



# Direct spectroscopic detection of binding formation by kneading of biomass filler and acid-modified resin



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## ABSTRACT

Compatibilizers added into filler-reinforced polymer composites are supposed to bring about the enhancement of mechanical properties by binding with the filler and entanglement with the polymer matrix. We elucidated the binding of maleic anhydride-modified polypropylene (MAPP) compatibilizer and microcrystalline cellulose (MCC) filler. This is usually not readily detectable by spectroscopy. For this, we adopted a set of enzymatic digestion and refined but simple spectroscopy. A series of binary composites of MCC and MAPP was prepared by kneading. By the cellulolytic treatment and an adequate heat processing, we obtained clear IR signals due to the binding. Furthermore, by gel (swollen)-state NMR method which has attracted attention for analyzing plant cell wall, we acquired interface-specific liquid-state NMR spectra giving the information of the bonds between these components insoluble in commonly used solvents. Such analytical methods provide a useful perspective on the relationship between the microstructure and compatibility of composite materials.

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## 1. Introduction

What is the role of acid-modified polyolefins as compatibilizers in filler-reinforced polymer composites? Briefly, their performance is supposed to combine with the filler and to intertwine with molecular chains of the matrix resin. Mechanical properties of the composites are likely improved by these effects. Although such understanding is very common in the industrial sector as well as the academic community, has there been the direct experimental evidence of these effects of the compatibilizing agents? In general, it is just ideal to improve the mechanical properties of the composites with the addition of as a small amount of compatibilizer as possible. Approaches to analyze the role at the molecular level thus seem to be rather inactive. However, by clarifying the binding sites that compatibilizers can form, we believe the possibility of further

enhancement of physical properties. In turn, we expect that it will lead to the impactful applications of filler-reinforced polymer composite materials, such as weight saving for automobiles.

We here focus on the bond formation in the composite systems of cellulose and acid-modified polyolefin resin [1]; the action mechanism appears to be easy to understand, among a number of combinations of fillers and compatibilizers. We study a binary composite system prepared by kneading microcrystalline cellulose (MCC) powder and maleic anhydride-modified polypropylene (MAPP).

The binding of cellulosic filler and MAPP is assumed as follows: hydrogen bonds between the surface hydroxyl groups of cellulose and the acid modification part of MAPP are rather less involved [2], whereas ester bonds between them are formed and they are mainly working positively [2,3]. The monomeric maleic anhydride is highly reactive to form ester bonds with cellulosic solids in the absence of solvent and catalyst at 60 °C or higher [4]. Although commercial MAPP products have different modification rates and molecular weights depending on the brand name, it is generally believed that acid anhydride moieties introduced as succinic anhydride groups

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by bonding to PP main chains can react by kneading at  $\geq \sim 130$  °C at which the MAPP is in molten state. The kneading process is supposed to give monoester or diester linkage between cellulose and MAPP, as illustrated in Scheme 1.

In previous prominent studies, IR spectroscopy useful for analysis of solids has been employed to demonstrate the formation of the covalent bonds in cellulosic filler/polyolefin composites containing the compatibilizer [2,3]. In these examples, in order to obtain the spectroscopic evidence, experimental efforts have been devised, such as solvent-extraction of the free (unbound) polyolefin component and heat-treatment of MAPP to activate (ring closure) acid functional groups. However, in general, the modification rate (acid unit weight fraction) of the acid-modified resins is as low as several percent. Since the amount of acid-modified resin added to the entire composite is also usually a few percent, it is actually difficult to directly detect the binding state by the spectroscopic method.

In the present study, we elucidate the fact that covalent bonds are formed between cellulosic filler and MAPP, not only by the solvent extraction which has been attempted so far, but also by a selective enzymatic digestion of the cellulosic component. This accomplishes a condensation of the binding sites of cellulose and MAPP and the sensitivity of the ordinary IR spectroscopy can be improved. In addition, we also make effective use of NMR with higher resolution; for this purpose, we adopt a modern method called “gel (swollen)-state NMR”, which has recently been drawing attention in analysis of plant cells [5,6]. This is the same procedure as the conventional liquid (solution)-state NMR which is useful as a method for quantitative identification of molecular structures. By using this swollen-state NMR method, the surface and interface of samples are selectively swollen by the deuterated NMR solvent and the molecular mobility of those parts is improved. It is thus suitable for analysis of the interface of composite materials. We show that the binding of cellulosic filler and acid modified resin can be detected by a series of experiments including condensation of binding sites and spectroscopy.

## 2. Experimental section

### 2.1. Materials

Avicel PH-101 with a maximum particle size of 50  $\mu\text{m}$  was used as the MCC, which was purchased from Sigma-Aldrich Co. LLC. Kayabrid 006 was used as the MAPP, which was produced by Kayaku Akzo Corporation (Japan). The nominal MA grafting level (wt%) and weight-average molecular weight were 2 wt% and 75,000, respectively. The MA grafting level of 2 wt% corresponds to the incorporation of one MA-derived anhydride moiety per 126 repeating units of PP. Melt flow rate (MFR) of the MAPP was 50 g/10 min at 180 °C/2.16 kgf. Industrial cellulase “Meicelase” derived from the fungus *Trichoderma viride* is a product of Meiji Seika Pharma Co., Ltd. (Japan) and was used for the enzymatic hydrolysis of the

cellulosic component. 0.1-mol/L acetate buffer (pH 5.0 at 20 °C) was purchased from Nacalai Tesque Corporation (Japan). Xylene (Nacalai Tesque, Inc. (Japan)) was used as an extracting solvent for the polyolefin ingredient, containing xylene 90% of xylene and 6% of ethyl benzene according to the manufacturer. Dimethyl sulfoxide (DMSO)- $d_6$ , (Wako Pure Chemical Industries, Ltd. (Japan)), pyridine- $d_5$  (Cambridge Isotope Laboratories, Inc (MA, USA)), and  $\text{CDCl}_3$ - $d$  (Wako Pure Chemical Industries, Ltd. (Japan)) were used as solvents for liquid-state NMR procedures.

### 2.2. Preparation of MCC/MAPP binary composites

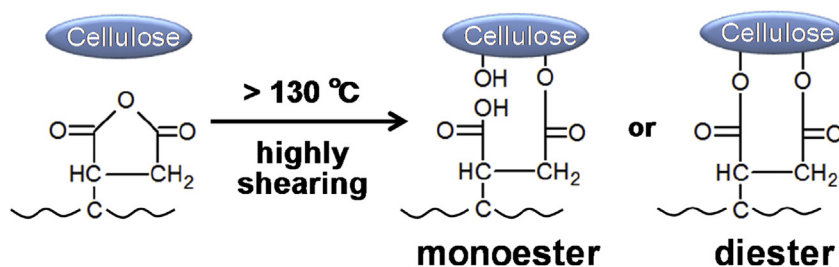
MCC and MAPP were first premixed in a plastic bag by shaking for 10 s. The MAPP content was fixed at 10 wt% in the mixture (MCC/MAPP = 90/10 in weight). The premixed MCC/MAPP mixtures were kneaded using a triple-arm planetary mixer Trimix (TX-0.5, Inoue Mfg., Inc. (Japan)). The series of MCC/MAPP composites were prepared by kneading at 120 or 160 °C for 5 or 10 min at 125.6 rpm (rotation) and 40.9 rpm (revolution). Thus obtained composites were all in a powdery state. A naming code MCC/MAPP-x-y indicates the composite sample prepared by kneading at x °C for y min.

### 2.3. Enzymatic digestion of the cellulosic component for MCC/MAPP

The MCC/MAPP samples were dried in vacuum at 40 °C for 24 h before use. 2.5 g of a MCC/MAPP composite was added into a flask and mixed with 675 mL of 50-mM acetate buffer and 180 mL of 1-mg/mL enzyme solution. The solid-liquid mixture was mechanically stirred at 45 °C and 300 rpm for 48 h. The additive amount of cellulase coincides with 19 filter paper unit (FPU)/g-MCC component [7]. After that, the mixture was filtrated with a 60-mm $\phi$  filter paper (No. 4, Kiriya Glass Co.) and the recovered solid part was washed with distilled water. Subsequently, the solid residue was freeze-dried for 5 h and then it was provided for further 24-h enzymatic treatment. Finally, enzymatically hydrolyzed MCC/MAPP (coded as MCC/MAPP-E) was washed and lyophilized for 5 h and vacuum-dried at 40 °C for 24 h.

### 2.4. Extraction of MAPP by hot xylene

The MCC/MAPP samples were dried in vacuum at 40 °C for 24 h. 2.0 g of the MCC/MAPP was loaded in a filter paper thimble (No. 84 (25  $\times$  90 mm), Toyo Roshi Kaisha, Ltd. (Japan)) and the thimble was set in a 1000-mL separable flask. 500 mL of xylene was poured into the flask and the system was heated at 150 °C to reflux. After three sets of the reflux for 8 h with adding fresh xylene for each, the extracted MCC/MAPP (coded as MCC/MAPP-X) samples were vacuum-dried at 40 °C for 24 h.



**Scheme 1.** Reaction scheme for mono- and diester formations between MCC and MAPP by kneading at higher than 130 °C.

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