

## **THE EFFECT OF CROSS-LINKED POLYETHYLENE AS A SURFACE MODIFIER ON CRYSTALLIZATION OF POLYPROPYLENE**

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(Received September 18, 1998; in revised form February 10, 1999)

### **Abstract**

The effect of addition of silica on the parameters of isothermal crystallization of polypropylene has been investigated. It was found that the covering of the silica surface by a layer of low-density polyethylene leads to a deactivation of the filler regarding the positive effect on the polypropylene crystallization rate parameters. Cross-linking of the surface polyethylene layer results in a stronger attachment of the modifying polymer to the filler surface and the deactivation effect of the silica surface modification is more pronounced.

**Keywords:** cross-linking, isothermal crystallization, kinetics, modification, polypropylene, silica

### **Introduction**

The addition of an inorganic filler into a matrix of semi-crystalline polymer is rather a common way of tailoring the properties of the material. Changes of mechanical properties, especially stiffness, are the most striking and also desired features. Other effects are less obvious but important as well.

The presence of the inorganic filler also affects the crystallization behaviour of the crystallizable matrix, mainly due to a substantial nucleating effect [1–4]. The morphology of the matrix is significantly changed in many cases by a way that results in a considerable effect on the ultimate properties of the material.

A surface modification of a filler is a common procedure when introducing the filler in a polymer matrix. An improvement of either processability or ultimate properties is the main reason. In the latter case the effect consists mainly in an improved interaction between the polymer matrix and the filler surface leading to an optimal adhesion on the interface. Usually the role of modifier includes a chemical or physico-chemical attaching onto the filler surface and an interaction with the polymer matrix at the same time. A large number of low-molecular compounds are commonly used as modifiers, silanes [5–7], titanates, or fatty acid [8] being those most commonly applied.

Oligomers of various nature have been tested as well [8, 9]. An application of polymeric modifiers is rather rare; in all cases some sort of chemical or physico-chemical interaction between the filler surface and the reactive groups of the modifier is required. Maleic anhydride and acrylic acid are the most frequently used ones as grafting co-monomers [10, 11]. In this paper we tried to use a modification of the filler surface by a polyolefin where no direct interaction between the filler surface and polymer via chemical or physico-chemical processes would be anticipated. A certain degree of attachment of the modifier onto the filler surface could be accomplished by cross-linking of the modifier at certain stage. This procedure should help to fix the modifying layer onto the surface.

It is assumed and demonstrated in many cases [12] that the modification of the filler surface can influence the effect of the filler on the crystallization behaviour. The effect of the modification on the morphology can be estimated from crystallization behaviour by such a way. In this paper we used this simple procedure to investigate the effect of a filler modification in a polypropylene matrix. To determine the parameters of isothermal crystallization, the DSC method can be used.

For calculation of the rate of isothermal crystallization from DSC Avrami equation [13, 14].

$$\ln[1-x(t)] = -kt^n \quad (1)$$

is commonly applied where  $k$  is the crystallization rate constant and  $n$  is the Avrami coefficient characterizing the mode of the crystal growth. More simple empirical procedure, consisting in a calculation of the relative overall crystallization rate  $v_c$  have been used in several cases [15], based on the determination of the slope of the dependence of the crystallizing portion  $x(t)$  on time

$$x(t) = f(t) \quad (2)$$

where

$$x(t) = \frac{A_t}{A} \quad (3)$$

$A_t$  corresponds to the heat generated in the crystallization time  $t$  (the area under the DSC curve in time  $t$ ) and  $A$  is related to the overall crystallization heat (the total area under the DSC curve).

The last described method allows neither to calculate a crystallization rate constant nor estimate the different mode of crystal growth. It should be used only for comparison of similar materials in a narrow temperature range, where no change of a crystallization mechanism can be assumed.

In this paper, the effect of a modification of silica by a layer of low-density polyethylene (LDPE) on isothermal crystallization of isotactic polypropylene (iPP) was investigated. The LDPE layer was cross-linked (XLDPE) before mixing the filler into the iPP matrix.

## Experimental

Polypropylene Tatren TF 411 (Slovnaft, Bratislava, MFI=8 g min<sup>-1</sup>, 230°C, 21.18 N, ISO 1133) and low-density polyethylene Bralen RA 2-19 (Slovnaft, Bratislava, MFI=2 g min<sup>-1</sup>, ISO 1133), were used. Silica Ultrasil VN3 (Degussa, surface area 140 m<sup>2</sup> g<sup>-1</sup>) was used as a filler. 2,5-dimethyl-2,5-ditertbutyl peroxy hexyne (Luperox 130, Luperox GmbH, Germany) was used as a peroxide initiator of the cross-linking.

All the mixtures have been prepared by using a Brabender Plasticorder PLE 331 internal mixer with a 50 cm<sup>3</sup> mixing chamber. The first set of samples was made by simple mixing of silica in respective polymer. 200°C was applied when polypropylene was used as a matrix. These samples were used as reference materials. Mixtures of silica with polyethylene with or without peroxide were prepared at 150°C, i.e. under conditions when peroxide decomposition is negligible. LDPE/silica mixture were used as master-batches for preparation of other samples. Cross-linked polyethylene (XLDPE) was prepared in the same way. The second set was made by mixing LDPE/silica master-batches without peroxide into iPP at 190°C. These samples were used for the estimation of the effect of covering the filler surface by LDPE on nucleating ability of the filler. The third set of samples was similar to the second one but LDPE was cross-linked before mixing the filler in iPP. Cross-linking proceeded in Brabender mixing chamber at 190°C for 15 min. The master-batch was mixed into iPP at 190°C. It was supposed that the surface LDPE layer would be permanently fixed onto filler surface and should withstand the mixing procedure with PP. In all cases the amount of master-batch added was calculated so that the total concentration of silica in the polypropylene was 2 mass%.

The measurements of the isothermal crystallization were studied by means of a Perkin Elmer DSC model 2 with an on-line connection to a Tektronix 31 calculator. Indium and lead were used as temperature standards and indium for the heat of fusion.

Isothermal crystallization was carried out using 5 to 6 mg samples. They were heated to 473 K at a heating rate 80°C min<sup>-1</sup> and left for 10 min. They were subsequently cooled at a cooling rate 80°C min<sup>-1</sup> to the crystallization temperature. Two different temperatures of isothermal crystallization were chosen (399, 403 K). Rather narrow temperature range could only be investigated because of experimental reasons. A certain induction period is necessary before the beginning of crystallization on one hand and the crystallization rate has to be high enough considering the sensitivity of the equipment on the other hand.

## Results and discussion

The calculated values from DSC measurements for all samples, i.e. iPP mixed with LDPE or cross-linked LDPE, as well as filled with silica, silica covered by LDPE and silica covered by a layer of cross-linked LDPE, are shown in Tables 1 and 2.

*The effect of LDPE and XLDPE addition in iPP crystallization*

Before investigating the effect of silica covered by LDPE on iPP crystallization parameters, the influence of LDPE and cross-linked LDPE without filler had to be observed. It is seen that the addition of polyethylene leads to an increase in the iPP crystallization rate comparing to the iPP without LDPE (Table 1). However, with increasing LDPE content the effect is less pronounced. The addition of small amounts of cross-linked LDPE has the same effect (Table 1). At higher XLDPE content the crystallization rate decrease is higher compared to uncross-linked LDPE.

**Table 1** The changes of the relative crystallization  $v_c$ , Avrami coefficient  $n$  the rate constant  $k$  as the functions of the LDPE, resp. XLDPE content in the mixture with iPP at the temperatures of isothermal crystallization 399 and 403 K

PE/ mass%	$v_c \cdot 10^2 / s^{-1}$		$n$		$k \cdot 10^3 / s^{-n}$	
	LDPE	XLDPE	LDPE	XLDPE	LDPE	XLDPE
399 K						
0	0.34		3.3		2.97	
4	0.73	0.73	3.7	4.0	5.87	5.89
10	0.56	0.46	3.6	3.3	4.58	4.10
20	0.54	0.30	3.6	3.3	4.46	3.34
403 K						
0	0.14		3.3		1.42	
4	0.30	0.29	3.5	3.7	2.90	2.59
10	0.24	0.18	3.5	3.2	1.94	1.52
20	0.24	0.09	3.6	2.7	1.99	1.08

In these experiments the isothermal crystallization of iPP was performed above the melting temperature of LDPE. Under these conditions the effect might be ascribed to a contribution to a nucleation introduced either by the LDPE presence itself or by some additives (antioxidants, impurities) introduced by LDPE and transferred to iPP phase during mixing. Certain increase of iPP mobility resulting in higher crystallization rate due to an addition of small amount of LDPE can also be considered. The increase of LDPE concentration, however, results in a more extensive diluting the crystallizing polymer and the above mentioned effects are less pronounced. It is somewhat surprising that the XLDPE has the same effect. It may mean that for achieving the crystallization rate increase observed, nucleation plays a more important role, since the small amount of low-molecular nucleating agent can be supplied from the XLDPE or the nucleating agent can be cross-linked polymer itself.

Certain decrease of the crystallization rate with increasing LDPE content is more important for XLDPE. At higher XLDPE content, the crystallization rate is even lower in the presence of the additive compared to the iPP homopolymer. This is quite understandable since the molten LDPE has to be squeezed out from crystallizing regions of iPP. This is much more difficult to achieve with cross-linked LDPE if

uncross-linked LDPE is present. The dependence of Avrami coefficients on the composition of the blend supports this idea. An addition of LDPE results in an increase of the  $n$  indicating that the three-dimensional growth of the crystals is somewhat easier. The increase of LDPE content does not influence the values of  $n$ . On the other hand, the increase in the XLDPE content leads to a drop of  $n$ , indicating that spatial obstacles may play a role in the crystallization process.

The changes of the kinetic parameters of isothermal crystallization calculated for two different temperatures show the same tendency in all cases (Table 1).

#### *The effect of silica and modified silica addition on iPP crystallization*

An addition of 2 mass% of silica leads to a substantial increase of all the crystallization rate parameters (the comparison Tables 1 and 2). A ten-fold increase of the filler concentration has only a marginal effect on the relative crystallization rate  $v_c$  and almost no effect on the Avrami rate constant  $k$ . On the other hand, further growth of the Avrami coefficient  $n$  was observed. The covering of the filler surface by LDPE results in diminishing the effect of the silica addition (Table 2), regarding the relative crystallization rate and crystallization rate constant.

**Table 2** The changes of the relative crystallization rate  $v_c$ , Avrami coefficient  $n$  and rate constant  $k$  as the functions of SiO<sub>2</sub>/LDPE, resp. SiO<sub>2</sub>/XLDPE content in iPP at the temperatures of isothermal crystallization 399 and 403 K

SiO <sub>2</sub> /PE/ mass%	$v_c \cdot 10^2 / s^{-1}$		$n$		$k \cdot 10^3 / s^{-n}$	
	LDPE	XLDPE	LDPE	XLDPE	LDPE	XLDPE
399 K						
2/0	1.68		4.5		12.57	
2/4	1.46	0.57	4.7	3.8	12.27	6.05
2/8	1.12	0.80	3.7	4.0	9.65	6.57
20/0	1.18		5.0		12.99	
403 K						
2/0	0.62		3.6		6.21	
2/4	0.55	0.24	3.5	3.4	4.55	2.10
2/8	0.47	0.30	3.6	3.4	4.16	2.56
20/0	0.68		4.5		5.86	

These results indicate that considering the nucleation effect, the surface of silica is deactivated to certain extent by the presence of LDPE. It is worth noting that, comparing the mixtures iPP/LDPE and iPP/(silica/LDPE) (Tables 1 and 2), the relative crystallization rates and Avrami constants are approximately double in the mixtures containing silica for the same or similar LDPE content. This fact may indicate that during mixing the silica/LDPE master-batch into iPP, part of LDPE is removed from the filler surface and affects the crystallization behaviour similar to the LDPE without

silica. Another explanation may be that the filler surface is not covered completely and the increase in the LDPE portion in the master-batch with silica leads to higher surface deactivation resulting in lower both relative crystallization rate and Avrami rate constants.

The Avrami coefficients  $n$  differ in dependence on the LDPE content in the master-batch. At lower LDPE content the  $n$  is similar to that for unmodified silica while at double LDPE concentration  $n$  is close to the value for iPP/LDPE blends without silica, indicating, again, much more perfect deactivation of the nucleation ability of the silica surface.

#### *The effect of cross-linking of the surface LDPE layer on iPP crystallization*

The cross-linking of the surface layer results in a significant decrease in both the relative crystallization rate and Avrami rate constant compared to both blends with unmodified silica and with silica covered with uncross-linked LDPE (Table 2). The crystallization rate constant is almost identical with the  $k$  for the blend iPP/XLDPE containing 4 mass% of (Table 1) and no large difference was found when comparing the values of relative crystallization rate. This observation indicates that rather perfect covering of the silica surface was achieved by the layer of cross-linked LDPE which was not removed from the surface during the mixing of master-batch with iPP. It means that the cross-linking leads to the fixation of LDPE layer on the filler surface.

However, the increase of XLDPE content in the silica/XLDPE master-batch results in opposite effect compared to that for uncross-linked LDPE layer, namely, the increase of rate parameters ( $v_c$ ,  $k$ ,  $n$ ) with rising XLDPE content is observed. This rather surprising fact is to be explained considering the same behaviour as for the addition of LDPE only. Assuming that the addition of small amounts of LDPE leads to an increase of crystallization rate, as demonstrated by the investigation of iPP crystallization in the presence of LDPE (Table 1), this effect can also be expected in the presence of XLDPE due to certain portion of uncross-linked LDPE which could be partially extracted from the cross-linked part during mixing well above the LDPE melting temperature. This amount is not high enough to be able to influence the crystallization substantially at overall XLDPE content 4 mass% since, unlike for the blends in absence of silica, certain amount of uncross-linked LDPE content can be irreversibly immobilized at the filler surface. When increasing the XLDPE content, the uncross-linked portion can be expected to rise to about 10 mass% of the total XLDPE content, making around 1 mass% of free LDPE in the blend. Even a part of this amount can be sufficient to be able to affect the crystallization rate in the observed extent. This behaviour is not found for the uncross-linked LDPE layer since in this case much more of the LDPE is expected to be removed from the filler surface during the mixing. Therefore similar behaviour is observed as for the mixtures with higher LDPE content, where further increase in the LDPE content results in a drop of both relative crystallization rate and rate constant (Table 1).

It should be mentioned that kinetic analysis based on Avrami equation suffers a little from rather narrow experimental temperature range. Nevertheless, the fact that the

dependences of the kinetic parameters on composition factors are very similar for both experimental temperatures (Table 2) supports the general validity of the conclusions.

## Conclusions

It was shown that parameters of isothermal crystallization of polypropylene can be influenced by covering the silica surface by a layer of low-density polyethylene. The effect of the cross-linked polyethylene layer on the silica surface is more pronounced compared to the filler covered with uncross-linked LDPE layer. The results indicate that cross-linking leads to an immobilization of the polyethylene layer on the filler surface, resulting in a permanent modification of the filler surface.

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The financial support from Slovak grant agency VEGA (Grant No. 2/5032/98) is highly appreciated.

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