

# Preparation and Properties of Novel In-situ Composite Materials Based on Polyethylene-Polyamide Oriented Blends

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**Abstract.** The objective of this study is to manufacture and investigate novel nanostructured polymer composites (NPC) based on oriented blends of high-density polyethylene (HDPE) and polyamide 6 (PA6). Conventional polymer processing techniques are used for this purpose including extrusion blending, cold drawing and compression molding. Thus, various polymer blends are prepared comprising 10 and 20 wt% of PA6 and 0-10 wt% of a copolymeric compatibilizer. These blends are cold-drawn to high draw ratios and the oriented strands so produced are further compression molded at various temperatures between the melting points of HDPE and PA6. All NPC obtained are characterized by microscopy techniques, solid state NMR, mechanical tests and wide- and small-angle X-ray scattering from synchrotron. The mechanical and structural data of NPCs are discussed with relation with the polyamide fibrils' orientation, as well as with the effect of compatibilizer at the matrix-fibrils interface.

## Introduction

More than a decade ago, a new type of *in situ* fibrous polymer composite was developed with suppressed incompatibility and possibilities for improved adhesion between the fiber and matrix [1-4]. The reinforcing elements in these materials are fibrils built of bundles of flexible, organic macromolecules embedded in an isotropic, thermoplastic polymer matrix. Since the typical diameters of the fibrils were found to be within the upper size limit of nanocomposites (100–1000 nm), they were designated as nanostructured polymer composites (NPC). The preparation of NPC comprises three basic steps. First, *melt-blending* is performed of two or more immiscible polymers with melting temperatures ( $T_m$ ) differing by 30°C or more. In the polymer blend so formed, the minor phase should always originate from the higher-melting material and the major one from the lower melting component or could even be amorphous. Second, the polymer blend is drawn at temperatures equal or slightly above the glass transition temperatures ( $T_g$ ) of both components leading to their orientation (i.e. *fibrillation*). Finally, liquefaction of the component with the lower melting temperature is induced thus causing a nearly complete loss of orientation of the major phase upon its solidification, which, in fact, constitutes the creation of the composite matrix. This stage is called *isotropization*. It is very important that during isotropization the temperature should be kept below  $T_m$  of the higher melting and already fibrillated

component. In doing so, the oriented crystalline structure of the latter is preserved, thus forming the reinforcing elements of the NPC. To carry out the NPC preparation at an industrial scale, continuous setups are used where polymer blending, forming and cold drawing of the initial strands is performed in a twin-screw extruder coupled with one or more stretching haul-off units [5,6]. The isotropization stage is performed by either compression or injection molding techniques.

There is a great variety of polymers used for the preparation of NPC. In this study high-density polyethylene (HDPE) was employed as matrix material and polyamide 6 (PA6) for the reinforcing fibrils. A copolymeric compatibilizer was used so as to improve the miscibility of HDPE and PA6 by enhancing the adhesion at the matrix-fibril interface. The structure-properties relationship in NPCs with various composition and thermal prehistory was flowed in order to select those blend compositions and processing conditions resulting in optimal mechanical properties.

## Experimental

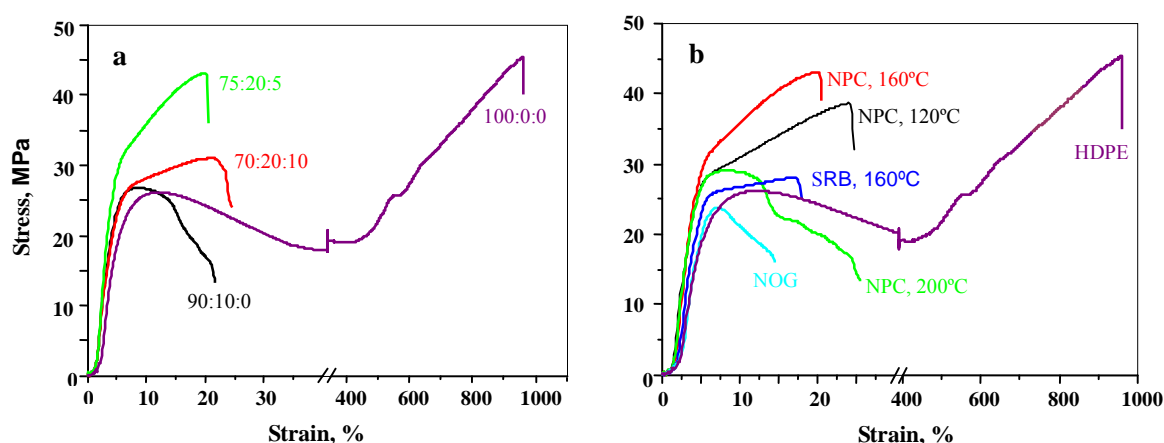
**Sample Preparation.** The corresponding amounts of granulates of HDPE and PA6 were premixed and fed at a constant rate by means of a gravimetric feeder to a Leistritz LSM 30.34 intermeshing co-rotating twin-screw extruder equipped with a pelletizing die of 2 mm diameter. The extrusion line included also two water baths and two haul-off units, as well a winder positioned downstream. The melt blending was performed at a set temperature of 230°C. The extrudate was cooled in the first bath with cold water, while drawing at a draw ratio (DR) of 2.6, in order to stabilize both its cross section and the line velocity. The final drawing was performed in the second haul-off unit, after heating the extruded strand to 90°C, the DR between the two haul-off devices being of ca. 6.0. In such a way, both melt-blending and cold-drawing stages were performed in the extruder line to get oriented strands of three HDPE:PA6:YP blends with the following compositions: 90:10:0; 75:20:5 and 70:20:10 (wt.%) where YP is the compatibilizer – a HDPE/maleic anhydride copolymer (Yparex, a product of DSM). The isotropization of the HDPE matrix was carried out by compression molding of parallel bundles of oriented strands at various temperatures and a constant pressure of 50 bar, followed by cooling to 80°C at 10°C/min.

**Sample Characterization.** Samples of all laminate plates (200x150x2 mm) prepared as indicated above were further studied by scanning electron microscopy (SEM) in a Leica S 360 microscope. Mechanical tests were performed in an Instron 4505 machine at 23°C and a constant cross-head speed of 50 mm/min using a temperature chamber and a load cell of 1 kN. The data were averaged over five equal test specimens cut out from each laminate plate. The solid state NMR studies were performed in a Bruker MSL 300P spectrometer operating at 75.5 MHz using magic angle spinning (MAS), high-power  $^1\text{H}$  dipolar decoupling (DD), and  $^1\text{H}$  -  $^{13}\text{C}$  cross polarization (CP) combined techniques. The X-ray patterns were obtained at the Soft Condensed Matter beamline A2, HASYLAB-DESY, Hamburg using a sample-to-detector distance of 105 mm for WAXS or 2840 mm for SAXS, incident beam wavelength  $\lambda = 0.15\text{nm}$ .

## Results and Discussion

**Mechanical Tests** Figure 1 displays the stress-strain curves obtained at room temperature with various HDPE:PA6:YP NPC compositions and also with the HDPE matrix material. The mechanical behavior of the NPCs and of the pure HDPE is clearly different. HDPE yields at a strain  $\epsilon$  of ca 10%, up to  $\epsilon = 400\%$  there is a cold-flow region, after which a strain hardening takes place until the sample failure. The NPC composites do not show yield point or cold flow and break at  $\epsilon = 20\text{--}25\%$ . The compatibilizer has an important impact on the maximal stress values  $\sigma_{max}$ , its optimal content being close to 5 wt. % (Fig. 1a). This NPC breaks at  $\sigma_{max} = 45\text{ MPa}$  displaying a Young moduli of 1.1 – 1.2 GPa. The values of the

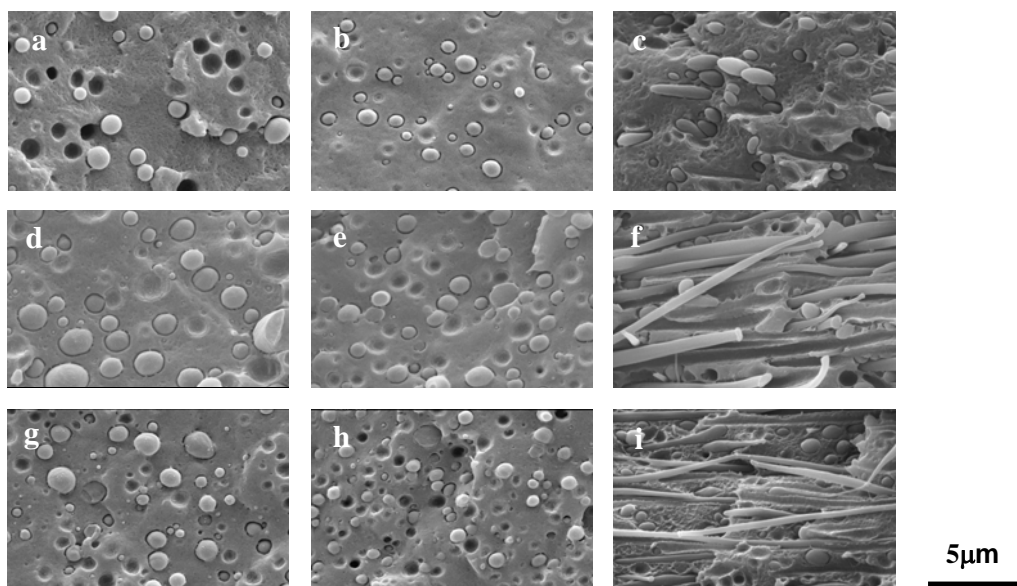
pure HDPE matrix material in the same strain region are 24.7 MPa and 0.7 GPa, respectively. Figure 1b reveals that annealing of NPC at 160°C after molding results in the highest tensile stress values. The tensile behavior of the NPCs is related also to the DR and the orientation of the reinforcing elements. Compression molding of palletized extrudate obtained after the 1<sup>st</sup> haul-off device (DR = 2-3) results in composites whose mechanical properties are worse than those of the pure isotropic matrix. Cutting strands collected after the 2<sup>nd</sup> haul-off unit (total DR = 13) and compression molding them produces an isotropic HDPE matrix reinforced by shorter, randomly oriented PA6 fibrils. The mechanical properties of these systems are comparable to those of the pure matrix material. Only long, parallel and highly oriented strands obtained after the 2<sup>nd</sup> stretching device molded and annealed at 160°C can give rise to NPCs of good mechanical properties.



**Figure 1** Stress-strain curves of (a) - HDPE:PA6:YP NPCs with various compositions; (b) – 75:20:5 composites obtained at different compression molding temperatures from precursors with various orientation: NPC – unidirectional strands after the 2<sup>nd</sup> haul-off; NOG – granules after the 1<sup>st</sup> haul-off; SRB – short, randomly oriented bristles obtained by cutting of oriented strands after the 2<sup>nd</sup> haul-off.

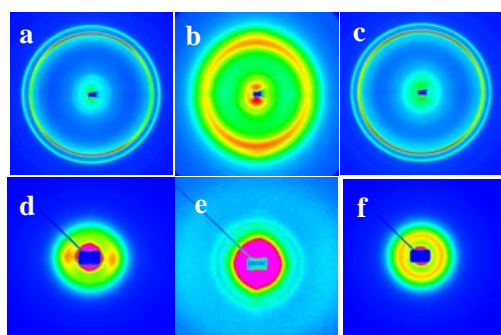
**SEM studies** Figure 2, (c), (f) and (i) visualize clearly the PA6 fibrils with diameters in the 300-600 nm range embedded in the HDPE matrix, thus proving undoubtedly the fibrillar structure of the reinforcement in the final NPCs. Apparently, the presence of compatibilizer is important for the formation of the reinforcing fibrils – in Fig. 2 (c) where there is no YP, the fibrils are shorter and poorly formed. Judging from the images of the final NPCs, the higher the YP concentration is, the thinner become the PA6 fibrils. Another conclusion based on the SEM data is that only stretching at high DR after the 2<sup>nd</sup> haul-off unit results in well-expressed fibrillar structure that results in the best reinforcing effect.

**Structural Studies by solid state <sup>1</sup>H NMR and X-ray scattering** Figure 3 displays the WAXS (a-c) and SAXS 2D patterns (d-f) of a 70:20:10 NPC obtained at various temperatures. The WAXS pattern of the NPC sample at 30°C (Fig. 3 (a)) shows the identity of the crystalline structure of both HDPE and PA6 whose main crystalline reflections coincide. The SAXS pattern (image d) reveals two long spacings of ca. 60 and 300 Å ascribed to the oriented PA6 reinforcing phase and to some amount of oriented HDPE formed by recrystallization of matrix material upon the oriented PA6 fibrils. One may observe also that the WAXS pattern at 160°C (Fig 3b) still displays some orientation along the horizontal draw direction. The respective SAXS image (e) shows one long spacing at ca. 70 Å, corresponding to the oriented reinforcing PA6 phase unable to melt at 160°C. After a heat treatment of 260°C both WAXS (c) and the SAXS patterns (f) become isotropic, of circular symmetry, the latter with three long spacings at 66, 122 and 252 Å, related to the isotropic PA6, HDPE-co-PA6 and neat HDPE phases, respectively.

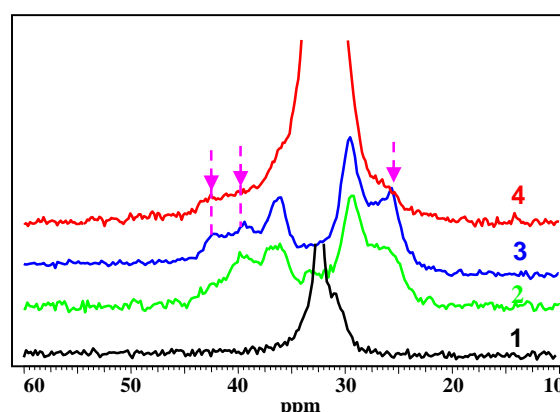


**Figure 2** SEM micrographs of HDPE:PA6:YP blends [(a)-(c): 90:10:0; (d-f):75:20:5; (g)-(i): 70:20:10] at various stages of its processing. Samples (a), (d) and (g) were obtained at the extruder die exit; (b), (e) and (h) – after the first haul-off; (c), (f) and (i) – final NPCs

The  $^{13}\text{C}$  solid state NMR curves in Figure 4 show the HDPE/PA6/YP composite (curve 4) compared to those of  $\gamma$ -PA6 (curve 2) and of the  $\alpha$ -PA6 polymorph (3). The NPC sample displays resonance lines above 40 ppm, which could only be ascribed to the  $\alpha$ -PA6 polymorph. This conclusion was confirmed in an in-depth study on the polymorphism in oriented and isotropic neat PA6. It was demonstrated that annealing at 160°C causes a well-expressed  $\gamma$ -to- $\alpha$  phase transition in the crystalline domains accompanied with some hardening of the adjacent amorphous phase [7,8]



**Figure 3** WAXS (a-c) and SAXS. 2D patterns (d-f) of a 70:20:10 NPC. Patterns obtained at: (a) and (d) – 30°C; (b) and (e) – 160°C; (c) and (f) - 30°C after melting at 260°C.



**Figure 4** Solid state NMR patterns of: HDPE (1);  $\gamma$ -PA6 polymorph (2);  $\alpha$ -PA6 polymorph (3); HDPE:PA6:YP = 70:20:10 NPC obtained at optimal conditions (4).

## Conclusions

The mechanical properties of the HPE/PA6/YP NPCs are controlled by the following interrelated factors: (i) the concentration of the compatibilizer; (ii) the diameter and orientation of the reinforcing PA6 fibrils; (iii) the temperature of HDPE matrix isotropization or of the subsequent annealing. By a careful selection and combination of all these parameters, composite materials can be obtained with Young modulus and tensile behavior being clearly superior to those of the HDPE matrix.

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