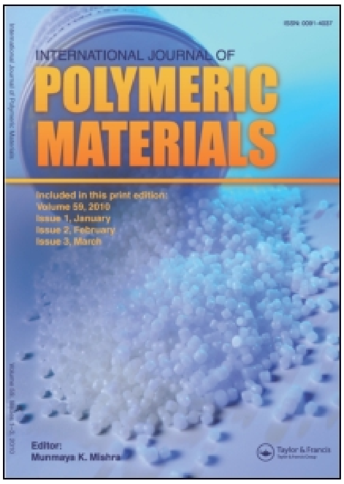


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

INFLUENCE OF THE PULLING OF EMBEDDED NATURAL FIBERS ON THE CRYSTAL STRUCTURE OF POLYPROPYLENE MATRIX

Józef Garbarczyk[a]; Sławomir Borysiak[a]
[a] Poznan University of Technology, Poznan, Poland

To cite this Article Garbarczyk, Józef and Borysiak, Sławomir(2004) 'INFLUENCE OF THE PULLING OF EMBEDDED NATURAL FIBERS ON THE CRYSTAL STRUCTURE OF POLYPROPYLENE MATRIX', International Journal of Polymeric Materials, 53: 9, 725 — 733

To link to this Article: DOI: 10.1080/00914030490498225

URL: http://dx.doi.org/10.1080/00914030490498225

International Journal of Polymeric Materials, 53:725–733, 2004
Copyright © Taylor & Francis Inc.
ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490498225

INFLUENCE OF THE PULLING OF EMBEDDED NATURAL FIBERS ON THE CRYSTAL STRUCTURE OF POLYPROPYLENE MATRIX

Józef Garbarczyk
Sławomir Borysiak
Poznan University of Technology, Institute of Chemical Technology
and Engineering Polymers Department, Poznan, Poland

The formation of hexagonal modification (β) of isotactic polypropylene (iPP) matrix, induced by motion of embedded natural fibers (NF) has been investigated by WAXS method. Untreated and chemically modified flax as well as hemp fibers were used as NF. The motion temperature of NF was found to strongly influence the content of hexagonal modification. If the temperature of motion of NF is lower, then the amount of β-iPP significantly increases. The content of β-iPP also depends on the rate of motion of NF; however, the chemical modification of NF surface reduces the content of this form.

Keywords: isotactic polypropylene, hexagonal modification, natural fibers, composite, WAXS

INTRODUCTION

The composites of engineering polymers (EP) with natural components such as wood, flax, hemp, ramie, and so on have recently been intensively studied because of the interesting properties of such materials [1–2]. Biodegradable natural fibers (NF) can act as a reinforcing component and, in consequence, a rise of the tensile and flexural

---

Received 9 July 2002; in final form 18 July 2002.

A preliminary report of this work has been presented at the World Polymer Congress IUPAC MACRO 2000 in Warsaw.

This work was supported in part by the State Committee for Scientific Research (Poland) project 7 T08E 068 18.

Address correspondence to Prof. Józef Garbarczyk, Poznan University of Technology, Institute of Chemical Technology and Engineering Polymers Dept., pl. M. Sklodowskiej-Curie 1, 60-965 Poznan 60-965, Poland. E-mail: Jozef.Garbarczyk@put.poznan.pl

strengths, as well as an impact on resistance and absorbing capacity of the product is observed. One of the essential problems in the technology of EP/NF composites is adhesion between the components, because EP matrices are hydrophobic whereas the surfaces of the NF are hydrophilic [3].

An additional important question, closely related to the properties of composites, is the supermolecular structure of the EP matrix, because the NF component can act as a nucleant for thermoplastic polymer causing changes in morphology or even changes in the arrangement of chains in the crystal lattice of the matrix [4–5].

In the authors' previous work they found that flax fibers (FF) and hemp fibers (HF) induce hexagonal (β) ordering of isotactic polypropylene chains that coexist with the monoclinic (α) form. The amount of the β-phase depends on the temperature and cooling rate of the injection mold [6]. On the basis of these observations and literature data [5], they put forward a hypothesis that one of the reasons for the β-phase formation is the difference in mobility of both components during solidification in the injection mold. In other words, the observed polymorphism can be considered as an effect of shear forces in the neighborhood of NF surfaces. To prove this hypothesis, model studies were carried out in such a way that the natural fibers were put in motion during crystallization of polypropylene.

EXPERIMENTAL

Isotactic polypropylene Malen F-401 (Orlen, Płock), ($MFI_{230/2.16}$ value 2.4–3.2, isotacticity 95%, $T_c = 113°C$, $T_m = 163–164°C$) and flax or hemp fibers (100 mm in length and about 20 μm in diameter) were used. In the experiments crude as well as chemically modified fibers were used. The crude fibers were taken directly from industry and were not washed or extracted before experiment. To improve the compatibility between the components, the NF were chemically modified by reaction with acetic anhydride or with γ-methacryloxy-propyl-trimethoxysilane (silane A-174, Union Carbide Co.). Before the chemical modification, the NF were mercerized by treatment with 16% solution of sodium hydroxide for 10 min and then were washed with water and methanol and dried in oven at 110°C [7]. During mercerization the waxes as well as fats are removed and in consequence the fiber surface becomes more accessible to chemical reagents. This process causes transformation of cellulose I (native form) into cellulose II. The degree of conversion of cellulose strongly depends on conditions of mercerization such as concentration of alkali and time of treatment [7–8].

Acetylation

The acetylating reaction was based on the procedure described in [9]. The dried mercerized fibers were placed in a xylene solution containing acetic anhydride (AA) (AA/NF- 3:1) and were kept for two hours at 120°C. After modification the fibers were washed with xylene and dried at 110°C in oven with circulating air for 8 h.

Silane Treatment

The NF in a mixture of methanol and silane A-174 (NF/A-174- 5:1) were heated under reflux condenser for 2 h. After that the fibers were washed with methanol and dried in the same condition as after acetylating reaction.

The efficiency of chemical modification of NF was characterized by IR method and changes in water sorption [7].

The untreated or chemically modified fibers were embedded in molten iPP (ca. 220°C) on one microscopic cover glass and held at this temperature for 5 min in order to destroy the thermal history of the sample. Subsequently, the samples were cooled down to room temperature at a rate of 5°C/min. During such non-isothermal

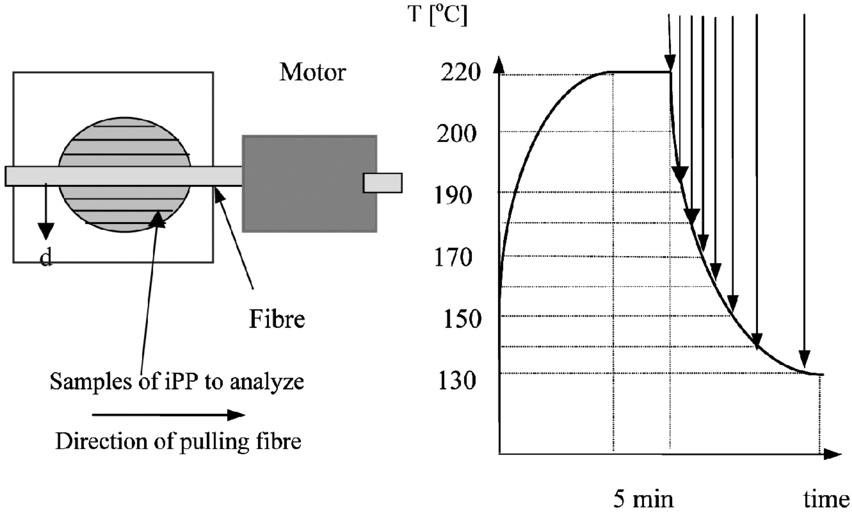


FIGURE 1 Scheme of the device for crystallization of PP with moving natural fibers and scheme of temperature program. The arrows indicate the points of temperature when the fibers were pulled (d = the distance from the surface of fibers).

crystallization, the fibers were pulled mechanically at different speeds and at different temperatures (T_{pull}) for 30 sec. To avoid the oxidation of NF and molten iPP, during experiments the surface of the samples was protected by argon. Schemes of the crystallization process and temperature program are presented in Figure 1.

The structure of iPP matrix was analyzed by means of wide angle X-ray scattering (WAXS) using Cu K_α radiation. The X-ray diffraction pattern was recorded in angle range of $2\Theta = 10-30°$. Deconvolution of peaks was performed by the method proposed by Hindeleh and Johnson [10], improved and programmed by Rabiej [11]. After separation of X-ray diffraction lines, the contents were determined of β-phase (k) by using the Turner-Jones formula [12] and degree of crystallinity (X_c) by comparison of areas under the peaks. The changes in the structure of iPP were analyzed as a function of the temperature at which the fibers were pulled, as a function of the speed of fiber pulling and as a function of the distance from the surface of fibers. To determine the last dependence the thin iPP film was cut into ca 1 mm stripes (Figure 1), which were analyzed separately. In such a way the values of k as well as X_c as function of distance from fibers were determined.

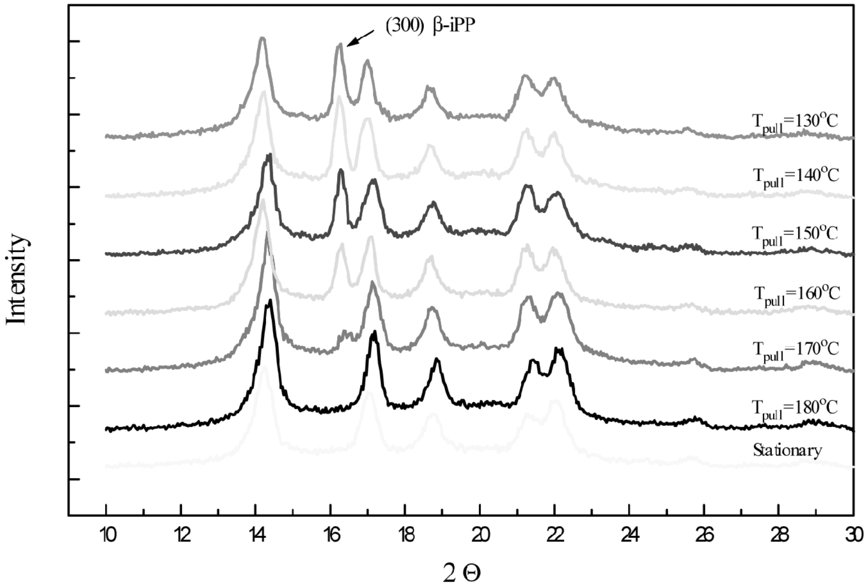


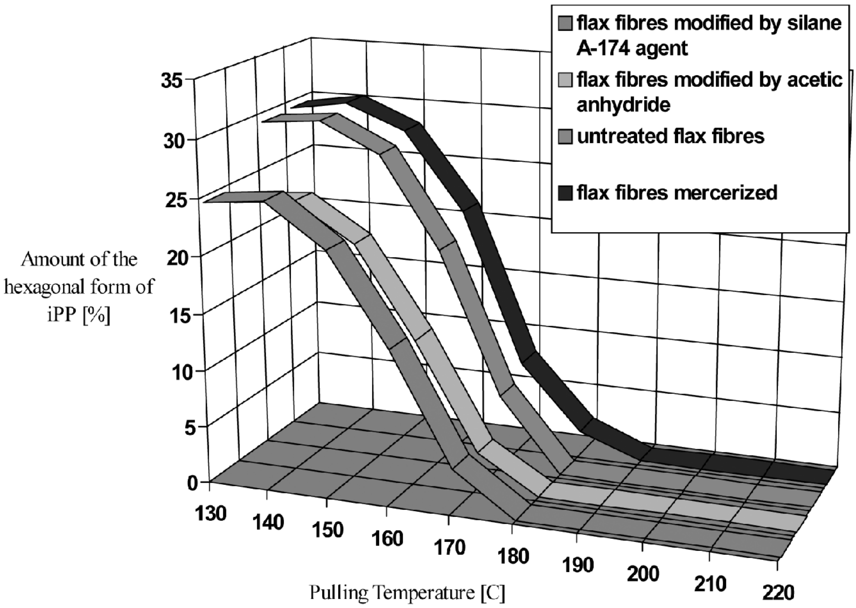
FIGURE 2 X-ray diffraction pattern of iPP/flax composites, where untreated fibers were pulled with speed 0.62 mm/s in range temperature 130–180°C.

RESULTS AND DISCUSSION

The X-ray diffraction patterns showed that the crystallization of iPP with stationary fibers results in the formation of α-form only. However, if the crystallization is performed with moving fibers, the β-iPP phase, beside the α-one, is observed (diffraction maximum at $2\Theta = 16.12^\circ$ in Figure 2).

The amount of β-iPP polymorph depends on the temperature at which the fibers were pulled. In the presence of untreated hemp fibers more β phase (36%) is formed than in the case of crude flax fibers (29%) (Figures 3a, 3b). In composites with mercerized fibers, the content of hexagonal form remained on the same level as in those with unmodified fibers. Surprisingly enough, the amount of β-iPP decreased after the chemical modification of fibers to 27% for hemp and to 24% for flax. The critical temperature of pulling, above which the β-iPP form was not generated was found to be 180°C (Figures 3a and 3b).

The analysis of k and X_c as a function of the distance from the surface of NF enabled the authors to determine the range of influence



(a)

FIGURE 3a Amount of hexagonal form of iPP vs. pulling temperature, for flax fibers.

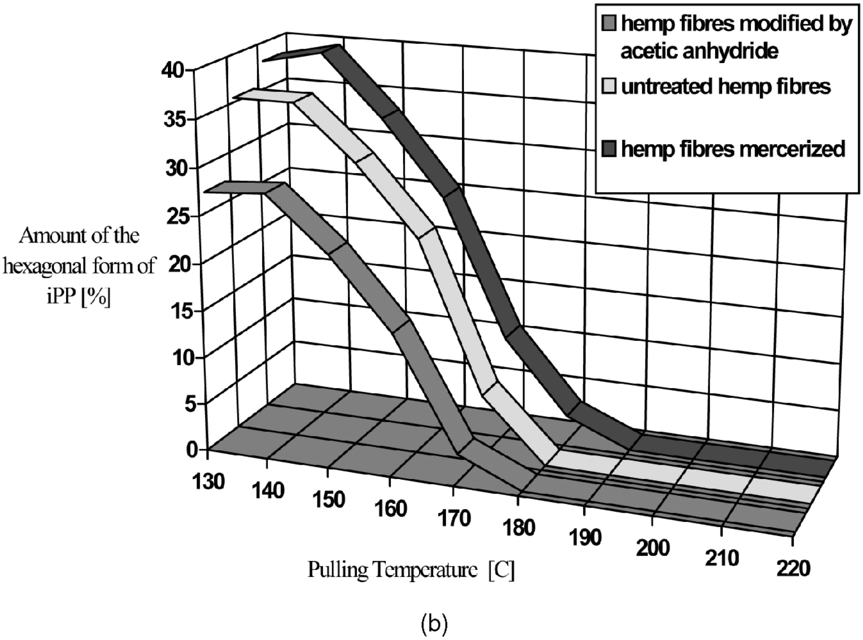


FIGURE 3b Amount of hexagonal form of iPP vs. pulling temperature hemp fibers.

of moving fibers on the formation of crystal structure of iPP matrix (Figure 4).

From diagrams shown in Figure 4, it can be seen that the optimal range of the influence of moving fibers on the structure of iPP is 2 mm. Most of the β-phase (27.7–30%) is formed and the degree of crystallinity reaches its maximal value (60–62%) up to this distance. At the distance of 3–7 mm, the values of k and X_c dropped sharply to 2% and 52%, respectively. Above 8 mm only the α-form of iPP was observed and X_c remained on the same, relatively low, level (51%). It is worth adding that the crystallinity of polypropylene matrix after crystallization with stationary NF was characterized by values (52–55%) similar to those recorded above 3 mm.

In the next experiments the authors found that the structure of iPP in the interlayer region strongly depends on the speed of NF motion (Figures 5a and 5b).

The shape of the curves describing changes in the amount of β-iPP phase as a function of the speed of NF V_{pull} is generally similar for all pulling temperatures (Figures 5a and 5b). The authors unexpectedly found that there exist a critical value (v_{cr}) of speed (for untreated flax

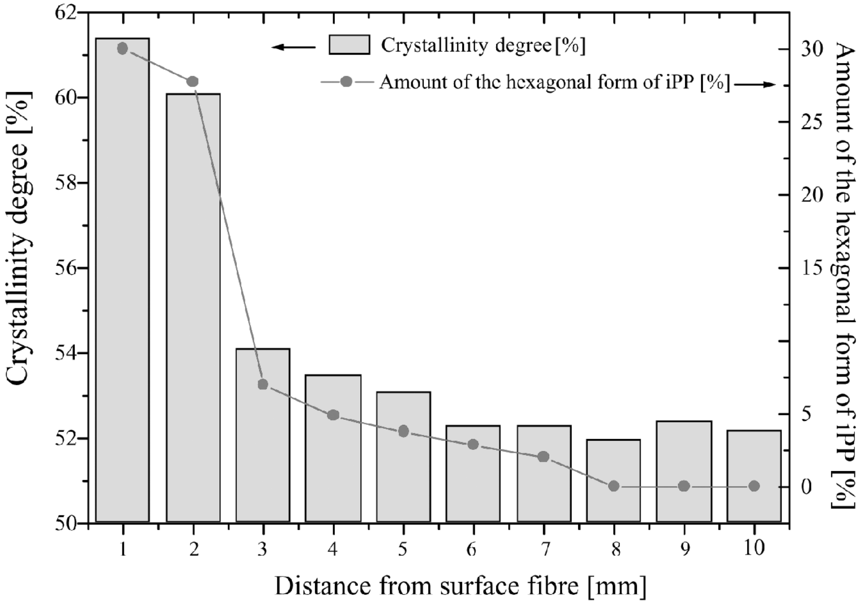
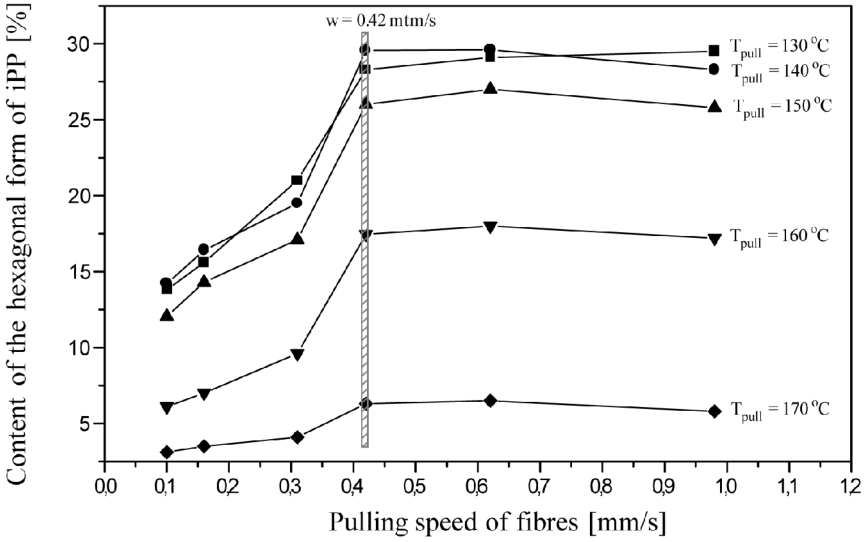
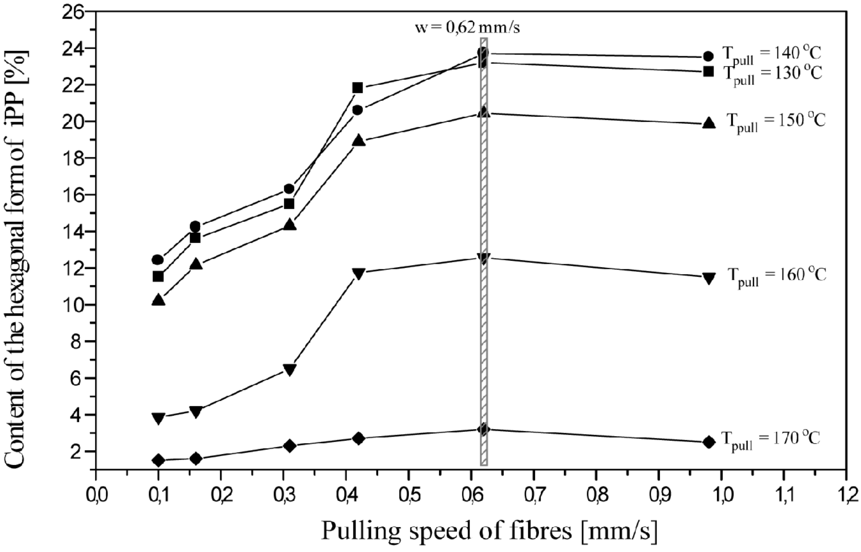


FIGURE 4 Degree of crystallinity of iPP and amount of the hexagonal form of iPP vs. distance from surface fibers.



(a)

FIGURE 5a Content of the hexagonal form vs. speed of fibers for untreated flax fibres.



(b)

FIGURE 5b Content of the hexagonal form vs. speed of fibers for flax fibers modified by acetic anhydride.

fibers $v_{cr} = 0.42\,mm/s$) above which the β-iPP content remains practically unchanged. It is interesting that up to v_{cr}, the dependence of k on V_{pull} is almost linear. Similar relationships were observed for the samples containing modified NF (Figure 5b). However, a comparison of results presented in Figure 5a and in Figure 5b, indicates that in each speed range, the untreated fibers result in the formation of more β-structure than the modified ones.

CONCLUSIONS

The results obtained in this study lead to a conclusion that when embedded fibers are in motion during non-isothermal crystallization of isotactic polypropylene matrix, then hexagonal form of the polymer matrix is formed. The amount of the hexagonal form depends on the temperature of the motion (above 180°C the β-form does not exist) and on the speed of the fiber motion. Moreover, the obtained results show that chemical modification of NF results in a decrease in β-iPP content. Therefore, it can be conclude that by improving compatibility on NF surface, favorable conditions for the formation of monoclinic arrangement of iPP chains are created.

On the other hand, on the basis of the obtained data, the authors cannot say that the creation of hexagonal modification of iPP depends only on shearing at the interface region, because the nucleation ability of NF as well as the rate of crystallization at the surface of fibers have to also be taken into consideration. This is a subject of the authors' further investigation [13].

REFERENCES

[1] R. Gauthier, C. Joly, A. C. Coupas, H. Gauthier, and M. Escoubes, *Polym. Composit.* **19**, 3, 287 (1998).

[2] J. Kuruvilla, T. Sabu, and C. Pavithran, *Polymer*, **37**, 23, 5139 (1996).

[3] A. K. Błedzki, S. Reihmane, and J. Gassan, *J. Appl. Polym. Sci.* **59**, 1329 (1996).

[4] J. L. Thomason, A. A. Van Rooyen, *J. Mater. Sci.* **27**, 897 (1992).

[5] J. Varga and J. Karger-Kocsis, *J. Polym. Sci. Polym. Phys.* **34**, 657 (1996).

[6] J. Garbarczyk and S. Borysiak, (1997). *Structure-Physical Properties Relationships of Block Copolymers and Polymer Blends*, (Technical University of Szczecin Press, Szczecin, Poland), pp. 162–163.

[7] S. Borysiak, Ph.D thesis, Poznan University of Technology (2000).

[8] J. Garbarczyk and S. Borysiak, *Fibres Textiles East Eur.* **11**, 104 (2003).

[9] David N.- S. Hon. (Ed.), (1996). *Chemical Modification of Lignocellulosic Materials*, (Clemson University, South Carolina), pp. 166.

[10] A. M. Hindeleh and D. J. Johnson, *Polymer*, **15**, 697 (1974).

[11] S. Rabiej, *Eur. Polym.* **27**, 947 (1991).

[12] A. Turner-Jones, A. Aizlewood, and D. R. Beckett, *Makromol. Chem.* **75**, 134 (1964).

[13] J. Garbarczyk, D. Paukszta, and S. Borysiak, *J. Macromol. Sci. Phys.* **41**, 1267 (2002).