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Transcrystallization of maleated polypropylene in the presence of various carbon fibers

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Summary

In this paper, the influence of the fiber surface sizing on development of transcrystallization, TCR, as well as the fiber-matrix interactions were analysed. Sized (CT) and unsized (CU) high-strength carbon fibers and maleated polypropylene, mPP, were used in model systems. Transcrystallization was followed by polarizing optical microscopy, in isothermal regime (Tc=124-130 ^{o}C). Besides the radius, distribution of the thickness and growth rate of the transcrystalline layer and the surface energetic parameters have been also determined. Lower value for $\Delta\sigma$ was obtained for the system with surface treated C fibers ($\Delta\sigma_{CT}$=1,145x10^{-7} J/cm^{2}) which also contribute for their higher nucleation activity. Using FTIR microscopy and model reaction, an attempt was made to analyse the chemical interactions at fiber/matrix interface.

Introduction

It is well known that the mechanical properties of thermoplastic composites depend not only on the properties of the fibers and polymer matrix but also on the interfacial properties. Transcrystallization represents special type of oriented morphology developed at the fiber/matrix interface under a proper conditions. The presence of TCR in thermoplastic composites has a technological importance due to the influence on the mechanical behavior and adhesion [1-6]. It was shown that TCR layer has a higher Young's modulus than bulk material [2]. Recently, the effect of TCR layer on the mechanical performance was evaluated by DMTA [7].

Although there is a significant number of papers on TCR, still many controversial results and comments could be find [3,5]. So far, the results suggest that the interfacial shear strength and the transcrystalline layer stiffness in the fiber direction, both increase by factor of cca 1.2-1.5. However, the evidence of this for real composites is not yet available. Because of that, the mechanism of TCR as well as the fiber/matrix systems where TCR can be developed are still a subject of interest [6-10].

TCR appeared when the nucleation density at the fiber surface is much higher and the spherulites can grow up only in perpendicular direction. As a nucleation controlled process, TCR depends on thermodynamic conditions, such as crystallization temperature, *Tc* and cooling rate, *Vc*. According the literature, TCR could be initiated by several factors [11-13]: topography of the substrates, shear induced crystallization, surface energy of the substrate, adsorption of small molecules, thermal gradients. Y.Cai and his coworkers have been worked on the TCR development in PP-based composites due to the fiber/matrix thermal gradients [13]. C.Wang and C.Liu have studied the effects of the difference in interfacial free-energies, $\Delta\sigma$, at the fiber surfaces and that in the bulk. [12]. They have compared the $\Delta\sigma$ values for different fibers and they have made gradation of nucleation activity of various fibers. Ishida and Bussi proposed an induction time method in studying the TCR of Polyethylene/Polycaprolactone composites [14]. TCR development of polypropylene, initiated by melt-shearing and fiber-pulling during the crystallization, have been followed by many authors [15-18]. Cylindritic forms have been formed at smaller shearing during the crystallization. This type of TCR was found in the presence of glass, polyamide, polyester, aramide and carbon fibers [16,17]. Varga and Karger-Kocsis have considered that the cylindritic microstructure is a row-nucleated structure and they described the difference between TCR and cylindritic crystallization [17,18].

Besides all these papers addressed to TCR, up to now only indirect indications for the assumed chemical interactions at fiber-matrix interface have been obtained. For that purpose, various spectroscopic methods were used, such as: FTIR microscopy [16], FTIR-ATR [19-22], transmission on thin films or pellets [23], and most of them mainly for epoxy based composites. The maximum extent of reaction to form secondary amine, alcohol and ether groups was found when the coupling layer was contacted with the polymer matrix. However, it was concluded that this procedure is not feasible in industrial practise. Analogue investigations were performed also for thermoplastic composites [24,25]. Using the model reactions and FTIR analysis, the mechanism of interaction between the silane coupling agents and the polypropylene matrix was studied [24]. Applying FTIR-ATR technique, Bayer and coworkers worked on a planar model system to investigate the interfacial reactions between the γ–APS coupling agent and thermoplastic polymer matrix [25].

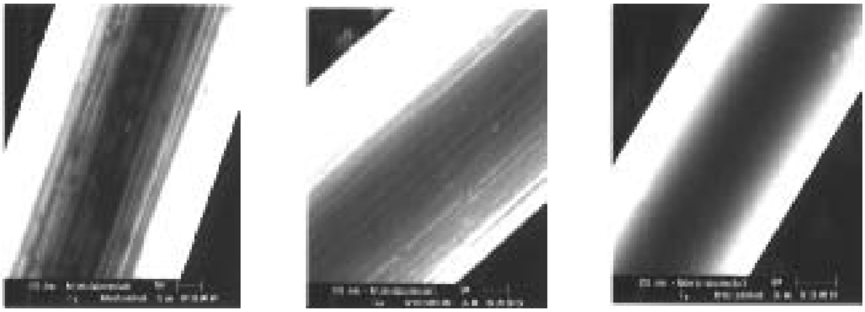
In this paper, besides TCR morphology and surface energy characteristics, the interaction among the components of surface sizings and polypropylene matrix using the model reaction were analysed.

Experiment

Transcrystallization was followed in model composites of maleated polypropylene, mPP (commercial product) and differently treated carbon, C, fibers (d=7.5μm). Sized (CT, Torayca and CH, Hercules) and unsized (CU, Tenax) high strength carbon fibers were used in model systems. Prior the crystallization, model composites were held at 200 °C 10 min in order to erase the previous thermal effects. Then the sample was rapidly cooled to the pre-determined crystallization temperature. TCR was observed by polarizing optical microscope (POM) (Leica, equipped with hot-stage and photo camera), in isothermal regime, *Tc* = 124- 130 °C. TCR was analysed in the composites based on PP- homopolymer and maleated one. In order to determine the induction time of crystallization (t_i) and surface energy characteristics, the model composites were analysed by DSC. DSC analysis was performed in the same isothermal regime using Perkin Elmer DSC-7 analyzer [26]. The chemistry of the interactions among the components of surface sizings and polymer matrix was followed on model reaction by FTIR microscopy. The reaction was performed in melt, at 180 °C for 1 h. After that, very thin films were prepared on teflone sheets. The obtained spectra were arithmetically treated by PC-programme GRAMS/32 using spectra substraction method.

Results

Fiber surface topography of the studied fibers, obtained by SEM are presented on fig. 1. Characteristic micrographs of TCR obtained by POM are presented on fig. 2 and fig. 3, which clearly show that nucleation occurs at the fiber surface and then the nuclei grow perpendicular on the fiber axis. Our investigations have proved the effect of the fiber-surface topography. Namely, TCR was obtained only in the presence of carbon fibers with fibrilized surface roughness (sized C-Torayca and unsized C-Tenax, see fig.1).



a) C-Torayca (x100) b) C-Tenax, untreated (x100) c)C-Hercules (x100)

Fig. 1. SEM micrographs of carbon fiber surfaces

Fig. 2. Transcrystalline morphology in CT/mPP model composites (t=8min, *Tc*=124 °C, x200)

TCR was developed only in the composites based on maleated PP, due to the higher nucleation ability of mPP as it was previously shown for glass fiber/mPP composites [27]. The changes of the TCR radius and growth rate with the time at different *Tc* are presented on fig.4. TCR radius increased with the crystallization time and decreased by increasing *Tc*. Nucleation rate and induction time decreased at higher *Tc*. It was shown that TCR has been influenced by the fiber surface sizing. The comparison has shown that higher effect exhibited sized carbon fibers (Torayca). They have higher nucleation activity and t_i of TCR layer on C-Torayca is lower .

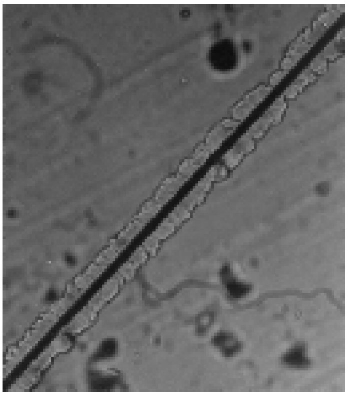
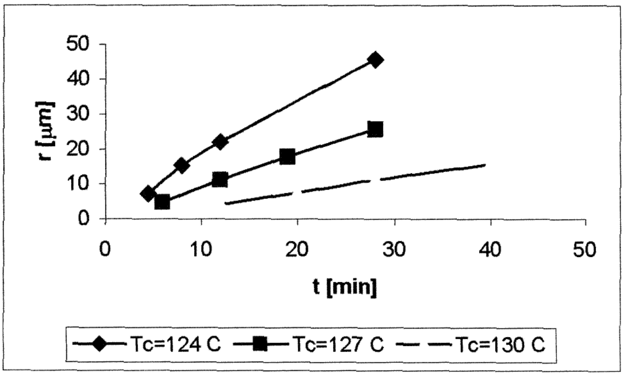
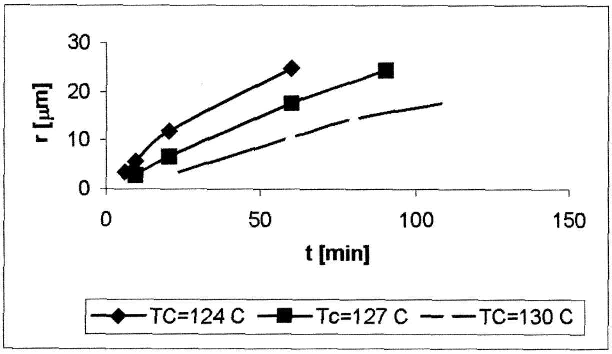


Fig. 3. Transcrystalline morphology in CU/mPP model composites (*t*=9.5min, *Tc*=124 °C, x200)



(a) CT/mPP



(b) CU/mPP

Fig. 4 Changes of TCR-radius, r [μm] with time at different *Tc*

At shorter times, up to 25 min, uniform thickness of the TCR layer was obtained. After 30 min, TCR layer impinged with the spherulites of the bulk matrix. The final dimensions of TCR layer are approximately 50-60 µm, which is comparable with literature data. According the theory, the TCR thickness mainly depends on the temperature, induction time and nucleation rate of polypropylene in TCR layer in relation to the neat matrix [6]. Fig.5 presents the changes of the radius of TCR layer, spherulites near the fibers and the bulk-spherulities. These differences actually represent the differences in the induction times and growth rates,*G*, although it was postulated that the growth rate is constant. According to Ishida's study on the heterogeneous crystallization, a linear relation between $ln(1/ti)$ and $ln\ \Delta T$ exists [10], which is also confirmed by our investigations (see fig. 6).

For the studied systems, some energetic parameters were calculated and the results are presented in Table 1. The surface energy parameter $\sigma\sigma_e\Delta\sigma$ was determined from the slope of the plot of $log(1/t_i) + U^*/2.303R(Tc-Tm,)$ versus $1/Tc(\Delta T^2)$, where U^* is the activation energy related to molecules transporting across the phase boundary. A value of $\sigma\sigma_e$ was determined from the slope of a plot of log G + $U^*/2.303R(Tc-Tm)$ versus $1/Tc\Delta T$ [12]. The obtained results are in agreement with literature data. Lower value for the interfacial energy difference function, $\Delta\sigma$, was obtained for the system with surface treated C fibers which also contribute for their higher nucleation activity.

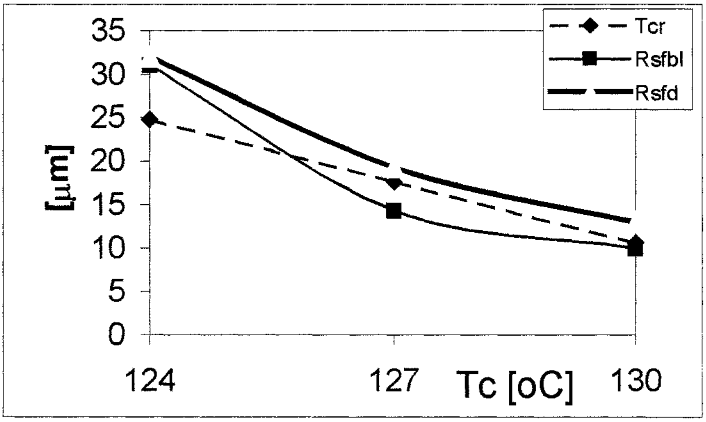


Fig. 5 Changes of TCR radius (Tcr), near spherulites (Rsfbl) and bulk-spherulites (Rsfd)

$\Delta\sigma$ for inter-mediate sized C-Torayca fiber ($\Delta\sigma=1{,}145x10^{-7}$ J/cm^2) is almost equal to $\Delta\sigma$ for high-modulus C-Torayca fiber ($\Delta\sigma=1{,}14\pm0{,}25x10^{-7}$ J/cm^2) [12], while $\Delta\sigma$ for the high-strength unsized C-Tenax fibers is higher. Besides $\Delta\sigma$, additional driving force for the nucleation of TCR could be also the thermal stress created at the fiber/melt interface when the samples are rapidly cooled from 200 °C to *Tc*. Due to the thermal expansion coefficient, α, of iPP melt and carbon fibers ($\alpha_{iPP}=300\ x10^{-6}$ $°C^{-1}$, $\alpha_{C-T,IM}=-0{,}1-0{,}5x10^{-6}$ $°C^{-1}$), inter-mediate modulus and high-tenacity C fibers, used in this work, can not induce TCR, contrary to high-modulus [12].

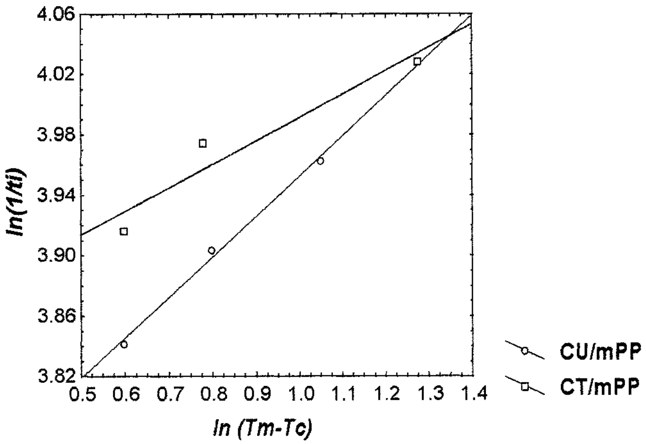


Fig. 6 Dependance of ln(1/*t*i) on ln $\Delta T = Tm-Tc$

Table 1. Energy characteristics

System	$\sigma\sigma_e\Delta\sigma$ $[J^3/cm^6]$	$\sigma\sigma_e$ $[J^2/cm^4]$	σ_e $[J/cm^2]$	$\Delta\sigma$ $[J/cm^2]$
CU/mPP T_m^o=176 °C	$0,261x10^{-18}$	$0,188x10^{-11}$	$0,17x10^{-5}$	$1,379x10^{-7}$
CT/mPP T_m^o=180 °C	$0,471x10^{-18}$	$0,412x10^{-11}$	$0,37x10^{-5}$	$1,145x10^{-7}$

Our results have confirmed that this is valid only for the systems based on neat PP homopolymer, but in composites based on maleated PP, TCR was also induced by intermediate and high-strength carbon fibers.

The chemistry of the interactions among the components of surface sizings and polymer matrix was studied by FTIR microscopy. Using the arithmetic tool of spectral substraction, it was shown that new bands have been created due to the reaction among the basic groups of the sizing (as previously shown by UV-spectroscopy [28]) and the acidic groups of the maleic anhydride grafted PP (see fig. 7). Assignation of the obtained bands is presented in table 2.

Table 2 Assignation of characteristic bands in FTIR spectra

cm^{-1}	group, bond
1532	-N-H
1689	-C=O
1720	-C=O
1806	-C=O (anhydrous gr.)
3376	-N-H (of the size)

The results of Pukanszky and Bayer obtained for similar model reaction confirmed that due to the chemical reaction among the primary amines of γ-APS and carboxyl groups of the maleated PP, secondary amides were formed which resulted in new deformation vibration of –N-H- bond in the range of 1518-1580 cm^{-1} and antysymmetrical vibration of C=O groups in the range of 1640-1690 cm^{-1} [24,25].

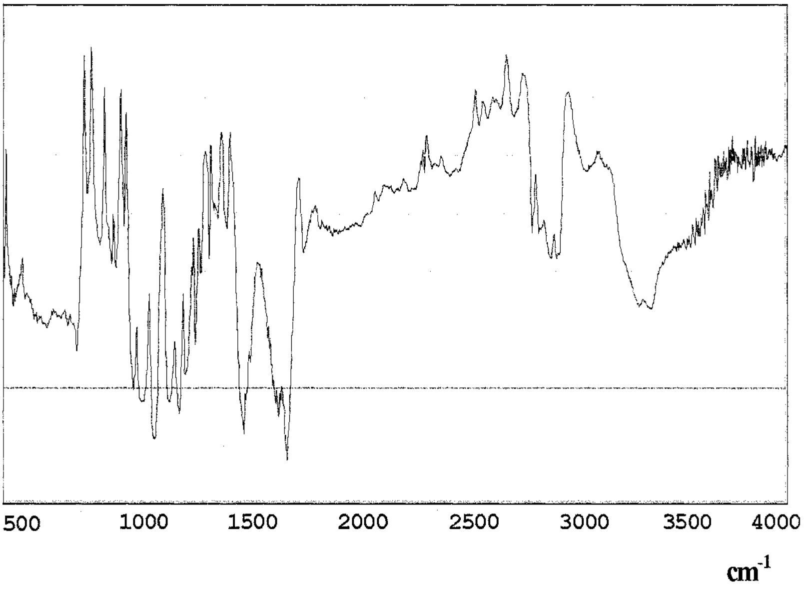


Fig. 7. FTIR substraction spectra of mPP and PP

FTIR-microscopy analysis of model systems might be useful tools for the detection of chemical interactions at the interface, which in turn is additional factor in creation of appropriate conditions for the growth of TCR layer [25]

Conclusions

TCR phenomena of Carbon fiber/mPP composites was investigated in terms of the effect of fiber surface sizing, crystal growth kinetics and chemical interaction at fiber/matrix interface. TCR was obtained only in the presence of carbon fibers with fibrillized surface roughness (C-Torayca and C-Tenax). For the system with surface treated carbon fibers lower value for $\Delta\sigma$ was obtained which also contribute for their higher nucleation activity. Using FTIR microscopy and model reaction, chemical interactions among the basic amine groups of the sizing and the acidic groups of the maleic anhydride grafted PP matrix were confirmed.

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