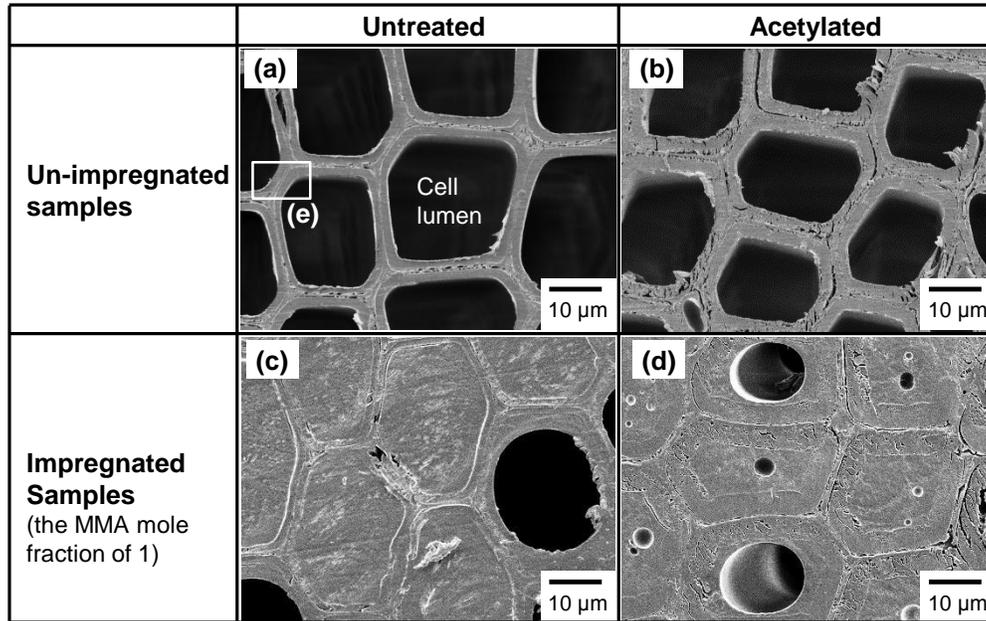


Fig. 5. Scanning electron micrographs of transverse sections of the wood (un-impregnated) and composite (impregnated) samples

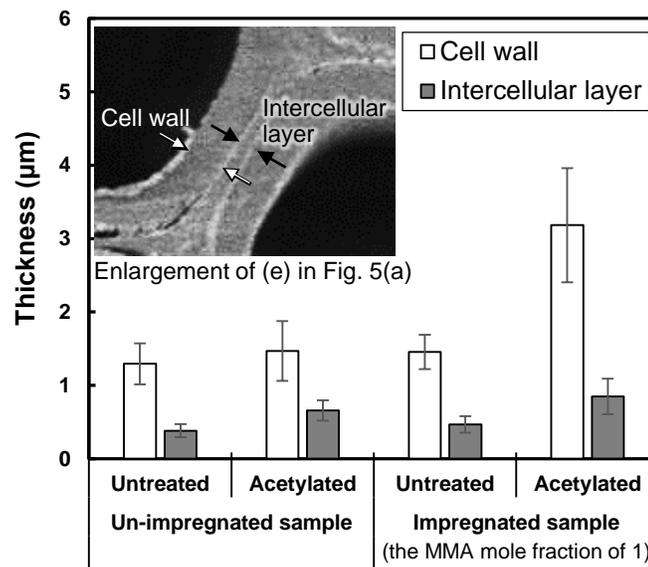


Fig. 6. Thicknesses of the cell wall and intercellular layer of the wood (un-impregnated) and composite (impregnated) samples

Extrudability of Wood-PMMA Composite

Figure 7 shows the load behaviour during capillary fluidity tests with both un-impregnated samples and samples impregnated with various concentrations of MMA solution (wood-PMMA composites). All of the results revealed an initial gradual increase in load, during which the samples were gradually compressed, underwent cell deformation, and became packed (Sandberg *et al.* 2013). Then, the load rapidly increased until the samples began to flow. Regardless of wood acetylation, the un-impregnated samples never

extruded at all through the capillary die. On the other hand, all of the impregnated samples extruded through the capillary die, and the load reached a relatively steady state.

Figure 8 shows examples of extruded materials obtained from capillary fluidity tests with untreated samples. Wood samples prepared with higher MMA concentrations were extruded continuously, and the strand shape was relatively uniform (Fig. 8(b)). On the other hand, the extruded materials that were prepared with lower MMA concentrations were extruded intermittently and did not attain a fixed shape (Fig. 8(a)). Extruded acetylated samples showed similar results. Therefore, the materials prepared with higher MMA concentrations contained sufficient matrix PMMA (as shown in Figs. 5(c) and (d)), which provided sufficient adhesion to hold the extruded samples together, whereas those prepared with low concentrations of MMA contained insufficient matrix PMMA (Fig. 4(a)).

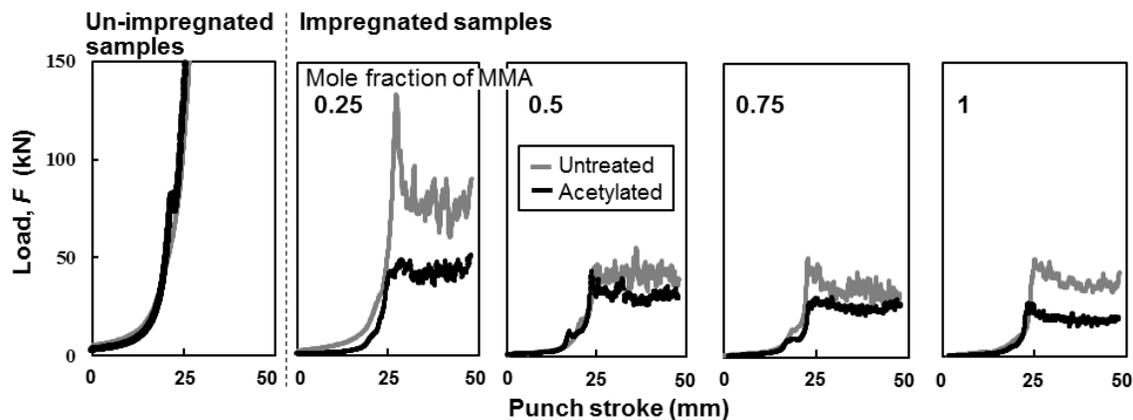


Fig. 7. Load behavior during capillary fluidity testing of un-impregnated samples and impregnated samples (wood-PMMA composites) prepared with various concentrations of MMA



(a) The MMA mole fraction of 0.25 (b) The MMA mole fraction of 1

Fig. 8. Extruded materials obtained from capillary fluidity tests of untreated samples

To compare the extrudability during extrusion between untreated and acetylated woods, the extrusion load F_E , the average load from 30 mm to 45 mm of punch stroke in Fig. 7, was plotted against the mole fraction of MMA in the impregnated solution and the polymer content, as shown in Figs. 9(a) and (b), respectively.

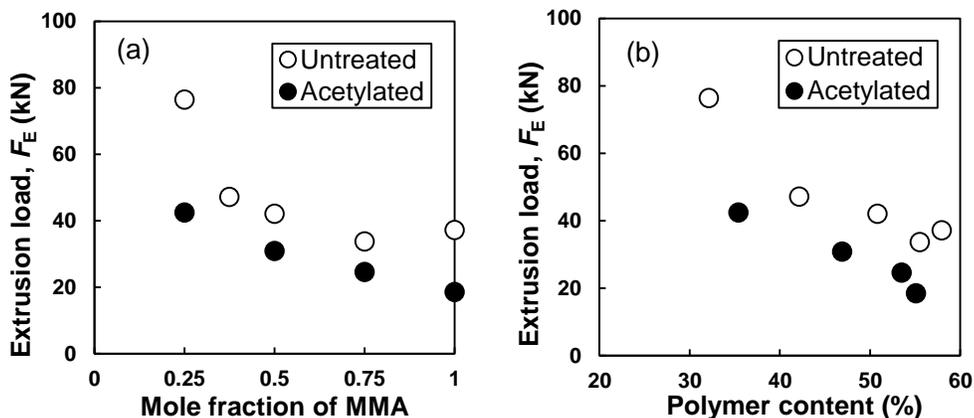


Fig. 9. Effect of (a) MMA concentration in the impregnated solution and of (b) polymer content on the extrusion load for acetylated and untreated wood-PMMA composites

The extrusion load in Figs. 9(a) and (b) tended to decrease with increasing MMA concentration and polymer content, respectively. These trends can be explained by the generally accepted belief that with more matrix resin present, the extrudability increasingly improves.

Comparison of the extrusion loads between untreated and acetylated samples indicates that the extrusion load of the acetylated samples was lower than those of untreated samples for all concentrations. This result suggests that the fluidity of wood-PMMA composites can be improved by wood acetylation. The difference in extrusion load between untreated and acetylated samples was larger for the lowest and highest MMA concentrations, as shown in Fig. 9(a). At the lowest concentration of 0.25 mole fraction, there was no difference in the polymer content or in the swelling of the wood samples, as shown in Fig. 4(b). Therefore, it seems that the fluidity difference at low concentrations can be attributed to the acetylation of the amorphous wood polymer, in which intermolecular hydrogen bonds are cut and hydroxyl groups are substituted with hydrophobic acetyl groups (Fig. 1). It is likely that this weakening of cohesive interaction in the wood polymer with acetylation markedly improves the composite fluidity when even a small amount of PMMA is added.

At higher polymer contents, the extrusion load of untreated wood remained high at higher concentrations, whereas that of acetylated wood decreased with increasing polymer content. It is speculated that the thermal softening characteristics of the acetylated wood may be changed due to the noticeable swelling of PMMA in the cell wall, as shown in Fig. 6. On the other hand, since the untreated wood contained less or no PMMA in the cell wall, it seems that the untreated cell wall needed a greater amount of energy to become small elements and go through the capillary. In future work we will attempt to evaluate the thermal softening behaviour of the acetylated wood impregnated with different concentration of PMMA.

Extrudability Change with Repetitive Extrusion

To investigate the extrudability changes during repetitive extrusion, capillary fluidity tests were conducted repeatedly using the same samples. All of the wood-PMMA composites were successfully repeatedly extruded several times. Figures 10(a) and (b) show the changes in the extrusion starting load, the load at the onset of extrusion in Fig. 7, and the extrusion load, respectively, with the number of extrusions for samples with the

highest MMA concentration. The extrusion starting load decreased with increasing extrusion repetitions, and it slowly approached a constant value in both wood samples. The extrusion load of the untreated wood showed a similar tendency to the extrusion starting load. However, the acetylated samples showed no marked change in these loads with increasing extrusion repetitions. The differences in the extrusion starting load and in extrusion load between untreated and acetylated samples gradually decreased as the number of extrusions increased.

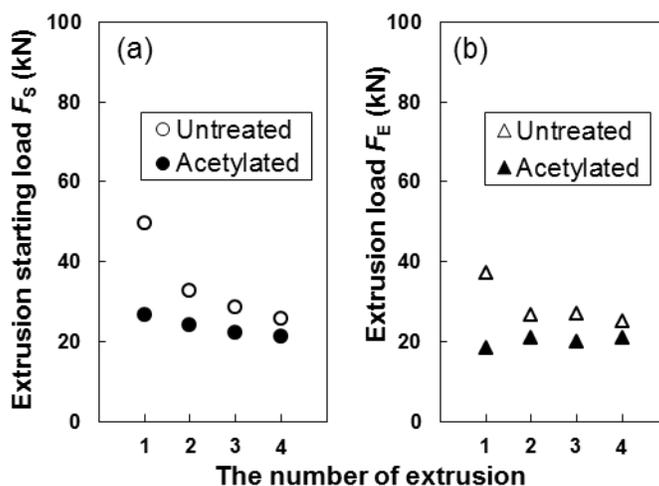


Fig. 10. Effect of repetitive extrusion on (a) the extrusion starting load and (b) the extrusion load for acetylated and untreated samples impregnated with the highest concentration of MMA (the MMA mole fraction of 1)

Figure 11 shows the microscopic images of wood particles obtained from the extruded materials after the PMMA-binder was leached out. The micrographs show that the size of the wood particles in both samples became smaller after repeated extrusion processes. It seems that these size changes in the wood particles during repeated extrusion resulted in a decrease in extrusion starting load with increasing extrusion repetitions, as shown in Fig. 10(a), because at first, the solid woods had to be fractured to fit through the capillary present in the extrusion die. From the result of wood size change during multiple extrusions (Fig. 10), the extrudability might become similar to WPCs using wood flour.

The morphological characteristics seemed to be different between the acetylated and untreated woods as shown in Fig. 11. In the first extrusion of the acetylated samples (Fig. 11(e)), some cells at the surface were almost peeled off. In contrast, untreated woods underwent no such peeling. After the second and subsequent extrusions, the acetylated wood particles appeared to be thin rod-like shapes and have more pointed tips than the untreated wood samples. The result indicates that the bundles of acetylated cells split easily during the successive extrusion.

Based on the results from Fig. 6, the thicknesses of intercellular layer in acetylated samples were larger than that in the untreated samples. This result suggests that the hydroxyl groups of wood polymer in the intercellular layer had been substituted with bulky hydrophobic acetyl groups. Rowell *et al.* (1994) also reported that the acetylated wood polymers exist particularly in intercellular layer form. It is speculated that the acetylated wood polymer in intercellular layer, where the original intermolecular hydrogen bonds were cut due to the acetylation, was the weakest point of the acetylated samples, and may

enable the acetylated cells to separate from each other with less fracture of the cell wall. We believe that this phenomenon in acetylated wood could be an advantage of the wood flow forming technique.

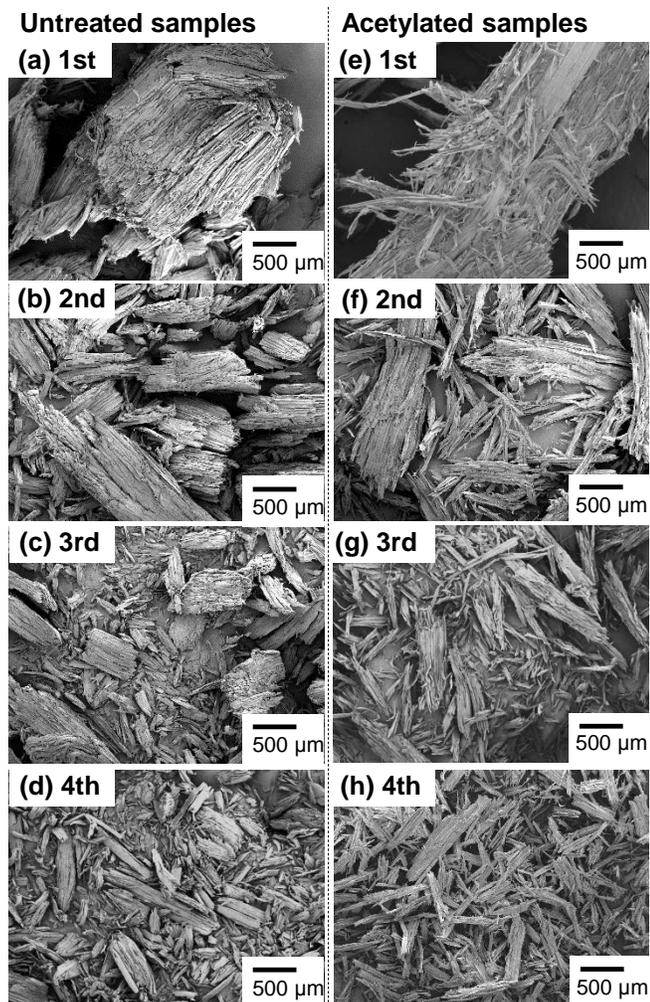


Fig. 11. Scanning electron micrographs of the wood particles in extruded materials after different numbers of extrusion (the MMA mole fraction used was 1)

CONCLUSIONS

1. Acetylated wood and its cell wall were found to undergo greater swelling with PMMA than untreated wood, especially at higher PMMA contents. The extrusion loads of acetylated samples were lower than those of untreated samples. The fluidity improvement by acetylation can be attributed to a weakening of the cohesive interactions in the wood polymer primarily caused by the acetylation reaction itself.
2. Acetylated wood-PMMA composites were successfully repeatedly extruded. The extrusion starting load was decreased with increasing extrusion repetitions, and slowly approached a constant value. The size of the wood particles in the extruded material became smaller as the extrusions were repeated. Therefore, the change in size of the wood particles resulted in a decreasing extrusion starting load with increasing extrusion

repetitions. Moreover, the acetylated wood cells were separated from each other with less fracture of the cell wall, whereas the cell wall in untreated woods fractured during the extrusion.

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