The Effect of Processing Conditions and Matrix Type on the Interface of Polyethylene-fibre/Polyethylene-matrix Composites

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A B S T R A C T

In this paper three different types of polyethylene, high density (HDPE), medium density (MDPE) and linear low density (LLDPE), have been used to prepare composites with ultra high molecular weight polyethylene (UHMWPE) fibres. Thermal behaviour of the matrices, the fibre and the prepared hot-pressed composites were investigated by differential scanning calorimeter (DSC) analysis. PE/PE Microcomposites were prepared from the above materials and their crystalline morphology of the fibre and matrice's interfaces were studied by a polarizing microscope. The hot-pressed samples and microcomposites were cooled by using different processing conditions, i.e. isothermal crystallization (ISO), air cooling (AC) and ice water quenching (IWQ). The DSC studies revealed that only HDPE had a crystallization condition similar to the melted fibres. The microscopic images showed a big difference between those samples prepared by HDPE matrix that cooled by ISO and IWQ methods. The ISO cooled sample contained a regular transcrystallinity (T_C) region having 25 μm thickness and consist of compact needle-like crystals set vertically on the fibre surface, while the IWQ cooled sample had a two-layer T_C region with irregular thickness. In the microcomposites prepared by MDPE and LLDPE as matrix and cooled by ISO method, a sever irregular T_C region appeared and there was no similarity with the microcomposites prepared by HDPE as matrix. With regards to the surface melting of fibres, it is probable to consider a three-layer region around the fibre core where the crystallization of interface begins from the internal layer, which is UHMWPE melt, and continues through the external layer that is matrix melt. The middle layer seems to be composed of a blend of UHMWPE and PE matrix chains.

INTRODUCTION

In comparison with other high performance fibres, outstanding physical and mechanical properties of PE fibres have spread their application in different sectors of composite industries. One group of the PE fibre composites is polyethylene-matrix/ polyethylene-fibre (PE/PE) composites, which have superior mechanical properties. Being made of PE both of fibre and matrix one could expect, apart from the environmental issues, astonishing proprties from these composites. On the other hand due to

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close melting points of fibre and matrix, there is a narrow temperature window for processing of these composites. Consequently special methods should be used for their preparation. Film stacking [1], solution impregnation [2], powder impregnation [3] and hot compaction [4] are the most common techniques that have been used to produce PE/PE composites. In addition the similar chemical structures of fibre and matrix, improve their interface adhesion in these composites. Like other composites, matrix-fibre adhesion is the most influential factor, which determines the mechanical properties of PE/PE composites. A good knowledge of the interface structure and method of formation is necessary to increase fibre-matrix adhesion.

Several researchers have studied the structure and formation of the interface in PE/PE composites [5-7], nonetheless there are still some uncertainties and contradictions in the obtained results which show that the interface nature is not completely known yet. Some researchers have compared the interface of PE/PE composites with other fibrous composites like PE/glass-fibre(GF), despite the fact that during the formation of PE/PE composites, a thin layer of fibre melts. This phenomenon shows a fundamental difference between the interface of PE/PE composites and other usual fibrous composites such as PE/GF. So to study the interface of this composite it should be noted that, in contradiction to other composites, the surface of the fibres could melt.

In this paper the effect of cooling rate and various types of polyethylene as matrix on the formation and structure of the interface in PE/PE composites have been studied.

EXPERIMENTAL

The UHMWPE fibre used in this study was Dyneema SK60 (DSM High Performance Fibers BV). The PE matrix materials were high density polyethylene copolymer grade (HDPE) with narrow molecular wieght distribution, trade name of Rigidex HD5218EA (BP Solvay), linear medium density polyethylene (MDPE), trade name of Rigidex HD3840UA-W (BP Solvay) and linear low density polyethylene copolymer grade (LLDPE) with narrow molecular weight distribution, trade name of M500026 (Sabic corporation). Some properties of these materials are shown in Table 1.

Table 1. Properties of PE matrices.

Test	HDPE	MDPE	LLDPE
MFI (2.16 kg,190°C)	18	4	50
Density (g/mL)	0.952	0.938	0.926
Melting point (°C)	131	127	124

For preparation of hot-pressed samples, PE long fibres were cut to equal lengths and unidirectionally oriented. To facilitate the wetting of fibres by matrix, the fibres were slightly unpacked and divided into several equal bunches, then a fine powder of PE matrix was distributed on the bunches. The powder impregnated bunches were placed between two PE films, having thickness of 100 micron. This preform was transferred into the mould. The mould pressure was adjusted on 5-7 bar during the moulding cycle and at the end of the moulding cycle it was increased to 100 bar to remove the probable air bubbles and providing better compression. The moulding temperature was controlled with the accuracy of –1 C during the moulding cycle, and then the mould was cooled by three methods: quenching in a mixture of ice and water (IWQ), air cooling (AC) by rate of about -3 C/min and isothermal at crystallization temperature as long as 1 h (ISO). To investigate the thermal analysis of the prepared composites, a differential scanning calorimeter (DSC) was used. The DSC curves of raw materials, PE fibre and PE matrices, were prepared as they received. Moreover DSC thermographs of the composites were also obtained and their thermal behaviour were scrutinized. To study the melting and crystallization processes, the DSC analysis was performed in heating and cooling modes. The samples heating and cooling rate was 5 C/min for all the DSC tests. To provide similar condition to moulding process, nitrogen purging was not used during the DSC analysis.

To study the interface of the fibre and matrix, suitable samples were prepared at proper temperatures by laying separately a few monofilaments between two matrix films with 100 μm in thickness and positioning the assemblage on a microscope slide and covering it by a glass cover. The interface of these samples was examined under a polarized light microscope. To investigate the effect of cooling rate on the interface, the samples were cooled by the same three methods. To

explore the matrix influence on the interface structure, three types of polyethylene as matrix were used.

RESULTS AND DISCUSSION

Thermal Analysis

Figure 1 shows the DSC graphs of UHMWPE fibres and three various types of polyethylene as matrices which have been used in this work. A brief outline of the information of these graphs are presented in Table 2.

Melting of UHMWPE fibres in DSC begins at around 127 C and appears as a doublet. The low temperature endothermic peak observed at about 147.3 C is the main melting peak. It is followed by a smaller peak at about 155.8 C. Beginning of the melting of UHMWPE fibre around 127 C is due to the melting of the low molecular mass macromolecules on the periphery of the fibre. The main melting peak at 147.3 C corresponds to the melting point of the main constitutive oriented orthorhombic crystals of the fibre. A solid state transformation of the previous crystals during this same step, transforms a part of the orthorhombic phase to a hexagonal form. This phenomenon is masked by the main endothermic peak of fusion. Finally a smaller

**Table 2.** Thermal information of matrices and fibre obtained from Figure 1.

Materials	Melting peak (°C)	Begining of crystallization (°C)	Crystallization peak (°C)
PE Fibre	147.3, 155.8	121.0	117.3
HDPE	130.3	120.1	117.7
MDPE	126.5	116.8	114.8
LLDPE	124.2	113.6	109.6

peak around 155.8 C is due to the melting of hexagonal form of the polyethylene generated in the latter step[8]. After completing the melting process in the forward part of the curve an exothermic peak appears at 188 C which is due to oxidative degradation of the fibres. This low degradation temperature could arise from particular treatment of fibres during their production. At the backward part of the curve only an exothermic peak corresponding to crystallization process was observed which begins at 121 C and reaches a peak at 117.3 C.

Figure 2 illustrates the DSC curves of the composites produced from three different types of PE as matrix and cooled by AC method. In heating route of three
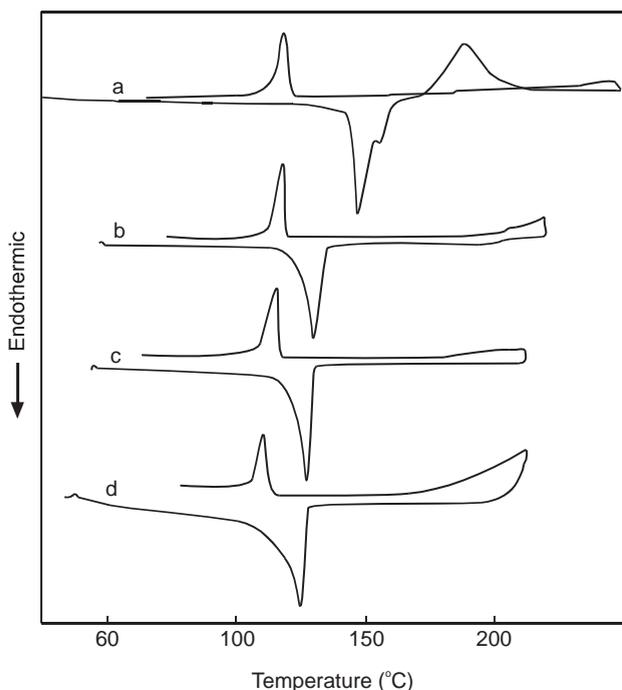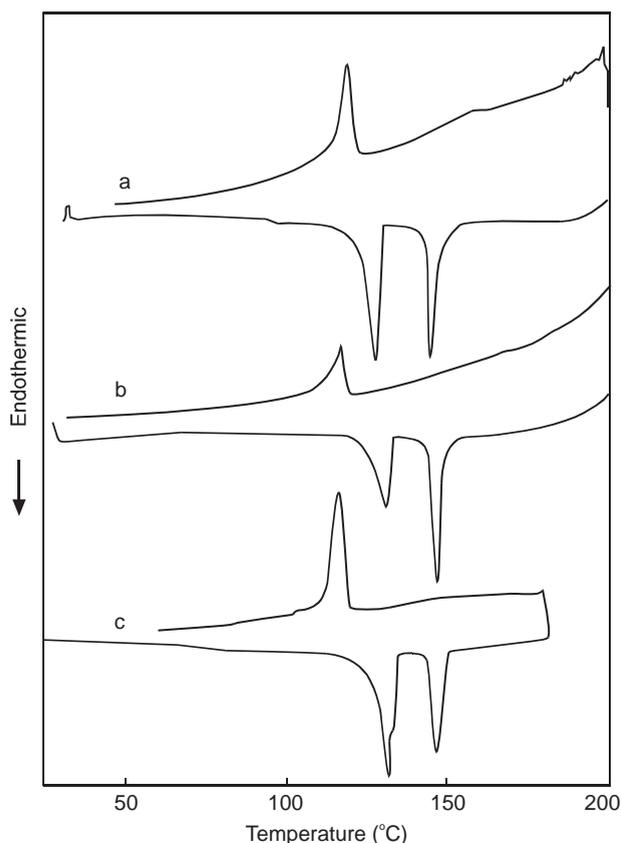

Figure 1. DSC Thermograms of: (a) PE fibre, (b) HDPE, (c) MDPE and (d) LLDPE.
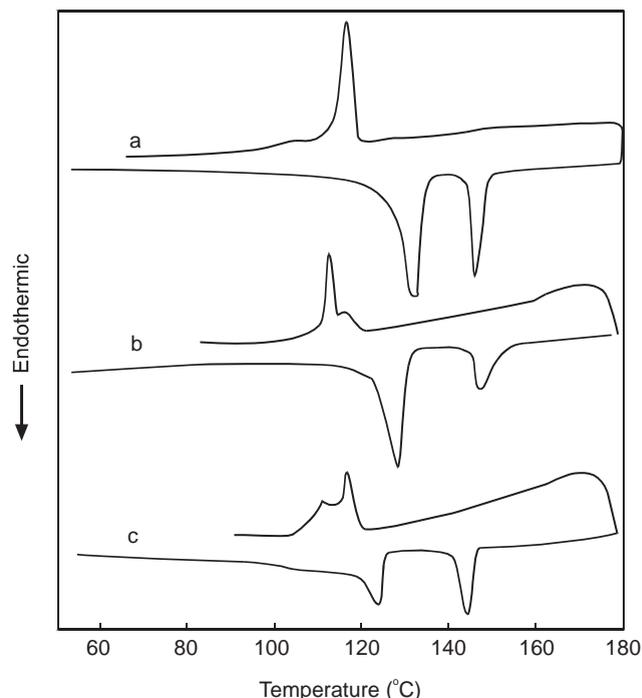
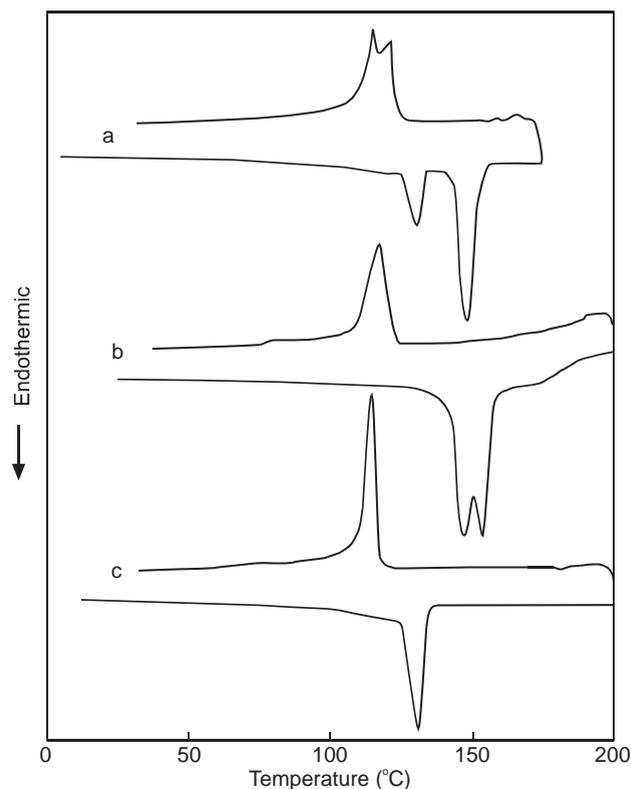**Figure 2.** DSC Thermograms of composites with: (a) HDPE, (b) MDPE, (c) LLDPE matrix.

curves two peaks appeared which the lower one corresponds to the melting of matrix and the other is related to melting of fibres. There is an interesting point in the cooling part of these curves. In curve 2a which belongs to a HDPE matrix type composite, only a sharp exothermic peak was seen in cooling, while in curves 2b and 2c which are related to MDPE and LLDPE matrix type composites, respectively, two exothermic peaks have been appeared. The composite with LLDPE matrix has two discrete peaks which, according to Table 2 it can be concluded that the first peak (observed at 117 C) corresponds to fibre crystallization and the second one at 110 C is the feature of LLDPE crystallization. The same explanation is applicable for MDPE matrix type composite, just considering this difference that because of closer crystallization points of MDPE and the fibre, the observed two peaks are not completely discrete. So, Figure 2 reveals that only the composite with HDPE matrix has one exothermic peak, therefore, the possibility of cocrystallization of the fibre and matrix in the interface could be conceivable.

To evaluate the effect of cooling rate on thermal behaviour of PE/PE composites the HDPE composite prepared by the three cooling methods have been investigated. Their DSC results are presented in Figure 3. As shown in curve 3a, which corresponds to IWQ cooling, the matrix and fibre have melted at 127 C and 144 C, respectively. Curve 3b relating to AC cooling, presents melting of matrix and fibre at 129 C and 145 C, respectively. Curve 3c which represents ISO cooling, shows melting of matrix and fibre at 132 C and 145.6 C, respectively. Therefore, as an interesting point it can be realized that by decreasing the cooling rate, the melting point of matrix increases due to rising crystallinity of the matrix and the interface of composites. In the cooling part of the three curves in Figure 3, there is only one exothermic sharp peak, asserting that the crystallization of HDPE matrix and fibre are happening at the same temperature.

Curves 4a, b and c in Figure 4 are the DSC results of a MDPE type composite, UHMWPE fibre and MDPE, respectively, moulded and cooled by ISO method simultaneously in a single mould. Two endothermic peaks at 130 C and 147 C are clearly seen

Figure 3. DSC Thermograms of HDPE matrix composites with various cooling rate: (a) IWQ, (b) AC, and (c) ISO.

Figure 4. DSC Thermograms of: (a) MDPE matrix composite, (b) PE fibre, and (c) MDPE matrix, with ISO cooling method.

on heating part of curve 4a which exactly conform to matrix and fibre melting points which are evident in curves b and c. The same results have occurred in the cooling part of the curve for exothermic peaks. So it can be concluded that crystallization takes place separately in different temperatures for MDPE matrix and fibres and a cocrystallization phenomenon could not be attributed to the interface of matrix and fibre of this kind of composite.

Interface Studies

To conduct more accurate investigatinon on the effect of cooling process and type of matrix on the interface of PE/PE composites, polarized light microscopy was used. Figure 5 shows micrographs of two composites with HDPE matrix that are cooled by ISO and IWQ methods. In ISO cooled sample an interface with a constant thickness of about 25 μm is clearly seen. This region is made of needle-like compact crystals propa-

(a)

(b)

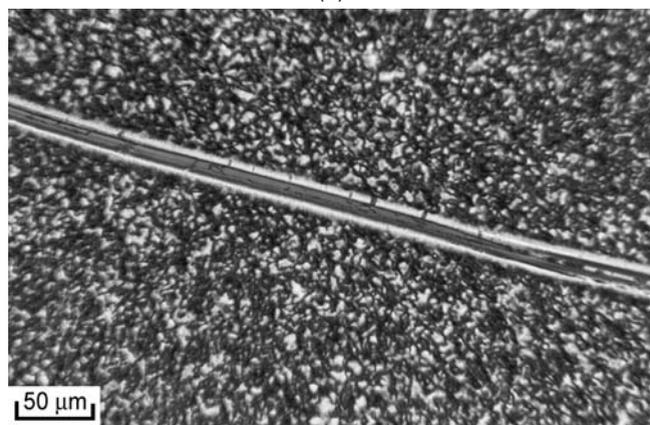**Figure 5.** Optical micrographs of HDPE-matrix/UHMWPE fibre microcomposites: (a) IWQ and (b) ISO.

gated vertically on the surface of fibre. The IWQ one has an irregular interface with variable thicknesses. The interface of this sample consisted of approximately two layers, with the internal layer, which is in contact with the core of the fibre, having more compact crystals compared to the second layer. The crystals in the external layer, are more or less similar to those in the bulk of the matrix, but packed tighter with respect to the bulk equivalents. This double-layered structure was not present in the ISO cooled sample. The double-layer structure of the IWQ sample is probably arises from the very rapid cooling of the sample. Since there is a melted layer of UHMWPE on the surface of the fibre, which is internally in contact with the fibre core and externally with the matrix melt. Because of the same crystallization temperature for fibre and matrix, quenching causes a simultaneous crystallization in the HDPE and UHMWPE and consequently a double-layer interface is formed which its external layer has similar crystals to the matrix crystals. The suggested mechanism is different for ISO sample. At first the UHMWPE chains in melt state begin nucleation on the surface of solid fibre core and reaches the matrix melt. At this time according to similar chemical structure and crystallization temperature of fibre and matrix, the T_C layer formed by UHMWPE continues by HDPE into the bulk of the matrix. In this situation the crystalline morphology in the interface did not look like the morphology of the crystals in the bulk of matrix.

To study the effect of matrix type on the interface, two microcomposite samples, based on HDPE and LLDPE and cooled by ISO method, prepared and their interfaces examined under a polarized light microscopy. Figure 6 shows the microscopic images of these two samples. The interface of the LLDPE composite is remarkably variable in thickness. In addition the crystalline structure at interface is extensively similar to that in matrix and its thickness even decreases to zero in some points. On the other hand a needle-like compact crystalline structure with roughly constant thickness, which was almost equal to the fibre diameter, was observed for HDPE composite. According to these results it is clearly understood that matrix type is one of the main factors affecting the crystalline formation at the interface.

The LLDPE composite cooled by ISO method does not show a compact crystalline layer. This could be
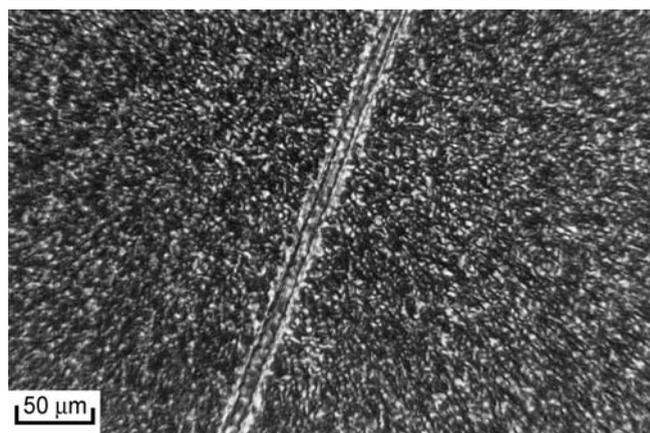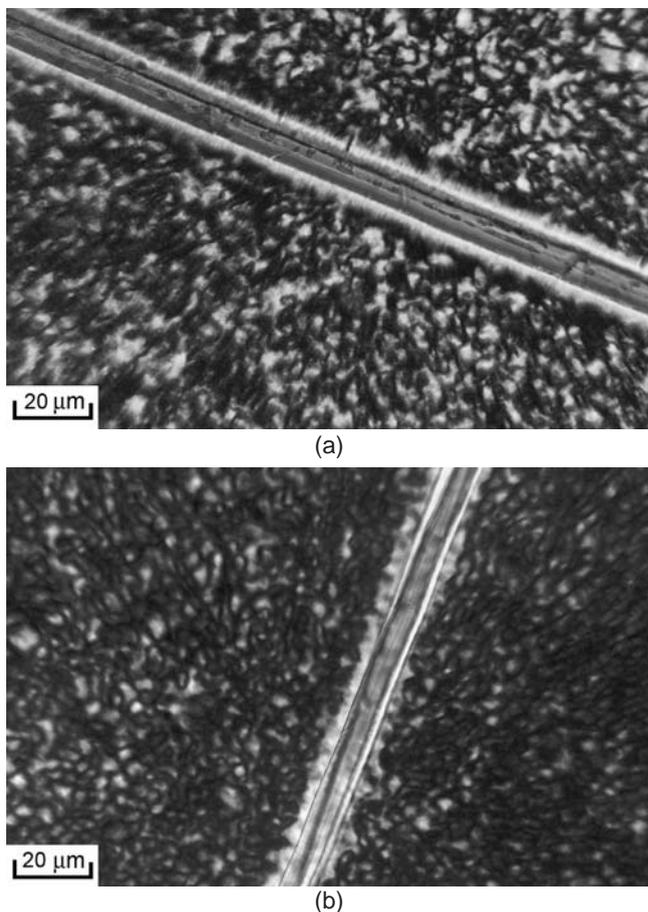
(a)

(b)

Figure 6. Optical micrographs of microcomposites: (a) HDPE matrix and (b) LLDPE matrix (ISO cooling).

related to the different condition in the crystallization process of this sample. At first the melt layer of UHMWPE begins the crystallization on the solid surface of fibre and while growing it reaches the matrix melt layer which its crystallization temperature is different from the UHMWPE melt. So at this point the crystallization development is stopped until the temperature
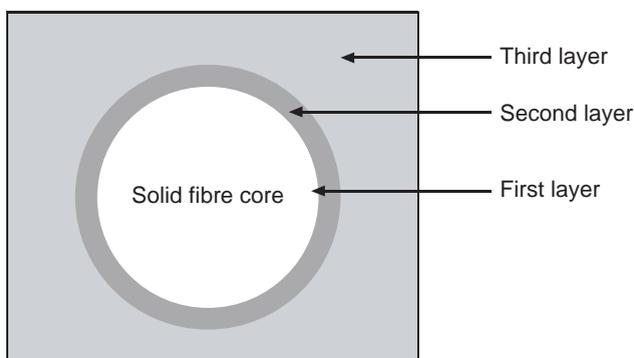
Figure 7. Schematic representation of layers in the interface.

decreases and meets the suitable temperature for the initiation of crystallization of LLDPE. Then the LLDPE melt continues the crystallization and finally a crystalline structure like that in bulk of matrix is created.

During the moulding of PE/PE composites, it can be proposed that in the melt state there are three different regions (layers) around the fibre core (Figure 7). The first layer in contact with the solid core of the fibre is the melted skin of the UHMWPE fibre. The second layer could be made of melted chains of matrix penetrating in UHMWPE melt. Compatibility of these two melts from the thermodynamic and rheological point of view is necessary to create the second layer. The third region is the matrix melt. The following order is strongly suggested for the crystallization process at interface; the first layer, adjacent to the solid fibre core, begins heterogeneous nucleation. Then, the crystals at the first layer grow from the solid surface of the fibre to the second layer, if such a layer does exist. At this time if the isothermal condition for crystallization of matrix and fibre is set, crystalline layer grows continuously along the previous crystals until they meet the third region which consists of matrix chains which, then grows in the bulk of matrix.

CONCLUSION

The best PE matrix to create a cocrystal region at the interface of PE/PE composites is such a polyethylene which its crystallization temperature is the same as that of melted PE fibre. Our results indicate that in addition to the type of matrix the processing conditions of composite manufacturing could also play a major role in the formation and structure of a proper interface. In this work a suitable co-crystal region was obtained with HDPE through ISO cooling method. When the samples were cooled by the IWQ method the observed structure at the interface was very similar to the bulk crystalline morphology, while in ISO cooling, no similarities were detected between the bulk and the interface. A three-layer interface around the solid fibre core was formed during the melting and consolidation of the composite.

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