AN EXPERIMENTAL DETERMINATION OF NEAR-INFRARED PROPERTIES OF POLYPROPYLENE AND COMPOSITE MATERIAL CONTAINING POLYPROPYLENE AND GLASS FIBERS

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Abstract

Polymer composite materials are nowadays widely used in structures where low weight in combination with high strength and stiffness are required. An effect of elaboration conditions of semi-crystalline polypropylene and glass fiber reinforced polypropylene on near-infrared optical properties is studied on the basis of spectral measurements of both normal-hemispherical reflectance and transmittance. The modified two-flux approximation is used to retrieve the volumetric absorption and scattering characteristics of the materials. New experimental results are expected to be useful in engineering practice concerning the manufacturing and subsequent use of advanced semi-crystalline reinforced materials.

1. Introduction

Knowledge of the radiative properties of thermoplastic composites is a crucial interest for the design of industrial systems where thermal radiation is an important mode of heat transfer. As in the case of the 1064 nm neodymium:YAG (Nd:YAG) laser [1]. Nd:YAG lasers typically emit light with a wavelength of 1064 nm, in the near-infrared. However, there are also transitions near 940, 1120, 1320, and 1440 nm. Nd:YAG lasers operate in both pulsed and continuous mode. In a polymer composite, the individual constituents are the polymer matrix and the added reinforcement (fibers or powders). In the present paper, near-infrared properties of two materials are studied: the pure polypropylene and a composite material containing both glass and polypropylene fibers. This is a part of more general study of wide-range optical properties of semi-crystalline polymers and composite materials.

Semi-crystalline polymers are characterized by a specific microscopic texture. In this work, the term texture stands for the spatial arrangement of the heterogeneities embedded within the host solid matrix as their respective size, orientation and shape distributions. To achieve this goal, we use the samples of polypropylene designed in the LTN laboratory by an injection process [2, 3]. The injection molding is one of the most widely employed methods for manufacturing polymeric products. Three main steps are recognized in the molding: filling, packing/holding and cooling. With this process we can pilot all the parameters of processing, like the temperature of mold, which will generate samples with parallelepiped shape (60mm x 60mm x 3mm). The samples are characterized by an infrared spectrometer equipped with an

integrating sphere system (∅ =75 mm) which allows the measurement of both diffuse and directional transmittance and reflectance for different samples developed at processing temperatures 40, 60, 80, 100, and 120°C in the wavelength range 0.5–20 μm of the radiation. The samples of polypropylene contain numerous sub-millimeter spherulites dispersed in a homogeneous matrix. This appeared to be important for the wide-range radiative properties of this semi-transparent material [1]. The composite material TWINTEX®RPP60N265 containing both E-glass and polypropylene filaments is also studied using the same experimental procedure. The radiative properties of both materials are identified using the method based on the modified two-flux approximation [4, 5]. The subsequent theoretical analysis of these characteristics should take into account the specific texture of the material formed at elevated temperatures. In particular, the evolution of the thermal kinetics properties can be considered to explain the observed effect of the processing temperature on polypropylene properties. Finally, a possible use of the infrared spectroscopy to analyze the material texture is discussed in the paper. The near-infrared range was chosen because scattering properties of materials in this spectral range are more sensitive to fine elements of the material structure. This is important for possible subsequent analysis of specific effects of the processing parameters on the material morphology [6].

2. Experimental procedure

2.1. General description of materials

Regarding the polymer matrix, a commercial homopolymer of isotactic polypropylene "iPP" with melt flow index 4g/min for 2.16 Kg total mass at 230°C was chosen for this study. The mold cavity is a square slab of size 60 x 60 x 3 mm. The material was injected in a SANDRETTO injection press. The melt temperature was set to 220°C; the hold pressure at the nozzle was 80 MPa, the holding time and the cooling time was equal to 15 and 20 s, respectively. One processing parameter was varied in the study: the mold temperature. This temperature was taken equal to 40, 60, 80, 100, and 120°C.

The TWINTEX®RPP60N265 is a commercial composite material sample of 1.4 mm thickness, 152 mm of internal diameter and 305 mm of external diameter containing about 60% of fiberglass and polypropylene provided from FGI, Amsterdam, New York, USA was chosen for this study. Consolidation is done by heating the roving above the melting temperature of PP matrix (180°C-230°C / 360°F-450°F) and applying a pressure before the cooling stage of the process.

2.2. Polypropylene sample preparation

The studied zones were located at 19 mm (zone A) and 44 mm (zone B) from the gate, close to the center of the part (Fig. 1). Samples of size 25 x 25 mm were cut from the central part of the molded plats which are used to make measurements using Fourier spectrometer Bruker Vertex 80V. Then in order to observe morphology changes with the mold temperature, the slices of 3 μm using a Leica slit microtome were cut from the middle of the slab.

2.3. Optical microscopy and crystallization experiments for polypropylene

In order to observe the morphology changes with mold temperature, a polarized light optical microscopy Olympus BX61 was used. It was found that an average diameter of spherulites increases from about 34 μm to 56 μm with the mold temperature. To obtain more information

on a morphology change, another study was conducted which shows that the spherulite diameter is about 56 µm at processing temperature 120 °C. Polarized optical microscopy with a LINKAM TMS94 hot stage was used in these experiments.

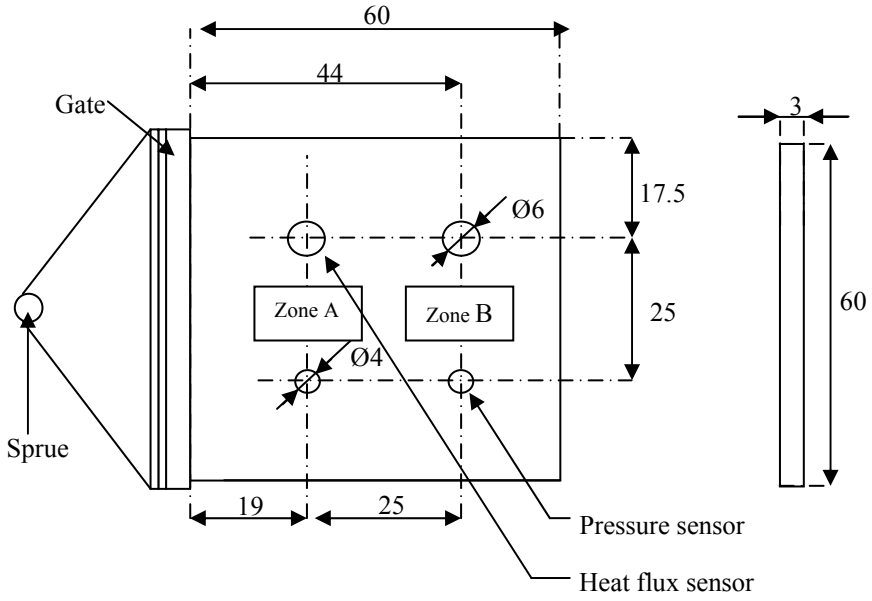
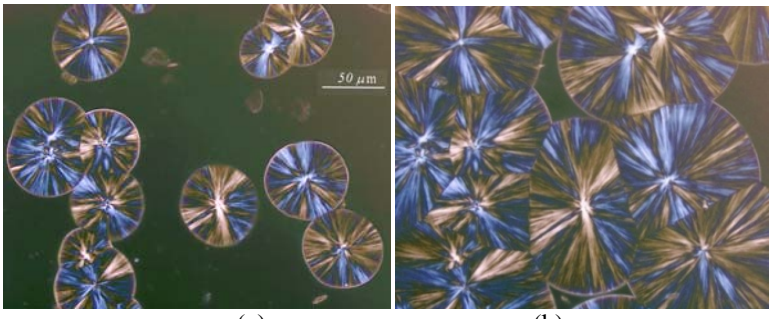


Figure 1. Geometry of the injected plate, localization of the sensors and of the measured zones.

The growth rate of spherulites was observed on thin films of thickness 30 µm, which are prepared by pressing the film between two cover glasses at 220°C. After that, the samples were hold at 220 °C for 4 min on the hot plate in order to remove effects of the preliminary thermal treatment. Finally, the samples were cooled to crystallize the polymer at T_{pr} =120°C. The fragments of typical photographs taken during the crystallization are presented in Fig. 2. One can see that spherulites of various sizes are really almost spherical and consist of numerous lamellas as well as they grow with time during the isothermal crystallization.



(a) (b)

Figure 2. Microphotograph of typical spherulites in the polypropylene sample during isothermal crystallization at T_{pr} = 120°C : (a) – 54s, (b) – 105s.

2.4. Optical microscopy for TWINTEX®RPP60N265

A Scanning Electron Microscope (SEM) Merlin (Carl Zeiss) was used to understand the repartition of glass fibers. One can see in Fig. 3 that glass fibers are parallel and close to each other.

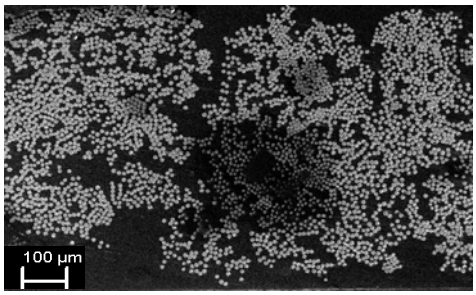


Figure 3. Microphotograph of a cross section of TWINTEX®RPP60N265 sample.

3. Analysis of experimental results

3.1. Polypropylene

The studied small samples (25×25×3 mm) were cut from the central part of the polypropylene slices. The spectral values of normal-hemispherical transmittance and reflectance were measured using Fourier spectrometer Bruker Vertex 80V from Bruker Optics, equipped with an integrating sphere of 75 mm in diameter, both installed on flexible sample holders. The first integrating sphere was made with a diffuse gold coating for investigating wavelengths from 1.25 to 16.7 µm. The second integrating sphere was based on a diffuse Teflon coating, which allows measurements for wavelength going from 0.67 up to 1.67 µm. The conception of the Vertex 80V spectrometer allows the combination a set of optical components to cover with a high accuracy the spectral range of this work. Thus, two detectors were successively used to investigate the whole spectral range. The MCT detector with a 2×2 mm active cell made by Infrared Associates Inc. for the mid infrared range used with the gold integrating sphere, which covers a spectral range from 1 to 16.7 µm. This detector was cooled by liquid nitrogen. The Silicone Diode detector with a 2.4×2.4 mm active cell for the near infrared range used with the PTFE integrating sphere, which covers a spectral range from 0.4 to 1.11 µm, operates at room temperature. The experimental technique of this type is widely used in studies of semi-transparent dispersed materials. We do not reproduce here the experimental setup schematics, which can be found elsewhere [7-9]. Some results of wide-range-measurements are shown in Fig. 4, whereas the measurements in a short-wave spectral range of semi-transparency at different orientations of five samples of polypropylene are presented in more detail in Fig. 5. The measurements of the normal–narrow-cone transmittance, T_n, in the main long-wave regions of semi-transparency are also presented in Fig. 4.

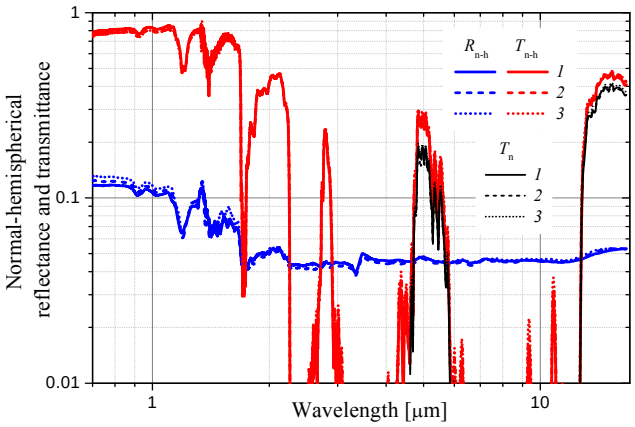


Figure 4. The measured normal-hemispherical reflectance and transmittance and normal–narrow-cone transmittance: 1 – T_{pr} = 40°C, 2 – 80°C, 3 – 120°C.

The values of T_n are very close to $T_{n\text{-}h}$ because of small scattering, and this experimental result can be used in the analysis of experimental data [10]. It is interesting that an effect of processing temperature is considerable in the short-wave range only. The latter leads to important simplifications in heat transfer calculations [10]. It is obvious in Fig. 4 that one can distinguish several spectral ranges characterized by quite different behavior of the radiative properties of polypropylene.

The short-wave range of semi-transparency $0.667 \le \lambda \le 1.17\,\mu m$ is characterized by a considerable volumetric scattering. It can be used to study the morphology of the samples as it was done recently by the authors [6]. As usually, the size of scattering particles is comparable with the wavelength [5]. It means that numerous lamellas are responsible for radiation scattering in this range.

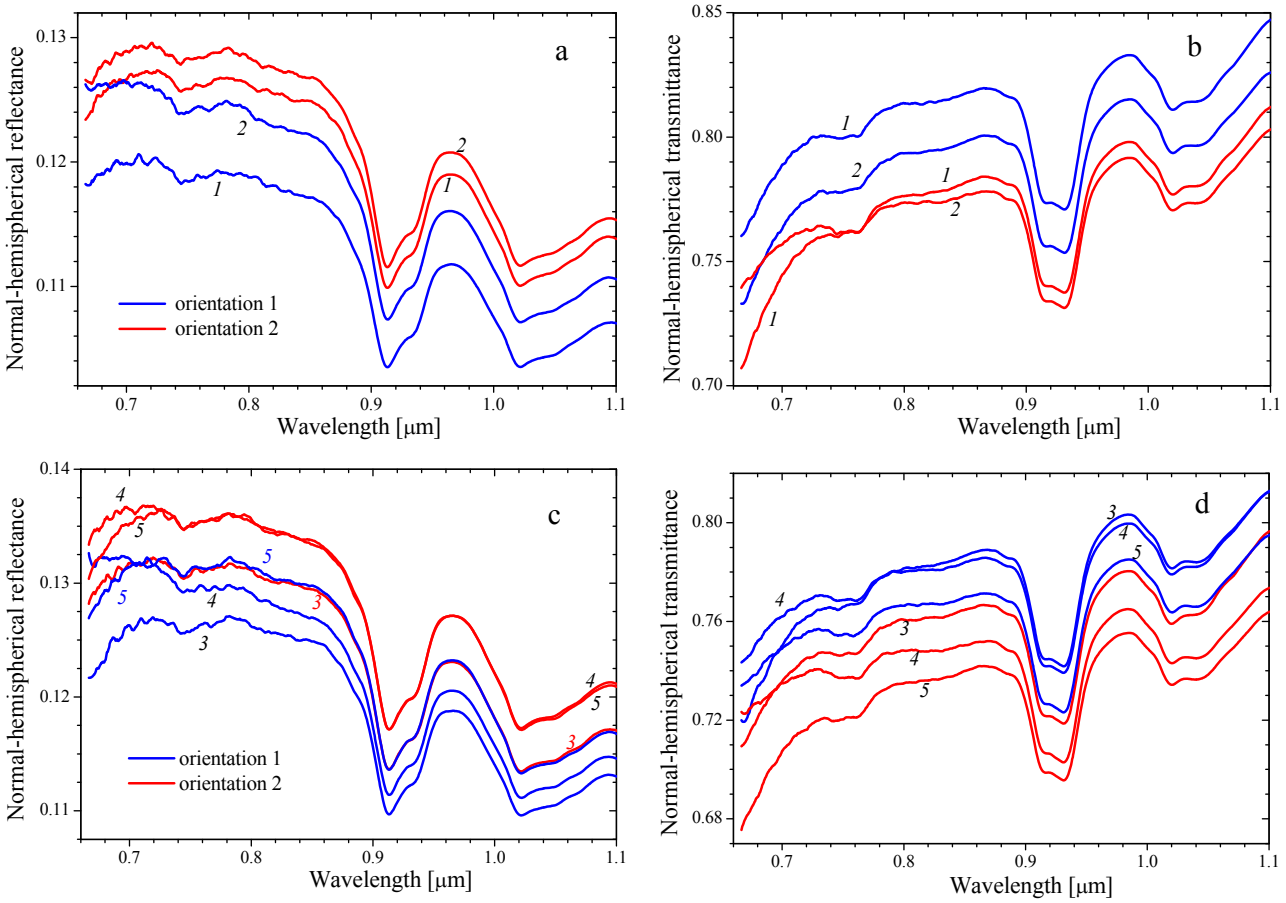


Figure 5. The measured normal-hemispherical reflectance (a, c) and transmittance (b, d) at different orientations of the samples: 1 – T_{pr} = 40°C, 2 – 60°C, 3 – 80°C, 4 – 100°C, 5 – 120°C.

There are several other ranges of semi-transparency: $1.74 < \lambda < 2.25\,\mu m$, $2.7 < \lambda < 2.9\,\mu m$ $4.7 < \lambda < 5.6\,\mu m$, and $12.8 < \lambda < 16.7\,\mu m$. In these ranges, the scattering is small and its effect on reflectance is negligible. A strong decrease in scattering with the wavelength confirms the above conclusion that thin lamellas are responsible for scattering. One can also see in Fig. 4 several strong absorption bands, where the samples are almost opaque. The reflectance due to superficial effects is also negligible in these ranges. The above dividing the whole spectral range into the sub-ranges of quite different radiative properties makes justified a separate consideration of particular problems. Note that both the normal-hemispherical reflectance and transmittance depend on the sample orientation. This asymmetry is related with specific conditions of cooling when the stage of crystallization has finished [6, 9]. The correct way to

determine volume-averaged optical properties of inhomogeneous samples is an averaging of the optical properties retrieved from the measurements for two different orientations of the sample [6].

3.2. TWINTEX®RPP60N265

A sample of size 25 x 25 mm was used in this study. The results of the spectral measurements are shown in Fig. 6.

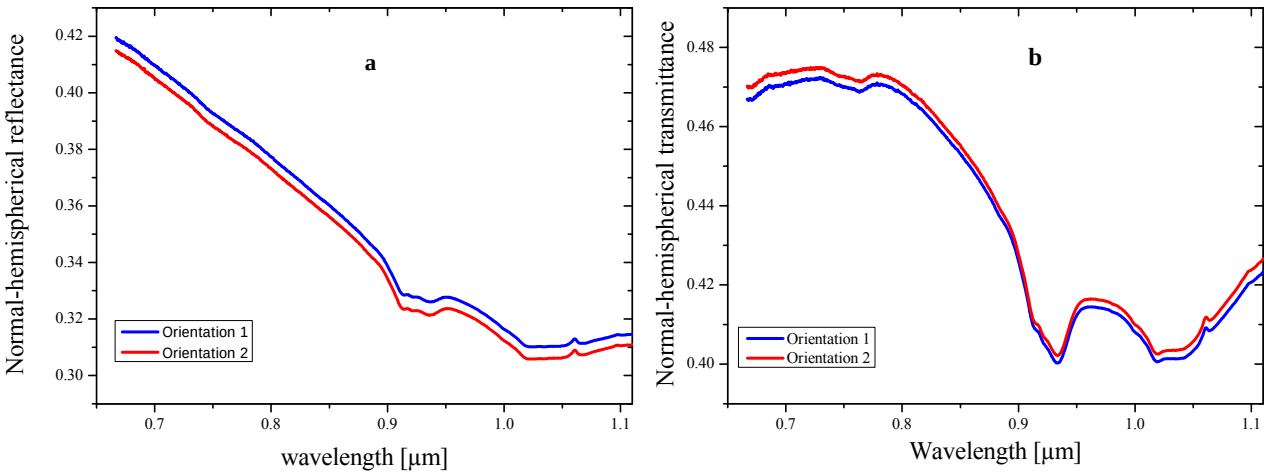


Figure 6. The measured normal-hemispherical reflectance (a) and transmittance (b) at different orientations of the TWINTEX®RPP60N265 sample.

One can see that both the normal-hemispherical reflectance and transmittance are almost independent of the sample orientation. This can be treated as an indirect confirmation of the uniform optical properties across the sample.

4. Identification of optical properties

In this paper, the identification procedure is based on transport approximation of the scattering phase function and the modified two-flux approximation for radiative transfer [4, 5, 11]. This method. takes into account the effect of total internal reflection at the interfaces.

4.1. Optical properties of polypropylene

The resulting spectral dependences of the absorption coefficient and transport scattering coefficient after arithmetic averaging of the volumetric optical properties retrieved from the measurements for two different orientations of the sample are presented in Fig. 6 taken from recent paper [8]. The calculations were conducted at an approximate constant value of index of refraction $n = 1.5$ [12] because both α and σ_{tr} are weakly sensitive to small variations of the refractive index. One can see in Fig. 7 that the scattering is predominant in the main part of the spectral range under consideration. Considerable values of σ_{tr} indicate that there are some scattering particles in the sample and the characteristic size of these particles is comparable to the wavelength. It should be recalled that only scattering can be used to retrieve some data on the material structure in the case of optically soft dispersed materials. The absorption coefficient of such materials is insensitive to the morphology, and it is simply proportional to the partial volumes of the absorbing substances [5,13].The decrease of scattering with the wavelength is typical for the case when an average particle size is less than

the wavelength [5]. It is important that the curves of $\sigma_{tr}(\lambda)$ for different samples are similar to each other. Physically, it means that a geometrical similarity of the scattering objects in polypropylene samples produced at different processing temperatures is proved. One can assume that these scattering particles are randomly oriented lamellas or the gaps between them, which can be observed in the microphotographs (see Fig. 2).

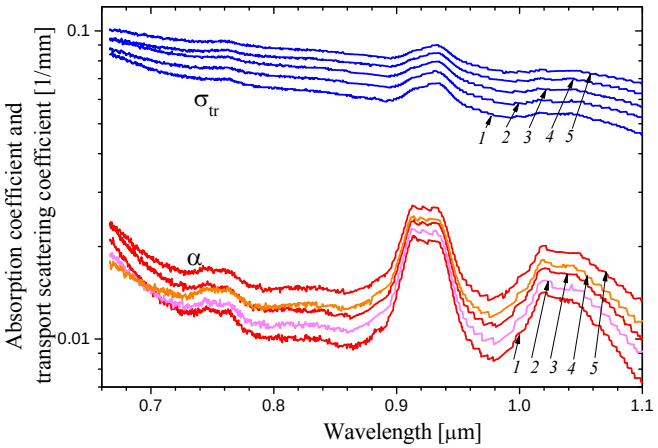


Figure 7. Averaged absorption coefficient and transport scattering coefficient: 1 – Tpr = 40°C, 2 – 60°C, 3 – 80°C, 4 – 100°C, 5 – 120°C.

4.1. Optical properties of composite material containing polypropylene and glass fibers

The retrieved volumetric optical properties of TWINTEX®RPP60N265 are presented in Fig. 8. It is seen that both the absorption and transport scattering curves are not monotonic and have strong resonances at λ=1.2 μm. It is interesting that the spectral dependences of absorption and transport scattering coefficients are quite similar to those in the case of the so-called scattering by absorption [14].

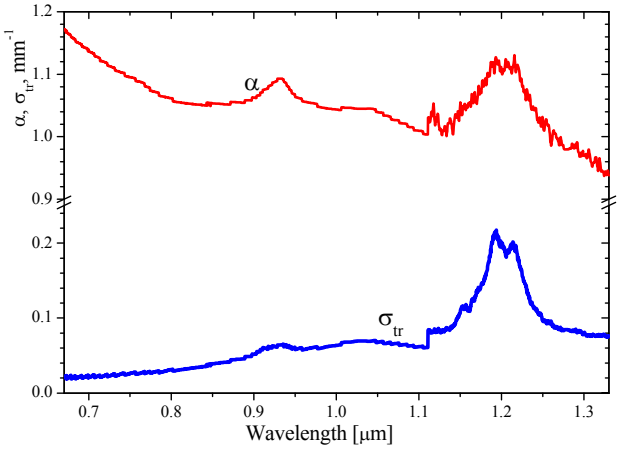


Figure 8. Spectral optical properties of TWINTEX®RPP60N265 sample of 1.4 mm thickness.

It is seen that there are two absorption peaks for wavelength λ= 0.93 μm and 1.05 μm. These absorption peaks are typical for polypropylene [15]. Note that transport scattering curves are quite different from those in Fig. 7. It is partially explained by the absence of small-size lamellas responsible for the short-wave scattering.

5. Conclusion

Visible and near-infrared optical properties of semi-transparent polypropylene samples, prepared at various processing temperatures from 40 to 120°C, were studied using the measurements of both normal-hemispherical reflectance and transmittance. The effect of a relatively strong scattering at the absorption peaks was observed for polypropylene at the absorption peaks at wavelengths measuring about 0.93 and 1.04 μm. It was shown that this effect is the same for every sample and is insensitive to the morphological differences between the samples. The short-wave scattering of a composite material containing about 60% of fiberglass and polypropylene appears to be quite different from that of pure polypropylene. This should be a subject of a further theoretical study.

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