Processing of Single Polymer Composites Using the Concept of Constrained Fibers

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The concept of "overheating" is one of the known methods for manufacturing single polymer composites. This concept is validated on two categories of semi-crystalline polymers: the drawable, apolar (i.e., isotactic polypropylene [iPP], ultra-high molecular weight polyethylene [UHMWPE]) and the less drawable, polar ones (i.e., polyethyleneterephalate [PET] and polyamides [PA]). The interchain interactions in apolar polymers are relatively weak and therefore a high degree of drawability can be obtained. Polar polymers on the other hand have relative strong interchain interactions, they are therefore less drawable. A shift higher than 20°C of the melting temperature can be obtained in case of highly extended iPP (draw ratios >14). Ultra-drawn PE shows only 10°C overheating upon constraining and this is mainly due to the change in chain mobility for PE in the hexagonal phase. In case of PET and PA6, only draw ratios of 4 could be reached; however, temperature shifts of about 10°C for constrained fibers compared to unconstrained fibers could be measured. A proof of principle of the potential of the constraining concept for the manufacturing of single polymer composites is obtained by the preparation of single fiber model composites. The effect of the post-drawing conditions on overheating is examined in details on the example of iPP. It is concluded that both post-drawing temperature and ultimate draw ratio have a significant influence on the degree of overheating. POLYM. COMPOS., 26:114–120, 2005. © 2004 Society of Plastics Engineers

INTRODUCTION

Polymer composites are being used in steadily increasing quantities in diverse fields, e.g., aerospace, automotive, electrical, microelectronics, infrastructure and construction, medical, and chemical industries, as a result of improved material performance, cost-effective production, and manufacturing flexibility (especially the thermoplastics). Compared to the widespread and widely documented activities on polymer recycling, the work on recycling of composites is still modest. However, as composites are more widely used in an increasing number of commodity products, the issue of composite recycling is becoming ever more important. Unfortunately, not all polymers are equally easy to recycle. Since thermoplastics can in theory be re-melted and cooled to solidify an infinite number of times, recycling of thermoplastic composites through material recovery is easier than for thermosets. While this is generally the case, each re-melting unfortunately causes the material to gradually degrade. The presence of additives or inclusions such as glass fibers limits further the application of the recyclate since glass-fiber reinforced thermoplastics, for example, can only be recycled into new fiber reinforced grades. Hence, there is a need for systems consisting of a minimum of different, compatible polymers. This in practice means mono-component systems or in other words single polymer composites.

Single Polymer Composites

The concept of single polymer composites is not new. Different methods have been proposed in the past for the processing of single polymer composites, referring mainly to polyethylene (PE) and polypropylene (PP). Mead and Porter presented 25 years ago the first attempts to prepare single polymer composites using different grades of polyethylene for the matrix and the reinforcement [1]. Since then a lot of effort has been given to bring single polymer composites in real applications. In order to increase the potential of single polymer composites it is essential to have polymer fibers and matrices optimized in structure, properties, and processing performance. Isotropic polymers have

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Contract grant sponsor: Economy, Ecology, and Technology (EET) program; contract grant number: Nr. EETK97104; contract grant sponsor: Dutch Government; contract grant sponsor: EU ORTHOFLEX Growth project; contract grant number: G5ST-CT-2002-50185.
DOI 10.1002/pc.20082
Published online in Wiley InterScience (www.interscience.wiley.com).
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relatively low mechanical properties because of the relative weak interactions that exist between the chains. Therefore high-performance fibers are needed in order to reinforce the matrix material. The development of high-performance polymer fiber has been in achieve and of research for the last 30 years and most approaches are based on forming the polymers into filaments and post-drawing them uniaxially in the solid state in order to orient the molecules in the direction of the applied load [2]. A high degree of chain-extension in combination with a high molar mass is needed for high-performance fibers. Because the molecular chains are in practice finite, chain overlap is needed for load transfer through the system, which means in practice the use of high molecular weight polymers. In the literature various processes have been described to orient the chains directly in the molten state. The problem of chain orientation and extension in the melt is that extensive relaxation processes, occur, i.e., the chains resist deformation and retract back to a random coil conformation. Consequently, in order to obtain a high degree of chain extension, drawing should be performed in a separate step, after processing and below the melting point, viz. in the (semi)solid state.

Next to good mechanical properties a clear difference in the melting temperatures of the fiber- and matrix-materials is required for manufacturing single polymer composites. This problem is generally tackled by using different polymer grades for the fiber and the matrix, e.g., UHMW-PE for the fiber and high density PE (HDPE) [3, 4]. However, in the case of true single polymer composites, the matrix and the fiber should originate from the same polymer grade, and hence should have similar melting temperatures. Therefore, it is difficult to combine the fiber with the matrix, without melting the oriented fiber and thus losing stiffness and strength developed in the drawing process.

The Concept of Constraining

Compared to the bulk material, drawn fibers can exhibit a shift of the melting temperature and an increased enthalpy of melting. If the same grade of polymer is used for the matrix and the reinforcement, the shift in the melting temperature of the drawn fiber is not always sufficient enough for the production of single polymer composites. As already discussed, in order to obtain a workable processing window for the preparation of single polymer composites, the difference in melting temperature between fiber and matrix has to be sufficiently high. A reasonable question would be, in what extent it is possible to control the melting point of either the matrix or the fiber. Based on Gibbs free energy theory, the melting point is given by the following equation: $T_m = \Delta H/\Delta S$, where ΔH and ΔS are the enthalpy and the entropy difference between crystal and liquid, respectively. The enthalpy of a polymer is determined by the interaction forces between the molecular chains, while the entropy is determined by the conformation possibilities of a molecular chain. Therefore it would be possible, in theory, to alter the crystalline melting point by the controlled change of either ΔH or ΔS, or by changing both of them. Disturbances in chain regularity, crystal imperfections, and small crystals could lower ΔH, and this would lead to a decrease of the melting point. Based on this fact, Teishev et al. [3, 4] prepared singe polyethylene (PE) composites consisting of high density PE matrix and UHMW-PE fibers which have at least a 20°C difference in their melting points. In practice, this means the use of two different polymer grades, which can be a limitation in terms of recyclability. On the other hand, the control of the crystallization speed and temperature gives only few degrees shifts of the melting temperature and a narrow processing window.

A different way to alter the melting point is by changing the conformation possibilities of the molecular chains. A polymer in the isotropic or in the liquid stage has several conformation possibilities. In the crystalline state, a polymer chain is in a single ordered conformation. This means that by going from the highly ordered crystalline state to the random coil conformation in the melt, there is a large change in entropy. Nevertheless, even if the crystals are highly oriented, upon heating, the molecules will try to re-establish their preferential isotropic structure and relaxation will occur.

It is possible to prevent this relaxation by constraining the chains. This would prevent the above-mentioned reorganization and by doing this the chain can be prevented from melting. The shift in melting temperature (T_m) results from an entropy effect, as the unconstrained and constrained fibers have the same enthalpy of melting (ΔH). The chains in the constrained fibers on the other hand have no freedom to move and to relax. This results in a reduction of the gain in entropy per monomer unit (ΔS) [5]. Since $T_m = \Delta H/\Delta S$ and ΔS is decreasing upon constraining, T_m shifts towards higher temperatures. This overheating behavior of constrained fibers has been reported [6–9] with melting temperature shifts of about 10°C. Unfortunately, constraining cannot always be effective. It is impossible to have a high degree of overheating when the molecular chains are folded or if the chain mobility is high.

In summary, for high performance fibers and effective constraining, highly extended chains are of considerable importance. The chain extensibility and drawability of some polymers is, however, questionable. The principle factors limiting chain extension appear to arise from constraints imposed by molecular entanglements, chemical interactions between chains, and crystallites [10]. However, these problems can be partially solved. It has been possible, for instance, to disentangle the molecules by using the solution (gel) spinning technique, devised at DSM. This involved employing semidilute solutions during spinning, but the elongation of chains is performed by drawing in the semi-solid state. This method was proven to be very effective in case of PE, where draw ratios of over 50 were achieved. The aforementioned approach, however, is not universally valid.

For apolar polymers where the interchain interactions are weak, the crystallites will provide little resistance to deformation and will unfold under low drawing stresses. This is

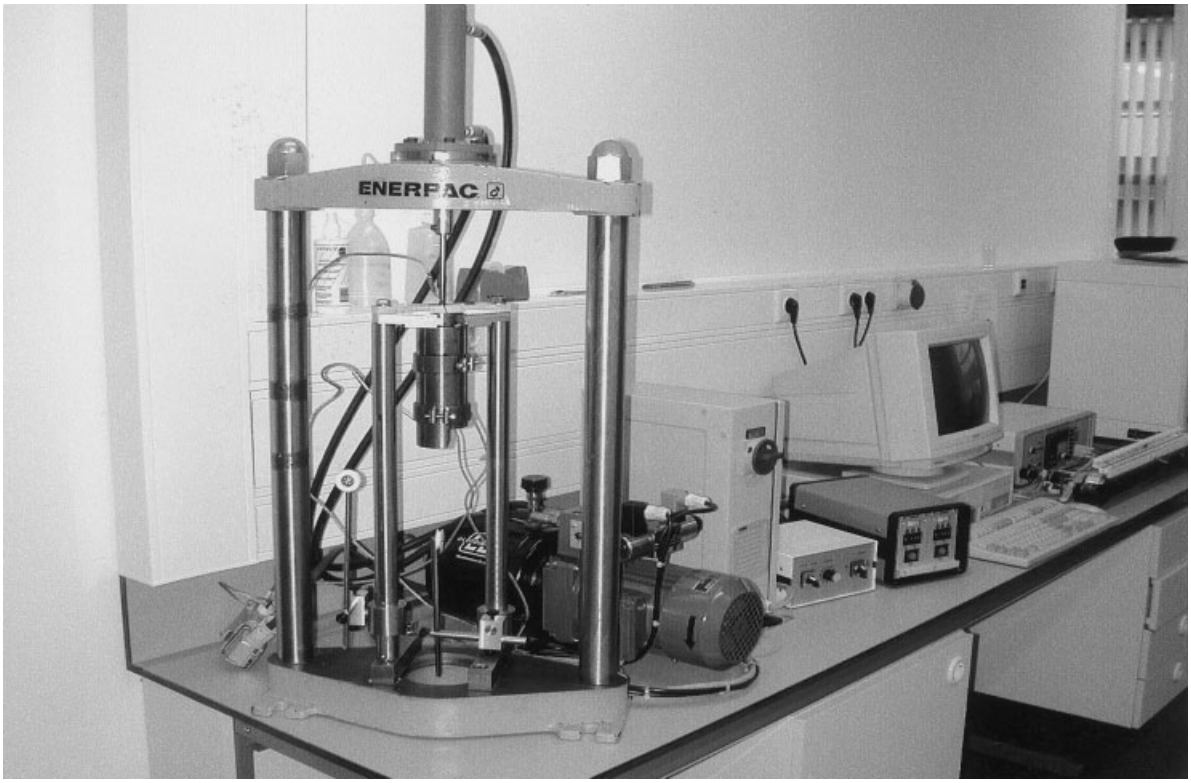


FIG. 1. Home-built lab-scale melt-spinning device.

possible at temperatures above the crystalline α relaxation temperature. For polymers with significant polar interactions, this is not so easy. These polymers possess strong secondary bonds (e.g., hydrogen bonds) and form folded-chain, which cannot easily be unfolded. This is because the crystallites in polar polymers will provide greater resistance to deformation at any temperature below the melting point. Even when solvents, as proposed in the gel spinning technique, are applied, the drawability in not improved, because, for example, the hydrogen bonds between the chains remain intact [2]. Typical examples of apolar polymers are PE and PP while Nylons and PET belong to polar polymers.

It is obvious from the previous discussion that the reason for overheating of different polymers is complicated. It depends on many different parameters including the crystallinity level, the crystal size, and the kinetics of melting of these crystals, and, in some cases, on the scan rate. Nevertheless, the main reason for overheating is the decreased conformational entropy of constrained amorphous phase upon melting. It exceeds the interest of this paper to investigate in depth the overheating due to other parameters beside those that affect the conformational entropy. Since drawability and extensibility of polymer chains and effective constraining are interrelated parameters that directly influence the degree of overheating, the main aim of our study is to validate the concept of constraining for manufacturing of single polymer composites on the example of PP, PE, PA6, and PET, and to find out under which circumstances this concept is applicable. These materials are chosen not only because they represent both polar and apolar polymers, but also because they are the most widely used engineering thermoplastics. Recycling of these materials will be a great contribution to the recycling of thermoplastic polymers. A further scope of our study is to create single polymer model composites as a proof of principle for the constraining concept. Next to that, it was recently reported that the post-drawing condition (draw ratio and drawing temperature) influences the morphology, the orientation of the induced crystals, and the mechanical properties of iPP fibers [11]. It is not known, however, how much these parameters influence the shift of the melting temperature. Using the example of iPP fibers, the influence of post-drawing conditions on the degree of overheating is finally investigated.

EXPERIMENTAL

A commercial iPP grade (Stamylan® P) kindly provided by DSM, The Netherlands, which has an average molecular weight of 280 kg/mol and a melt flow index of 13, is used to manufacture the iPP fibers. Solution (gel) spun UHMWPE fibers with exceptional high draw ratio (Dyneema SK65) were kindly provided by DSM, High Performance Fibers BU. The PA6 grade was Ultramid® BS 3300 provided by BASF, Germany, and the PET was a commercial fiber grade provided by Acordis, The Netherlands. All materials, except PE, were provided in pellet form. Before spinning, the PA6 and PET pellets were dried

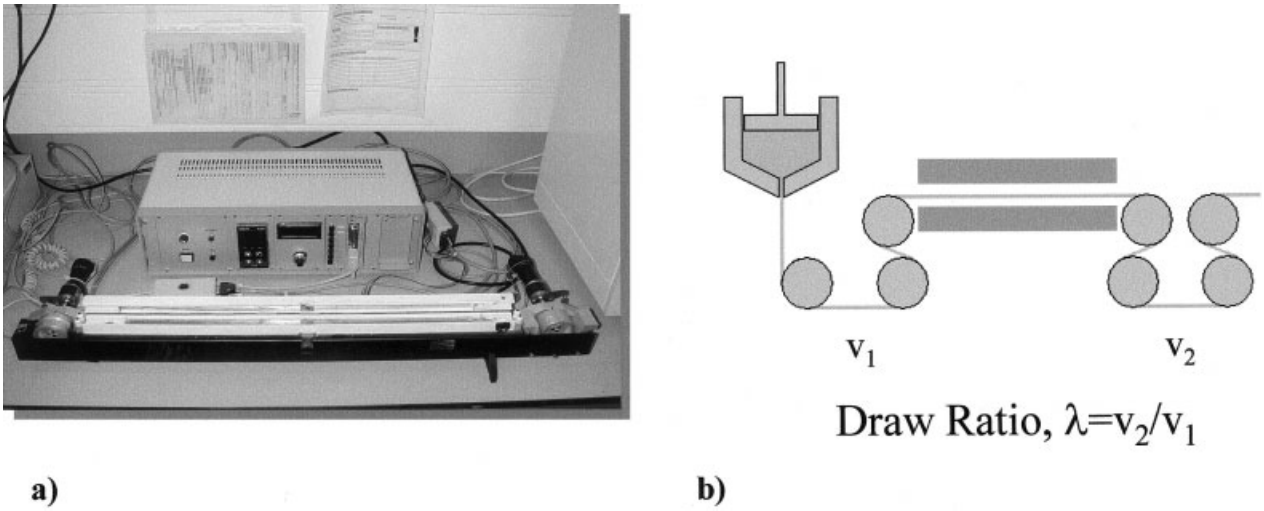


FIG. 2. Home-built stretching unit image (a) and schematic representation (b).

in a vacuum oven at 150°C for at least 24 h. The fibers were prepared using a home-built lab-scale melt-spinning device, which consisted of a double walled storage cylinder, which could accommodate about 10 g of material (see Fig. 1). The spinning temperatures were 200, 250, and 290 °C for PP, PA6, and PET, respectively. The spinning device was equipped with a capillary of 1.5 mm diameter and a length of 8 mm. The fibers were wound on a drum at rates varying from 5 to 120 m/min. The next step in the fiber preparation procedure was solid-state drawing of the filaments. Solid-state drawing was performed using a home-built stretching unit (Fig. 2a), consisting of two small drums of 48.5 mm diameter separated by a 600-mm long ceramic oven, which is schematically presented in Fig. 2b. Absolute speed, speed ratio of the two drums, and temperature are computer controlled. The PP fibers were post-drawn at temperatures varying between 70°C and 200°C with draw ratios (speed ratio of the two wheels of the drawing unit) varying between 2 and 14. The PA6 and PET fibers were post-drawn at different temperatures between their glass transition temperature (T_g) and their melting temperature in order to obtain maximum draw ratios.

The calorimetric measurements were performed using a Perkin-Elmer DSC-7 apparatus. The fibers were either placed unconstrained in the aluminum pans or wound on an aluminum rod to keep them constrained during heating. A heating rate of 10°C/min was used throughout this study. It was difficult to quantify the heat of fusion from these DSC scans because of the inferior contact of the fibers with the aluminum pan. As a consequence, comparison of the heat of fusion of unconstrained and constrained fibers as well as of the width of the melting peak is not applicable here. These measurements can, therefore, give information only on the melting point of the fibers.

For the production of single fiber model composites, both ends of the polymer fibers were fixed on glass slides in order to prevent relaxation during heating. Pellets from the same polymer grade were isothermally hot pressed. The resulting thin films were placed on the same glass slide as the fiber. These stacked samples were heated in a hot-stage, melting only the matrix material but not the constrained fiber. Afterwards, the samples were either air-cooled or isothermally crystallized in a hot-stage. The investigation of the composite morphology was performed using a transmission light microscope (Zeiss Universal) equipped with crossed polarizer.

RESULTS AND DISCUSSION

Figure 3 shows the differential scanning calorimetry (DSC) heating traces of an unconstrained and a constrained highly oriented iPP fiber (draw ratio of 10) [12]. A difference of 26°C in the melting temperature of the unconstrained and constrained fiber can be deduced which is fairly high and illustrates the efficiency of constraining on iPP. This was expected, since iPP belongs to the apolar polymers with high drawability and extensibility of the chains. Next to PP the constraining concept was validated on a sample of

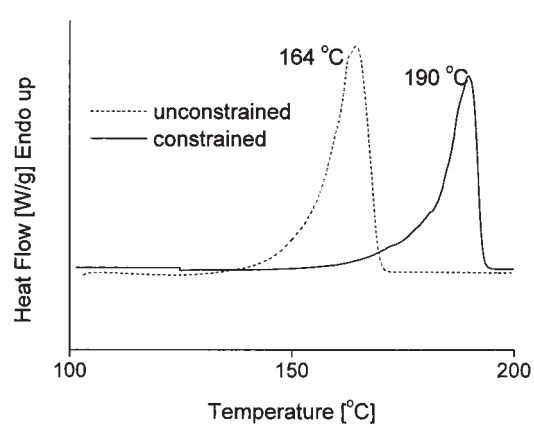


FIG. 3. DSC curve showing the effect of constraining on the crystalline melting point of an iPP fiber.

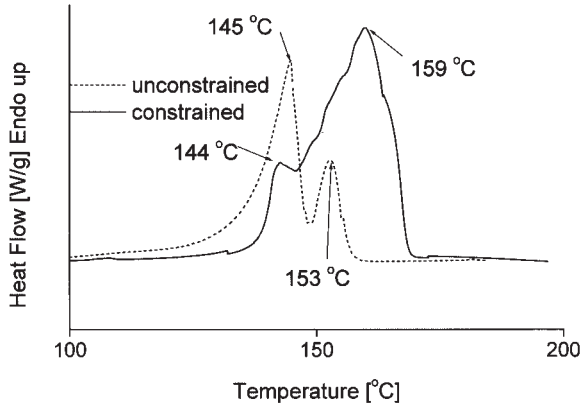


FIG. 4. DSC curve showing the effect of constraining on the crystalline melting point of a UHMW-PE fiber.

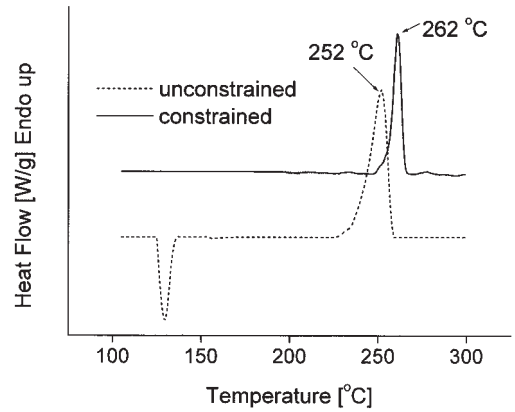


FIG. 6. DSC curve showing the effect of constraining on the crystalline melting point of a PA6 fiber.

gel spun UHMW-PE (see Fig. 4). In both curves (constrained and unconstrained fibers) multiple peaks can be deduced. This indicates the existence of different crystal structures, which is already known for PE. Beside the standard orthorhombic structure a hexagonal phase, which is a so-called "mobile" phase, exists in PE. The orthorhombic structure in PE fibers transforms in the hexagonal crystal structure at temperatures above 155°C. In the hexagonal phase the chain mobility is high and the fiber cannot sustain any load and, consequently, the fiber fails. This situation occurs only upon constrained heating. This explains why it is difficult to achieve a high degree of overheating for PE. Figures 5 and 6 present the DSC traces of constrained an unconstrained PET and PA6 fibers, respectively. The fibers were drawn to their maximum draw ratio, which was in both cases approximately 4. PET shows 10°C of overheating while PA6 shows a shift of 7°C upon constraining. This small shift is due to the limited drawability of both polymers, and therefore the question arises how to increase the drawability of PET and PA. In PET and to lesser extent in nylons, low initial crystallinity and crystallization during drawing can be exploited to achieve draw ratios >5 [13]. Multiple-stage drawing processes [14], zone-drawing, and zone-annealing processes [15–17] and other post-treatment methods [18] have been employed on PET and nylons. The general conclusion is that small improvements can be obtained, but no processing route has yet been devised to impart a structure of highly oriented, predominantly crystalline fibers with crystal continuity.

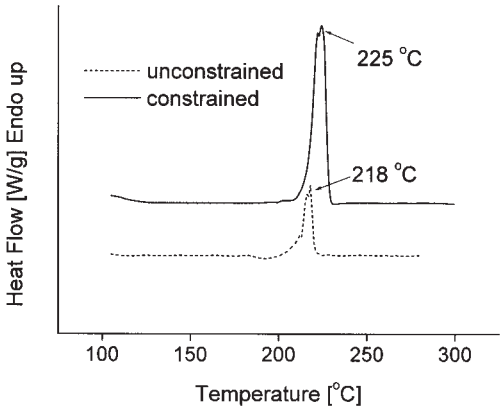


FIG. 5. DSC curve showing the effect of constraining on the crystalline melting point of a PET fiber.

In summary, the degree of overheating for PE, PET, and PA6 is not as high as for iPP but may still be large enough to create single polymer composites. Two polymers, one with a high degree of overheating (i.e., iPP) and one with a smaller shift in melting temperatures (i.e., PA6), were selected to make single polymer model composites. Single polymer model composites were prepared by embedding the constrained fiber in thin films of a matrix based on the same polymer grade (see Fig. 7). iPP was isothermally crystallized at 145°C for 3 days and PA6 at 200°C for 12 h. In case of iPP (see Fig. 7a), the composite morphology consists of three different regions: 1) the iPP fiber partially embedded in 2) a transcrystalline layer, surrounded by 3) the iPP matrix material consisting of spherulitic superstructures. The third region in Fig. 7b is not observed in case of PA6 and this can be mainly because of insufficient time of isothermal crystallization. Another reason could be the crystallization temperature (improper for spherulitic superstructures). Nevertheless, both pictures provide a proof of principle that the concept of constraining can be used to prepare single polymer composites.

As mentioned above, the effect of overheating becomes more pronounced with increasing chain orientation. The post-drawing conditions affect the induced orientation and crystallization; therefore, one would expect that they affect also the degree of overheating. PP was chosen since it is the one with the highest degree of overheating and allows us to observe differences that could not be deduced if the temperature window is narrow. Five different temperatures between 70°C and 200°C were selected to post-draw the iPP fibers, while a constant post-draw ratio of 7 was applied. When drawn at low temperatures, unconstrained samples show one melting peak, which is shifting towards higher temperatures. Fibers drawn at 160°C and 200°C present a

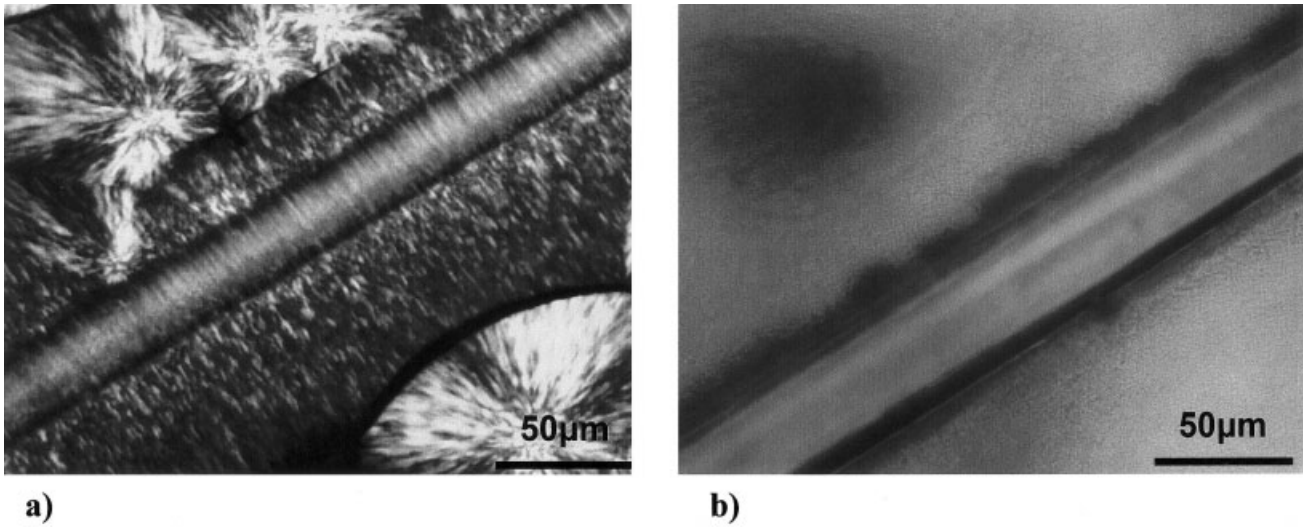


FIG. 7. Optical micrographs of single polymer model composites based on a constrained oriented polymer fiber embedded in an unconstrained non-oriented polymer matrix of the same grade as the fiber iPP (a) and PA6 (b).

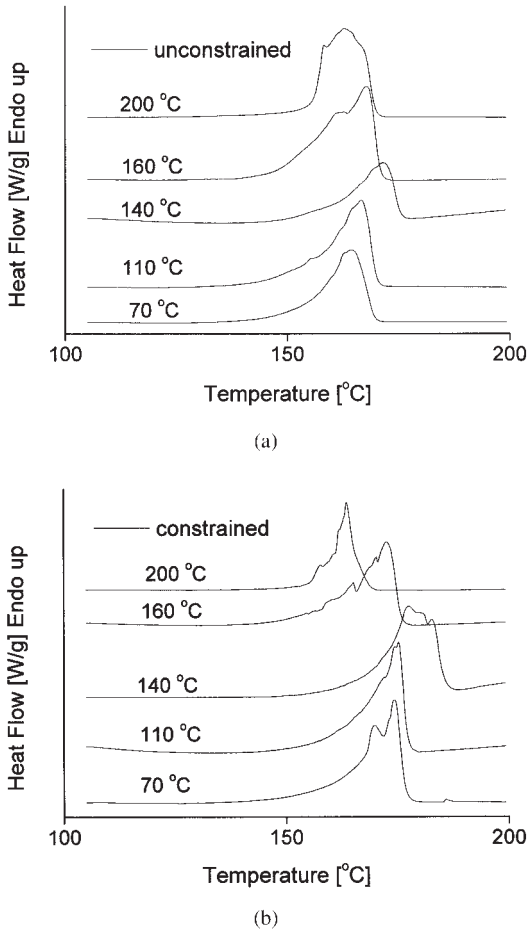
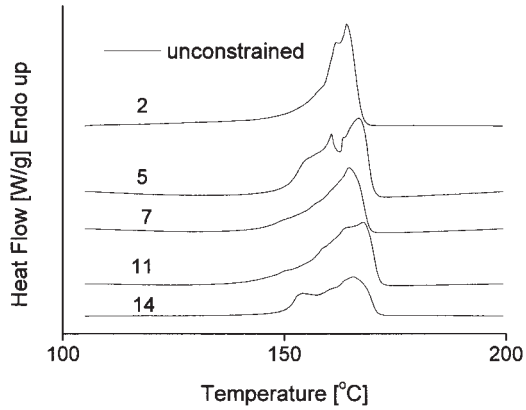


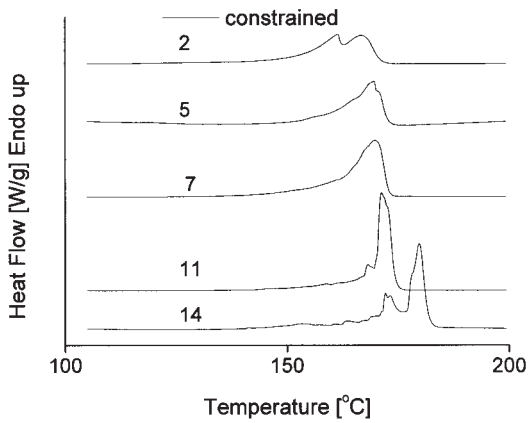
FIG. 8. DSC curve showing the influence of the post-drawing temperature on the overheating behavior of an unconstrained iPP fiber (a) and a constrained iPP fiber (b). Note: The draw ratio in both cases is 7.

shift of their melting peak back to lower temperatures (see Fig. 8a). Constrained samples give a similar picture (see Fig. 8b). At low drawing temperatures, double melting peaks are deduced. These peaks give an indication of the presence of two morphological forms (i.e., lamellar and fibrillar morphology in the same sample). Furthermore, the effect of overheating becomes less effective at drawing temperatures higher than 145°C, exactly as in case of unconstrained fibers. The aforementioned behavior can be explained as follows. At low post drawing temperatures (up to 145°C), the molecular mobility in the crystals is too low for effective relaxation processes on the time scale of the deformation process. At higher post drawing temperatures, the chain mobility in the crystals is increased. Relaxation processes directly accompany the deformation of the amorphous phase.

In Fig. 9a and b the effect of draw ratio on the melting point of unconstrained and constrained PP fibers is presented. It is shown in Fig. 8a and b that at post-drawing temperatures above 145°C relaxation processes take place and this temperature gives the maximum gain in terms of overheating. Therefore, the post drawing temperature was kept constant at 145°C and different draw ratios, varying between 2 and 14, were applied. In case of unconstrained samples (see Fig. 9a) the draw ratio seems to influence only the shape of the melting peak and not the absolute melting point. Low draw ratios give more narrow peaks. As the draw ratio is increasing the melting peaks become wider, but there is no shift in the melting point. Constrained specimens (see Fig. 9b) with draw ratios up to 10 present only a slight shift in their melting point. On the contrary, highly drawn constrained specimens present a further shift of more than 10°C. This behavior was expected, since the orientation of the chains induced at high draw ratios can be beneficial under constraining, but disappears when the specimen is free to shrink upon melting. On the other hand, the



(a)



(b)

FIG. 9. DSC curve showing the influence of the ultimate draw ratio on the overheating behavior of an unconstrained iPP fiber (a) and a constrained iPP fiber (b). Note: The post-drawing temperature in both cases is 145°.

draw ratio does not influence directly the morphology of the induced crystals; therefore, there is no change in the melting point of the unconstrained samples.

CONCLUSIONS

It was shown in this study that it is possible to use the constraining concept for both drawable (apolar) and less drawable (apolar) polymers in order to create single polymer composites. Nevertheless, if a wide processing window is needed the following prerequisites should be fulfilled: 1) the drawing temperature should be optimized in order to avoid relaxation processes in the amorphous phase while at the same time induce orientation and improvement of the crystals in terms of size and perfection; 2) the draw ratio should be high enough (above 7) in order to have chain unfolding and perfectly oriented (this does not easily apply on less drawable polymers); and, finally, 3) the chain mobility should be relative low for effective constraining.

ACKNOWLEDGMENT

N.-M.B. would like to acknowledge the EU (ORTHOFLEX Growth project, no: G5ST-CT-2002-50185) for financial support.

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