

Transcrystalline morphology and mechanical properties in polypropylene composites containing cellulose treated with sodium hydroxide and cellulase

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To evaluate the transcrystalline effects caused by various fibers, which were untreated, or treated with sodium hydroxide and cellulase, isothermal crystallization was performed. It was observed that the untreated and cellulase-treated cellulose fibers (cellulose I) had a nucleating ability to transcrystallize at PP matrix. Especially, cellulose fibers treated with Sodium hydroxide (cellulose II) transcrystallized at PP matrix. This result was different from other's. Cellulose fibers also transcrystallized at PP/MAH-PP matrix irrespective of the type of cellulose crystalline structure. In PP/MAH-PP/CELL system, MAH-PP was located around the fiber surface at initial crystallization time, but was gradually expelled from that with the increase of crystallization time, and existed at outer boundaries of transcrystalline region at the final crystallization time. These phenomena were confirmed by IR-IRS spectra. The tensile strength of PP/CELL and PP/MAH-PP/CELL composites decreased with the increase of isothermal crystallization time. Therefore, it is thought that transcrystallinity gives rise to negative effect of tensile strength. © 2000 Kluwer Academic Publishers

Nomenclature

| | |
|-------------------|--|
| 1) PP | isotactic Polypropylene |
| 2) CELL | Cellulose |
| 3) U-CELL | Untreated Cellulose |
| 4) N-CELL | Cellulose treated with NaOH |
| 5) E-CELL | Cellulose treated with cellulase |
| 6) NE-CELL | Cellulose treated with cellulase after pretreating with NaOH |
| 7) MAH-PP | Maleic-anhydride modified Polypropylene |
| 8) PP/MAH-PP | 6) + 7) copolymers |
| 9) PP/MAH-PP/CELL | 2) + 9) composites |
| 10) UPC | U-CELL/PPcomposites |
| 11) NPC | N-CELL/PP composites |

12) EPC

13) NEPC

14) UMPC

15) NMPC

16) EMPC

17) NEMPC

E-CELL/PP composites

NE-CELL/PP composites

U-CELL/PP/MAH-PP composites

N-CELL/PP/MAH-PP composites

E-CELL/PP/MAH-PP composites

NE-CELL/PP/MAH-PP composites

1. Introduction

Cellulose has many advantages, such as biodegradability and low density and cost [1–3]. However, cellulose also has disadvantages, such as low processing temperature and poor bonding with thermoplastic polymer [4, 5]. Among these disadvantages, interfacial

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interaction in the composite containing a hydrophillic cellulose and a hydrophobic matrix is the most problematical, because it has a significant effect on the final properties of composite.

A number of attempts have been made to improve adhesion between the phases. Previous studies are characterized into two categories. First, there are general methods using coupling agents [6–8], surfactants [9, 10], and compatibilizer [11–13] in order to improve the mechanical properties by the enhancement of dispersion, adhesion, and compatibility.

Second, the studies on the improvement of mechanical properties of composites by annealing and isothermal crystallization have been investigated. Among the various phenomena caused by the above treatments, most attention has been recently paid to the transcrystalline phenomenon in connection with the correlations between transcrystalline morphology and mechanical property.

Jenckel *et al.* [14] reported that in the case of thermoplastic/fiber composites, a transcrystalline region around fiber appeared when the polymer melt was cooled in contact with a fiber. This region grows perpendicular to the fiber surface with a columnar or disk-like morphology. However, the mechanism for the occurrence of transcrystallinity has not been fully identified. Several authors have reported that the presence of transcrystallinity on the fiber's surface can enhance the bonding of the matrix/fiber interface [15–17]. However, there were other results that indicate no, or a negative, effect on interfacial bonding [18–21].

In this study, we prepared various PP/cellulose composites, which contained celluloses treated with sodium hydroxide and cellulase, and with maleic-anhydride polypropylene MAH-PP as an additive, using compression molding techniques. The effects of nucleating ability of untreated or treated cellulose fibers against PP were investigated. The influences of MAH-PP in the transcrystalline morphology of PP were also studied. The changes of the microstructure and mechanical property in the composites under the isothermal crystallization were investigated.

2. Experimental procedure

2.1. Material

The isotactic Polypropylene (PP) and the low density polyethylene (LDPE) used as a matrix were SJ-170 (M_w : 197000, M_n : 35000) and G-5321 (M_w : 140000, M_n : 19000) produced by Honam Petrochemical Co., respectively. A commercially available maleic anhydride-g-polypropylene (MAH-PP) (6 wt% maleic anhydride) used as an additive was supplied by the same company. The ground hardwood pulp, cellulose short fiber, was used as a filler. The ground hardwood pulp in panel form, 10 × 10 mm, was ground with a grinder for 8 min. The aspect ratio (length/diameter) of the ground hardwood pulp was 12.8. Rayon fiber (30 denier) used as a filler was purchased from Ashai Kashei Co. The cellulase enzyme was Celluclast 1.5L (Novo Nordisk, Denmark). Sodium hydroxide (NaOH) was purchased from TEDIA. Sodium acetate and acetic acid, both purchased from Showa Chemical Co., Ltd., were employed to make a buffer solution.

2.2. Specimen preparation

2.2.1. Preparation of cellulose treated with NaOH

The pretreated cellulose was prepared by treating cellulose with a 20 wt% NaOH solution at 10 °C, for 3 and 30 min, and then washed and dried.

2.2.2. Preparation of cellulose treated with cellulase

Cellulase treatment of cellulose was performed at a cellulase concentration of 3 g/L, 50 °C, and bath ratio of 1 : 20 in the pH : 4.8 buffer solution, according to optimum conditions recommended by Novo Nordisk Co. [22]. The cellulase treating time on cellulose was 0.5 hr. After the cellulose was treated with cellulase, the cellulose was washed immediately with distilled water ~90 °C and then dried under vacuum for 2 days.

2.2.3. Preparation of cellulose treated with cellulase after pretreating with NaOH

The cellulose pretreated with NaOH was retreated with cellulase in the same manner as described above.

2.2.4. Preparation of composite films

PP/various cellulose composites with or without MAH-PP (10 wt%) were mixed at 180 °C on Haake Internal Mixer (Rheomix[®]82; 600). The mixtures were placed between two teflon sheets and laterally contained in a 2.5 mm thick steel frame. After the whole system was inserted within hot plates at 180 °C, the whole system was inserted to ice-water for quenching films, or was inserted to oven heated at 120 °C for 1, 3, 5, and 10 mins for isothermal crystallized films.

2.3. Observations

2.3.1. Morphological analysis

Crystallization behavior was observed using a hot stage (Mettler FP82 AT) under the Leitz optical microscope (Leitz Laborlux 12 POLS) fitted with polarizers. A Olympus camera was fitted to a microscope for taking micrographs. A small piece of the PP film, previously pressed at 180 °C for 10 mins between microscopic slide, was placed on a hot stage held at 180 °C. The untreated or treated fiber was set on the molten PP and, covered by a further piece of PP and cover slip. This was maintained at 180 °C for 10 mins. The sample was then allowed to cool at a rate of 20 °C/min to the desired crystallization temperature, 120 °C. The crystallization behaviors of these samples were recorded with a Olympus camera, and transcrystalline size was also determined by micrometer as a function of crystallization times. Crystalline morphology was also investigated of a cellulase treated fiber and rayon fiber systems using LDPE as a matrix under the same conditions.

2.3.2. Wide-angle X-ray diffraction (WAXD)

The wide-angle X-ray diffraction (WAXD) patterns of the untreated and treated celluloses and PP/various cellulose composites were recorded with a X-ray diffractometer (Ni-filtered Cu K_{α} radiation, Rigaku Denki, Japan) at 40 kv, 40 mA.

2.3.3. DSC characterization

Thermal properties of the various composites were examined with differential scanning calorimetry (DSC) (Perkin-Elmer, DSC7) at a heating rate of 10 °C/min.

2.3.4. Internal reflection spectroscopy

IR-IRS spectra (Internal Reflection Spectroscopy) (Magna IR spectrometer 550, Nicolet, USA) of composites containing with MAH-PP were performed to investigate the interaction between cellulose and MAH-PP in composites with crystallization time.

2.3.5. Tensile properties

Mechanical properties of the various composites were obtained with a Universal tester (Instron M/C, Series 4) at crosshead speed of 4 mm/min.

3. Results and discussion

Fig. 1 shows the optical micrographs of transcrystalline morphology of the PP containing a U-CELL which has been isothermally crystallized at 120 °C.

U-CELL acts as a nucleating agent to PP and nucleation occurs preferentially along the fiber axes. As



(a)



(b)

Figure 1 Optical micrographs of transcrystalline effect in the iPP/U-CELL samples crystallized at 120 °C with different time for: (a) 0.5 min, (b) 1 min.

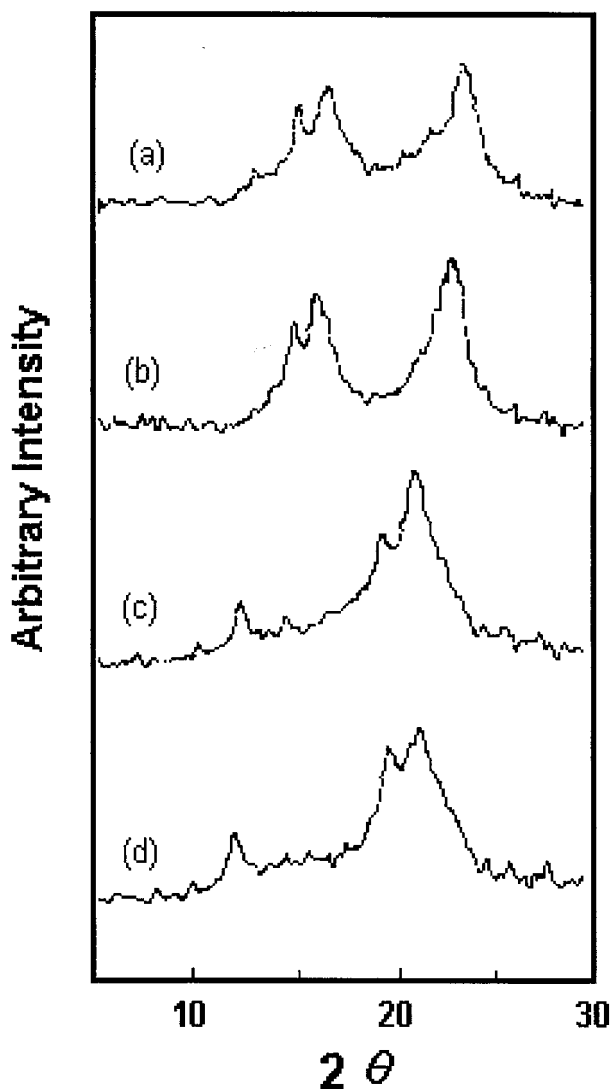


Figure 2 X-ray diffraction patterns of various cellulose: (a) untreated cellulose, (b) cellulose treated with cellulase, (c) cellulose treated with NaOH, (d) cellulose treated with cellulase after pretreating with NaOH.

the isothermal crystallization time increased, transcrystalline regions around fiber and spherulites in PP matrix propagated continuously. Their growths were terminated at certain time due to the impingement between them.

WAXD patterns of U-CELL, E-CELL, N-CELL, and N,E-CELL are shown in Fig. 2. The WAXD pattern of the U-CELL exhibits the diffraction profile based on the typical cellulose I. E-CELL has a crystalline structure of cellulose I, though cellulose fiber is treated with cellulase. That of N-CELL is changed from cellulose I to cellulose II. This phenomenon is in accord with the result by mercerization of cotton fiber. It can be seen that the crystalline structure of N,E-CELL, which is treated with cellulase after pretreatment of NaOH, was not changed, keeping cellulose II structure as well as that of N-CELL [23, 22].

Fig. 3 shows the transcrystalline morphology of the PP containing N-CELL, which has the crystalline structure of cellulose II, under the above conditions. It manifests that N-CELL has a nucleating ability to PP as well as U-CELL. The transcrystalline growth increased gradually with the increase of crystallization

time, though it was less effective in N-CELL than in U-CELL. The transcrystalline morphology of N-CELL treated with NaOH for 30 minutes also have the same trend, as indicated in Fig. 4b.

Gray *et al.* reported that no transcrystallization was induced on Fortisan or other regenerated cellulose fibers despite a variety of chemical and physical treatments, whereas the fibers such as cotton, purified wood fibers transcrystallized readily during crystallizations [24]. Quillin *et al.* also reported that when natural ramie fiber and rayon fiber were embedded in PP matrix during crystallization, the former had an ability to transcrystallize, but the latter didn't [25]. But our results contradict previous work as shown in Figs 3 and 4a and b.

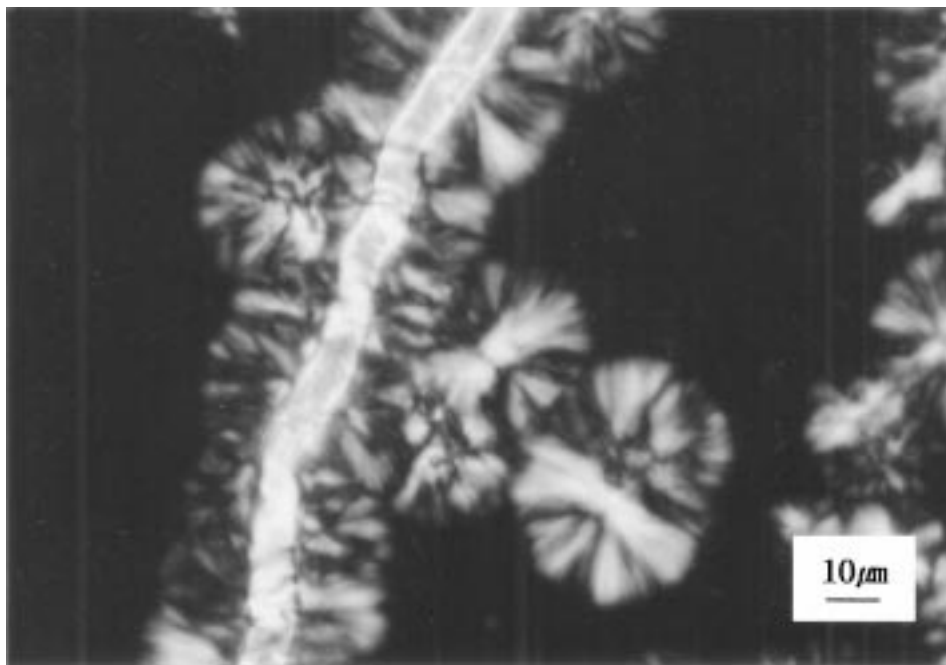
Fig. 4c and d show the transcrystalline morphologies of LDPE containing N-CELL and rayon fiber, respectively. It is also obvious from the optical microscopic results that N-CELL and rayon fiber have an ability to transcrystallize to LDPE even though their nucleating ability to LDPE was less effective than that to PP.

Among the various mechanisms [26–31] which account for transcrystalline phenomenon, the most noticeable mechanisms are those concerned with crystal structure matching between matrix and fibers.

Quillin *et al.* [25] explained that by using the mechanism of crystal structure matching noted by Wittman and Lotz [32], transcrystallinity was caused by providing sufficiently similar spacings of pyranose rings of cellulose I to methyl groups of PP in a flat manner; but, in the case of cellulose II, transcrystallinity did not occur because the cellulose II was not aligned in a flat manner. Felix *et al.* suggested that transcrystallinity occurred by the interaction of PP and cellulose at molecular level attributable to the adsorption configuration and the matching of interaction sites [33]. However, the mechanism suggested by Quillin cannot fully explain the phenomenon of transcrystallinity because in the case of cellulose II without sufficiently similar spacings to methyl groups of PP in a flat manner, transcrystallinity did also occur. In addition, in the case of cellulose II and LDPE system with absolutely different spacings, the occurrence of transcrystallinity cannot be explained. It is quite certain that Felix's mechanism is not complete because transcrystallinity occurred even though matrix and fiber had different adsorption configuration and the mismatching of interaction sites. Also, Bessel *et al.* reported that transcrystallinity occurred in the nylon 6/glass fiber system, but the lattice matching criteria for nucleation is invalid because of the amorphous structure of the glass [21]. However, in our results, it is also obvious that the more crystalline structure is similar, the more transcrystallinity is effective.

The transcrystalline morphologies of the PP samples containing E-CELL and NE-CELL are presented in Fig. 5. It was shown that transcrystallinity was occurred in both cases and the growth rate of E-CELL is higher than that of NE-CELL.

Fig. 6 shows the transcrystalline growth of the PP containing various celluloses as a function of crystallization time. The growth rate shows a linear



(a)



(b)

Figure 3 Optical micrographs of transcrystalline effect in the iPP/N-CELL samples crystallized at 120°C with different time for: (a) 0.5 min, (b) 1 min.

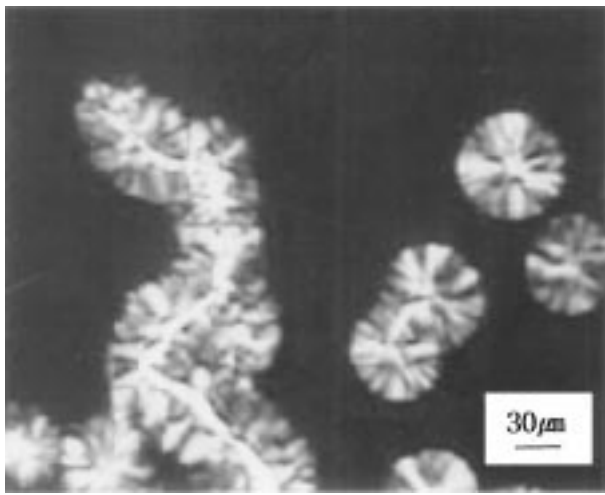
increase until the transcrystalline layer impinges on the spherulites at the bulk. The order of the growth rate is classified by E-CELL > U-CELL > NE-CELL > N-CELL. The growth rate of E-CELL is faster than that of U-CELL, though E-CELL and U-CELL have the same crystal structure (cellulose I). The growth rate of NE-CELL is more effective than that of N-CELL.

Bessell *et al.* [21] reported that as the number of nuclei increases the growing crystallites quickly impinge on their neighbors, and the difference in nucleating ability of filler is caused by crystallite size and the perfection and orientation of the filler lattice. They also reported that fiber surface topography such

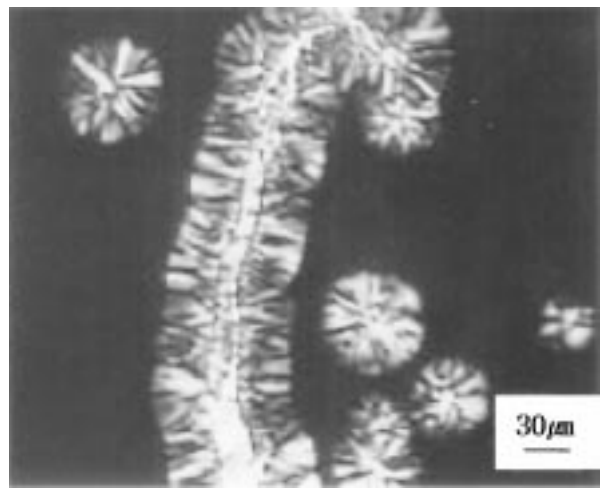
as smoothing and roughening didn't affect nucleation [21].

It is well known that treating cellulose with cellulase hardly affects crystalline region of cellulose. The crystalline structure of cellulose doesn't change by cellulase treatment as shown in Fig. 2. Therefore, we assume that the enhancement of the transcrystallinity growth rate can be caused by the enlargement of the effective surface areas and roughness in the cellulose surface due to cellulase treatments.

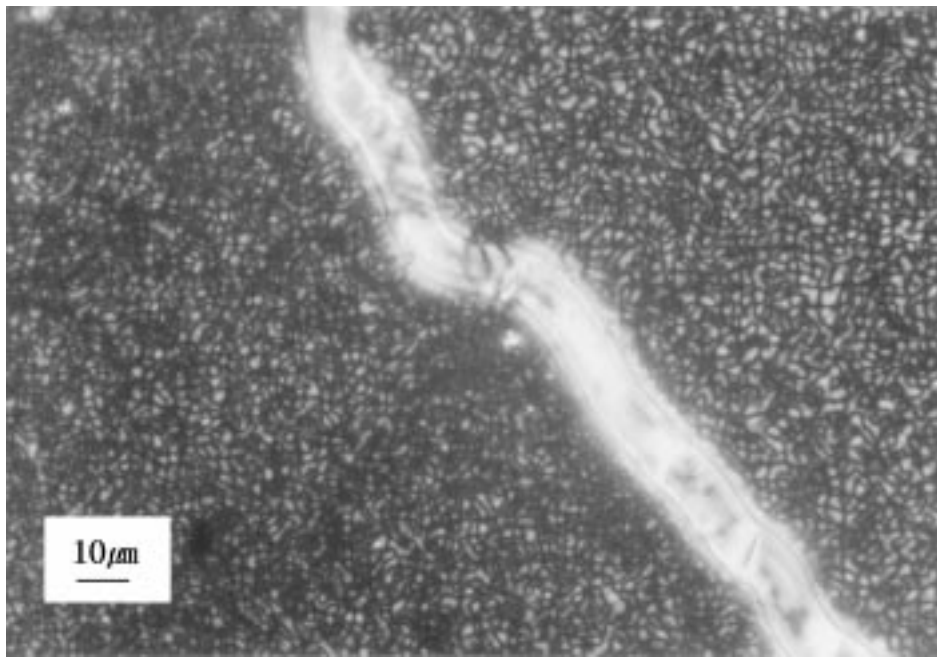
Fig. 7 exhibits the WAXD patterns of UPC and NEPC, which was manufactured by adding U-CELL and NE-CELL (30 phrs) to PP. In pure PP, the important peaks characteristic of the α -phase can be found at



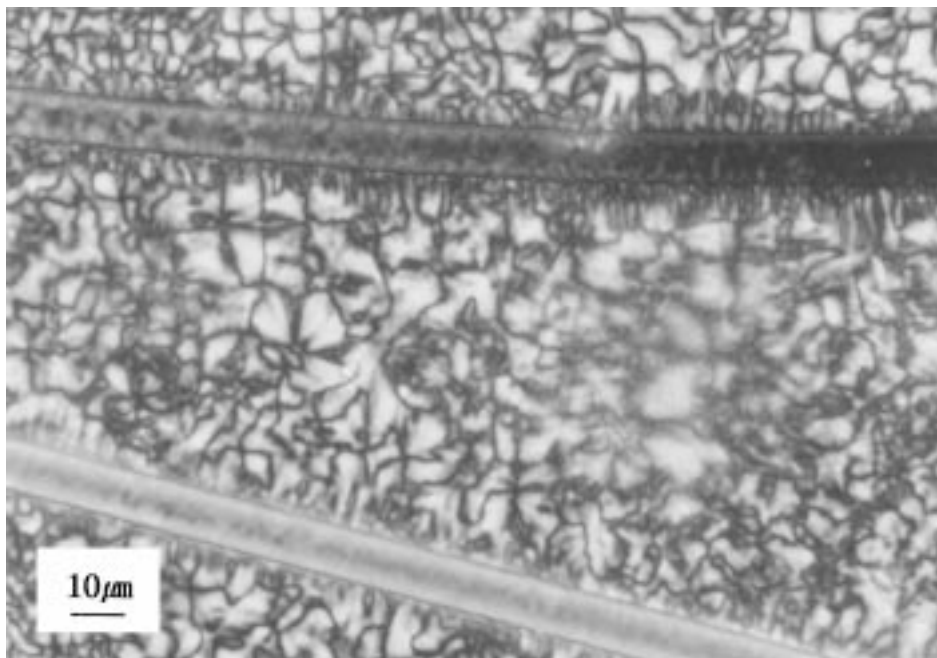
(a)



(b)

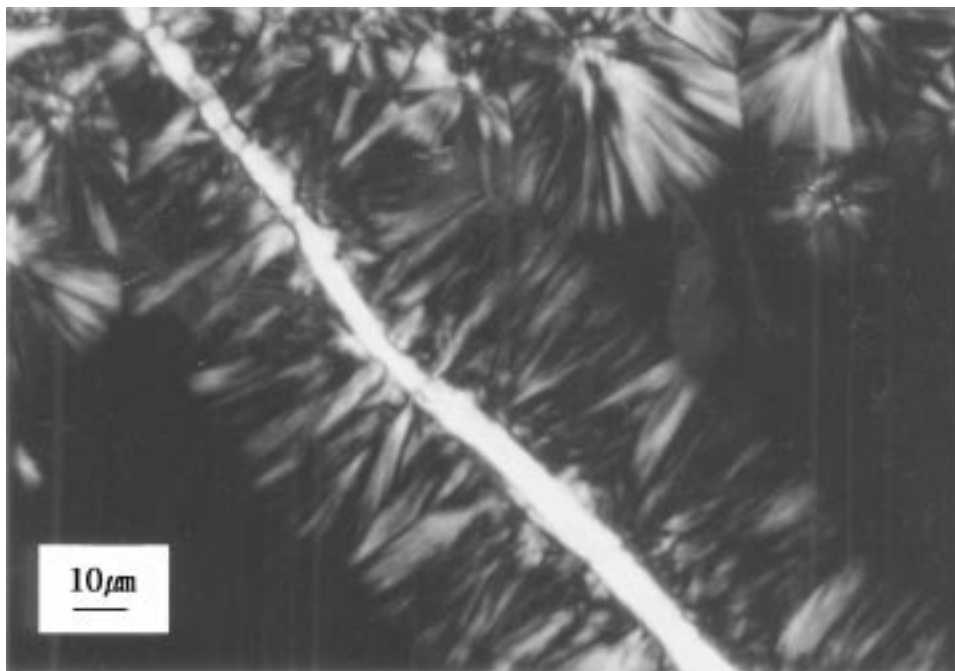


(c)



(d)

Figure 4 Optical micrographs of transcrystalline effect in the iPP matrix samples containig N-CELL pretreated with different NaOH treating times and in the LDPE matrix samples containing different fiber: NaOH treated for (a) 3 min and (b) 30 min. embedded fibers of (c) N-CELL and (d) rayon.



(a)



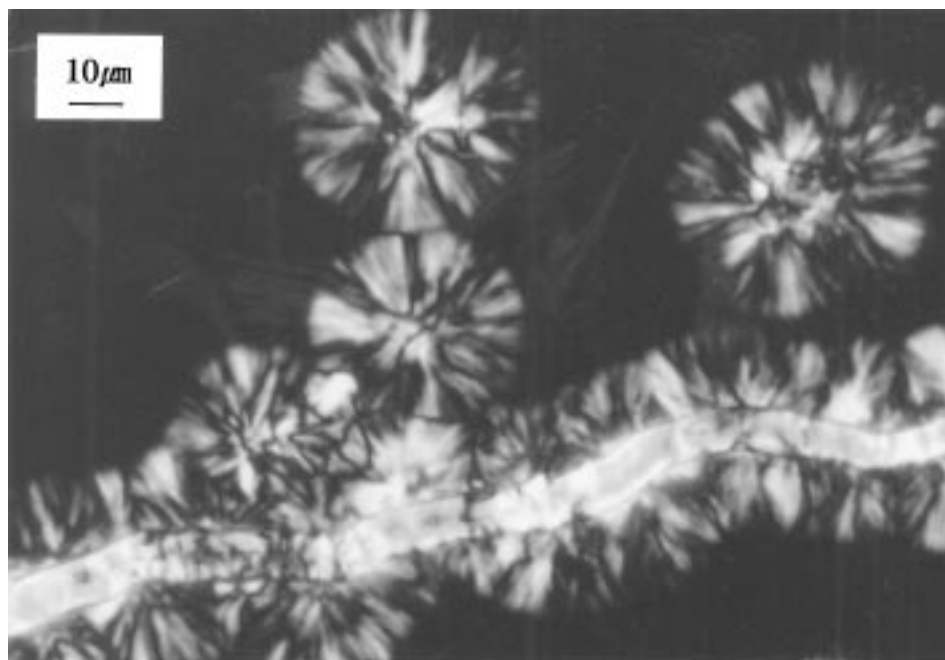
(b)

Figure 5 Optical micrographs of transcryalline effects in the iPP/E-CELL and iPP/NE-CELL samples crystallized at 120 °C with different time for: (a) iPP/E-CELL-0.5 min, (b) 1 min., (c) iPP/NE-CELL-0.5 min, (d) 1 min. (Continued.)

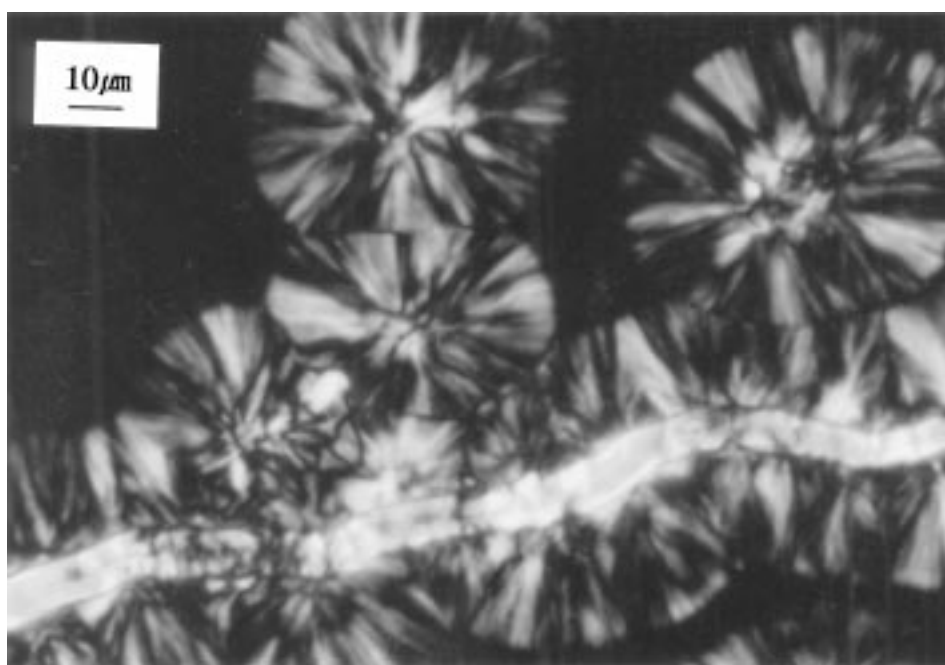
2θ of 14° (110), 17° (040), 18.5° (130), 21° (111), and 22° (131) and the β -phase can be detected by peaks at 16° (300), 21° (301) [34].

As shown in WAXD patterns of UPC and NEPC, there were no changes of 2θ values compared with that of pure PP. A small and weak β -peak and α -peaks were observed in quenched samples, but α -peaks were only observed in crystallized samples. With the increase of the crystallization time in the isothermally crystallized samples, the relative intensity increased and the half width of peak became narrower. These phenomena reflect on the fact that the crystallinity and the degree of order in the crystalline phase were increased.

Thermal properties of UPC and NEPC examined by DSC were shown in Fig. 8. The multiple endothermic peaks appeared in the quenched UPC and NEPC. The endothermic peak of 145 °C reflected on the β -crystalline phase as represented by X-ray result. The DSC results indicated that the quenched samples had the low degree of order in crystalline structure. Double endothermic peaks appeared in isothermally crystallized samples. With the increase of crystallization time, double peaks were transformed to the single endothermic peak, the width of peak became narrower, and the final peak was shifted into the higher temperature. These phenomena indicated that the degree of



(c)



(d)

Figure 5 (Continued.)

order in the crystalline structure was enhanced and the crystalline structure became more perfect during the crystallization. These results obtained by the X-ray and DSC experiments were similar with those obtained by Passingham and Vleeshouwers [35, 36].

Elastic moduli and tensile strengths of UPC, EPC, NPC, and NEPC are presented in Fig. 9. Elastic moduli increased slightly with crystallization time. These were consistent with the previous results of X-ray and DSC. However, it is assumed that the development of transcrystalline region barely affect elastic moduli because the increase in elastic moduli is very small irrespective of the previous results.

The tensile strengths decreased with the increase of crystallization time. Xavier *et al.* reported that trans-

crystallinity didn't influence the interfacial bondage [20]. Our result accord with these.

The quenched sample, which has a lower degree of order in the crystalline phase and has the β -phase that has a lower modulus and a lower yield stress, shows the largest value of the tensile strength, whereas those of the isothermally crystallized samples, which have a higher degree of order in the crystalline phase and a transcrystalline morphology, become decreased with the crystallization time. Therefore, it is thought that transcrystallinity negatively affect the interfacial adhesion in composites. Also, it may be assumed that because transcrystalline regions are bridged only by very few interspherulitic links with adjacent spherulites as postulated by Greco *et al.* [37], transcrystallinity negatively

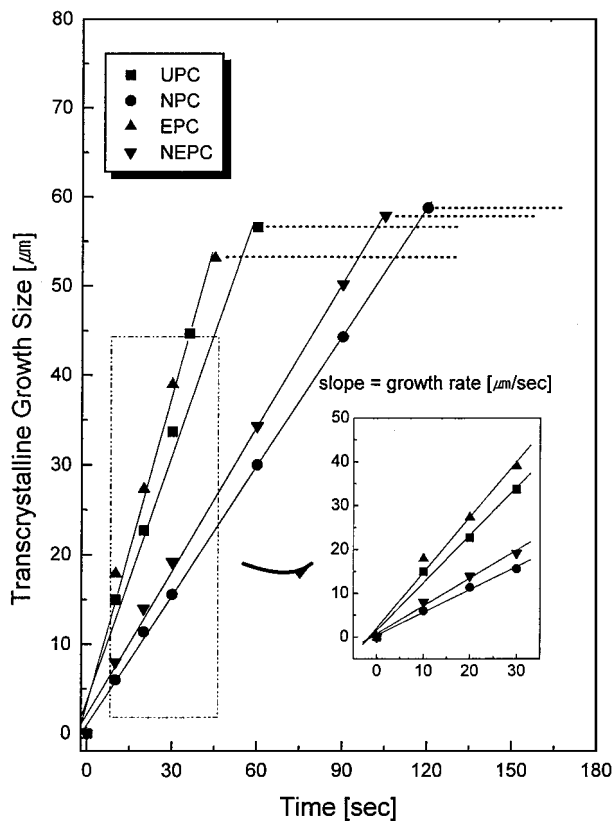


Figure 6 Plots for transcrystalline growth effects of different cellulose type embedded in PP samples crystallized at 120 °C.

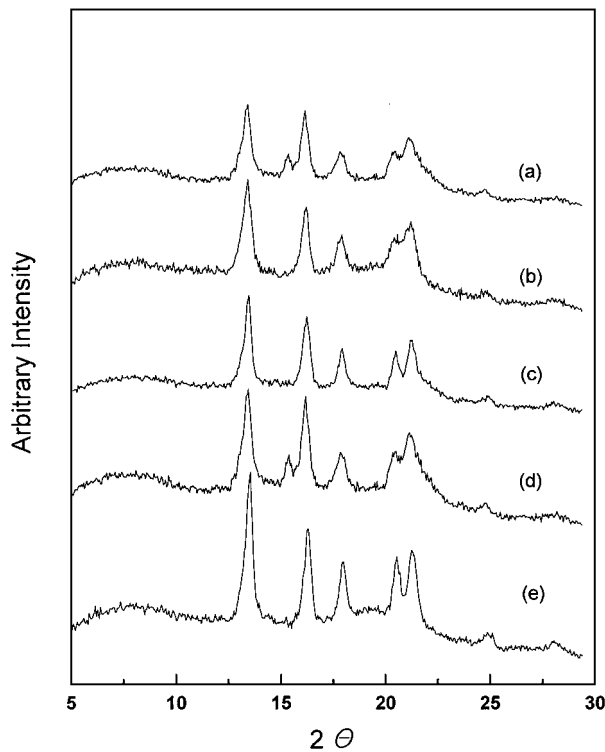


Figure 7 WAXD patterns of UPC and NEPC samples crystallized at 120 °C and quenched samples: (a) UPC-quenched, (b) UPC-crystallized for 3 min and (c) 10 min, (d) NEPC-quenched, (e) NEPC-crystallized for 10 min.

affects tensile strengths. However, it is still difficult to define how the transcrystallinity does affect on interfacial adhesion between fiber and matrix.

Fig. 10 shows the transcrystalline morphologies of UMPC and NEMPC, and the fully crystallized MAH-

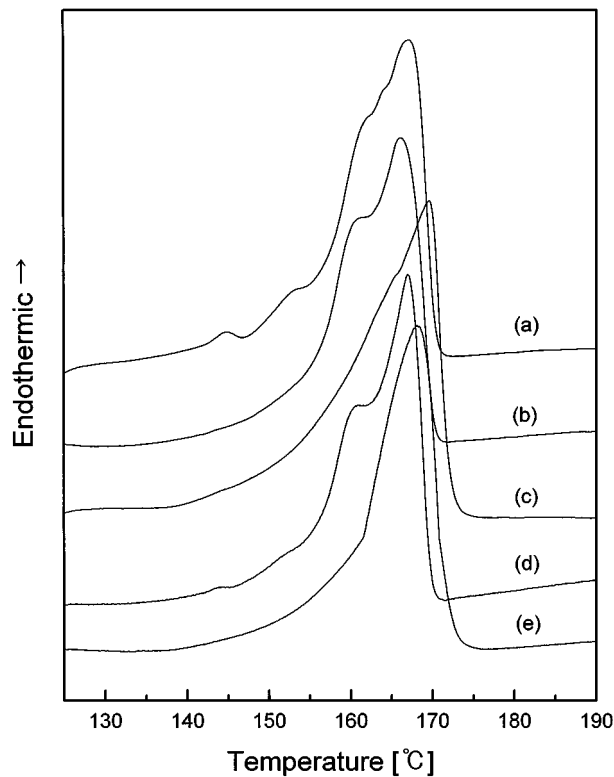


Figure 8 DSC traces of UPC and NEPC samples crystallized at 120 °C for different times: (a) UPC-quenched from 180 °C, (b) UPC-3 min, (c) UPC-10 min, (d) NEPC-quenched from 180 °C, (e) NEPC-10 min.

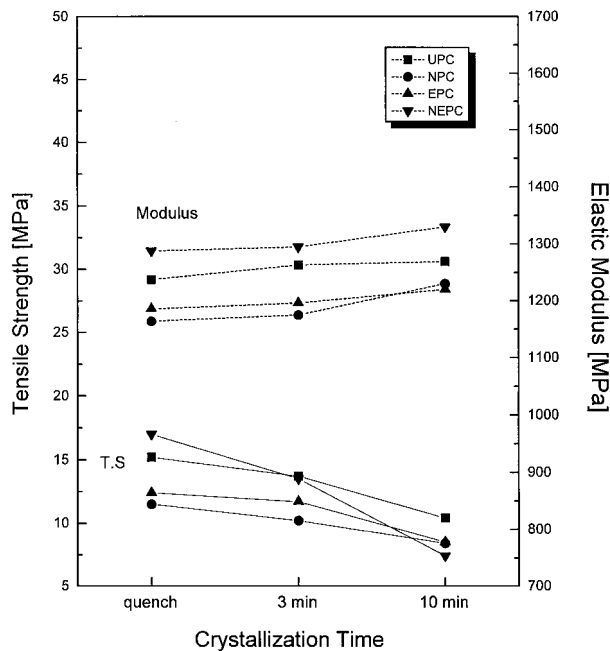


Figure 9 Variations of mechanical properties of each different iPP/CELL composites with crystallization time. Isothermal crystallization temperature was 120 °C.

PP under the same condition. Even though MAH-PP was added in composites, the transcrystallinity was occurred. The transcrystalline sizes of UMPC and NEMPC were smaller than those of UPC and NEPC. It was also found that MAH-PP existed at the outer boundaries of transcrystalline region. It was expected that MAH-PP, which was added to improve the interfacial interaction between cellulose and matrix, would be located at the interfacial region. According to this, we

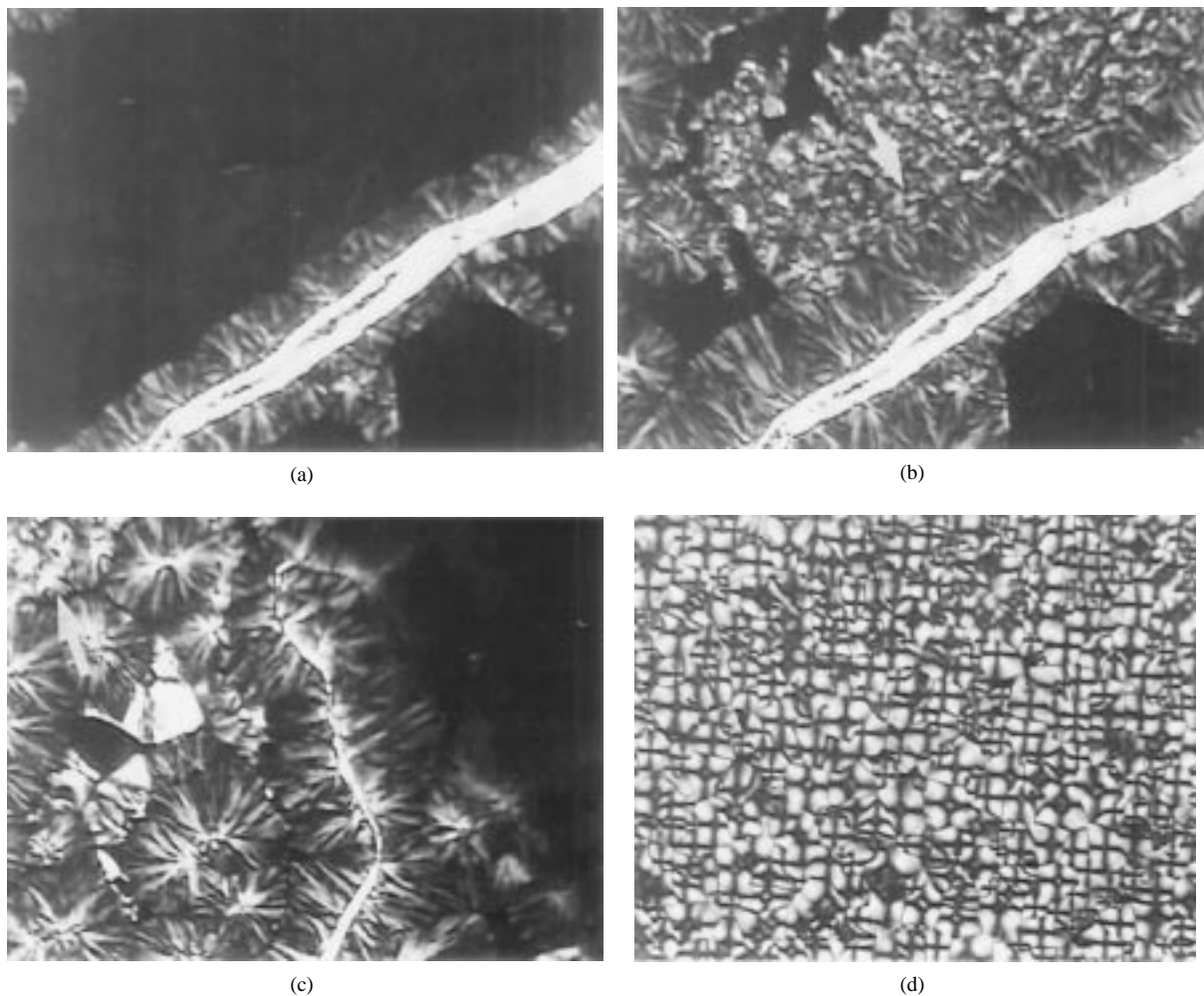


Figure 10 Optical micrographs of transcrystalline effect in the iPP/MAH-PP samples containing different type of cellulose fibers: (a) U-CELL embedded samples crystallized at 120 °C for 1 min and (b) 2 min, (c) N-CELL embedded samples crystallized at 120 °C for 2 min, (d) fully crystallized pure MAH-PP.

also expected that transcrystallinity would't appear, or barely appear by interrupting by MAH-PP. This phenomenon was opposite to our expectation.

Fig. 11 shows IR-IRS spectra of UMPC treated with quenching and isothermal crystallization at 120 °C. Felix *et. al* reported that characteristic peaks of dicarboxylic acid and cyclic anhydride form in MAH-PP appeared at 1717 cm^{-1} and 1786 cm^{-1} , respectively. And when cellulose was coated by MAH-PP, two new peaks located at 1739 cm^{-1} and 1746 cm^{-1} were observed. It was also reported that the peak of 1739 cm^{-1} arises from the hydrogen bond between the hydroxyl groups of MAH-PP and the cellulose, whereas that of 1746 cm^{-1} arises from ester bond between anhydride of MAH-PP and the hydroxyl groups of cellulose [4].

In the case of quenched pure MAH-PP, characteristic peaks of MAH-PP was also found at 1717 cm^{-1} , 1780 cm^{-1} as shown in Fig. 11a. In quenched UMPC, ester bondings between dicarboxylic acid, cyclic anhydride of MAH-PP and hydroxyl group of cellulose were mainly occurred at 1743 cm^{-1} ; (b). It was also shown that in the case of crystallized sample, ester bondings disappeared gradually and newly hydrogen bondings appeared at 1733 cm^{-1} with crystallization time; (c) and finally, all interactions described above disap-

peared with the increase of the crystallization time; (d). This result is coincident with the fact that MAH-PP was gradually expelled from the fiber surface as shown in Fig. 10 and as a result interactions disappeared gradually during the crystallization.

The mechanical properties of UMPC, EMPC, NMPC, and NEMPC are shown in Fig. 12. The elastic modulus and tensile strength of all composites decreased with an increase of crystallization time. The tensile strength of composites with MAH-PP decreased larger than those of composites without MAH-PP as shown in Fig. 9. It seems likely that MAH-PP used as a binder doesn't perform its function as shown in the previous results of Figs 10 and 11, and MAH-PP, which had lower mechanical properties than PP, acts as defects rather than binder.

4. Conclusion

Even in the case of cellulose II crystal structure, cellulose had an nucleating ability to transcrystallize PP matrix. Our observation was opposite to other's. However, it is also obvious that the more crystalline structure is similar, the more transcrystallinity is effective. The tensile strengths of polypropylene composites containing untreated and treated cellulose, which was

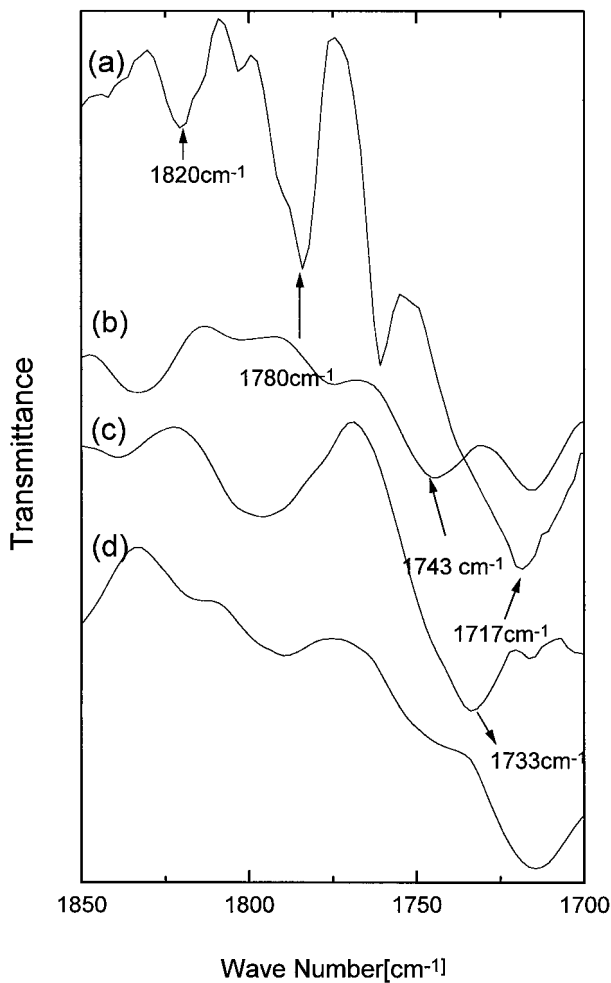


Figure 11 IR-IRS spectra of UMPC composites crystallized at 120 °C and quenched samples: (a) quenched pure MAH-PP, (b) UMPC-quench, (c) UMPC-crystallized for 3 min, and (d) 10 min.

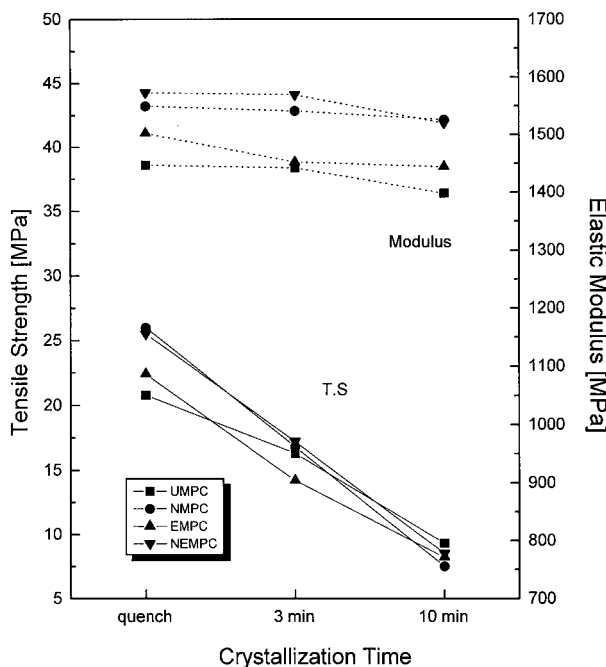


Figure 12 Variations of mechanical properties of each different iPP/MAH-PP/CELL composites with crystallization time. Isothermal crystallization temperature was 120 °C.

manufactured by isothermal crystallization, were decreased with increase of crystallization time and were inferior to those of the quenched samples. It could be found that in the case of MAH-PP added composites, the same trend was observed and decrease widths were larger than those of composites without MAH-PP. And, we observed that MAH-PP was gradually expelled from the fiber surface, no interaction between MAH-PP and cellulose was occurred in the final crystallization times. This phenomenon was also confirmed by IR-IRS analysis.

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