

# Formation of polypropylene nanofibers by solid state deformation during blending with molten polyethylene

(Rapid Communication)

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**Abstract:** A novel method for preparing all-polymer nanocomposites was described. The technique is based on enhanced susceptibility to deformation of a polymer having a lowered number of entanglements in the amorphous phase. Polymer powder remaining in the solid state was blended with a second molten polymer, and the shearing forces during compounding deformed the powder grains into nanofibers. After solidification of the matrix all-polymer nanocomposite was obtained. The effectiveness of the method was demonstrated on the example of ultra-high molecular weight polyethylene (PE-UHMW) composite containing PP nanofibers, produced *in situ* during compounding.

**Keywords:** polypropylene, polyethylene, all-polymer nanocomposites, entanglements.

## Tworzenie się nanowłókien polipropylenowych w wyniku deformacji w stanie stałym podczas mieszania ze stopionym polietylenem

**Streszczenie:** Opisano nową metodę otrzymywania nanokompozytów w pełni polimerowych (z ang. *all-polymer*). W metodzie tej wykorzystuje się zwiększoną zdolność do odkształcania polimeru mającego ograniczoną liczbę splątań w fazie amorficznej. Polimer w stanie stałym miesza się z drugim stopionym polimerem, a siły występujące podczas mieszania powodują przekształcanie się ziaren stałego polimeru w nanowłókna. Po zestaleniu matrycy powstaje w pełni polimerowy nanokompozyt. Skuteczność metody pokazano na przykładzie kompozytu polietylenu o bardzo dużym ciężarze cząsteczkowym (PE-UHMW) zawierającego nanowłókna polipropylenu (PP) wytworzone *in situ* w procesie mieszania.

**Słowa kluczowe:** polipropylen, polietylen, nanokompozyty w pełni polimerowe, zapętlenia.

All-polymer composites are usually produced by re-distributing ready-made polymer fibers within another polymer matrix [1, 2]. For some pairs of polymers the composite can be prepared by melt blending, if one of the polymers, dispersed in the form of droplets, is capable of converting into fibers under the action of forces [3]. The resulting blend is characterized by orientation of both components, so in the second step by melting and relaxation of a matrix the isotropic composite is formed. Known examples of such blends include polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polylactide (PLA) and polyamide 6 (PA6) pairs (PP/PET, PE/PET, PET/PA6 and PLA/PP). The composites based only on polyolefins were not successfully prepared with this method.

Some time ago another approach to producing all-polymer composites was proposed. It is based on the observation of easy deformation of highly crystalline nascent

poly(tetrafluoroethylene) (PTFE) powder. Nascent PTFE powder grains are easily deformed during compounding with another molten polymer while they remain in the solid state. As the result of shearing micro- and nanometer size PTFE fibers are formed [4]. The ability of the powder particles to transform into the fibers resulted from the low level of macromolecular entanglements in nascent PTFE grains. From the studies of plastic deformation of semi-crystalline polymers it is known that the presence of entanglements in the amorphous phase limits the possibility to achieve high macroscopic strains, because the network of entanglements gets strained and prevents from obtaining high degree of deformation. For micrometer size polymer grain with disentangled macromolecules the ultimate degree of deformation might reach several hundreds or even thousands of times and grains would get transformed into nanofibrils.

Successful experiment with deformation of PTFE was the motivation for us to investigate whether it would be possible to produce disentangled grains of polymers other than PTFE and whether a similar mechanism of deformation would be possible to obtain nanofibers of those polymers. We were interested in obtaining disentangled

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grains of PP and in deformation of those grains in a similar manner. Such procedure would lead to a manufacture of all-polymer composite based on polyolefins only in a single compounding process. For this purpose, it was necessary to obtain PP grains with a limited number of entanglements, and then to find a proper method of processing by melt blending into a composite comprising nanofibers dispersed in a polymer matrix. As a matrix we chose ultra-high molecular weight polyethylene (PE-UHMW).

## EXPERIMENTAL PART

### Materials

Polypropylene (PP) with trade name Novolen 1100N (BASF) was characterized by mass-average molar mass  $\overline{M}_w = 250$  kg/mol. Ultra-high molecular weight polyethylene (PE-UHMW) was GUR type (Ticona) with  $\overline{M}_w = 9000$ .

### Composite preparation

The idea to prepare a nanocomposite is illustrated in Fig. 1. The approach proposed by Lemstra group, developed originally for polyethylene [5], was used to obtain PP grains with reduced number of entanglements. PP was dissolved at 130 °C in xylene. The polymer concentration was 1–2 wt %, which guaranteed a small number of macromolecular entanglements in the solution. After 1 h of homogenization of the solution at 130 °C, the temperature was slowly lowered at the rate of 15 deg/h. At the temperature of 80 °C a gel appeared in the solution. After further cooling to 40 °C the gel was filtered out from the solution and dried to obtain a white powder.

In order to produce all-polymer composite the obtained PP powder was mixed with PE-UHMW which was designed to create the matrix of the composite. The components were compounded using Brabender internal mixer. PP content in the composites was 3 or 6 wt %. The blending took place at 150 °C, with blade rotation speed of 15 rpm and the time of blending was 15 min. The selected temperature ensured that PP remained in the solid state while the stress needed for plastic deformation of PP crystals was low. Although the temperature rise was observed during the compounding (8–10 deg), it was always below the melting point of most PP crystals, which was 165–166 °C as based on the DSC melting scan.

### Methods of testing

For confirmation of achieving a reduction in the number of entanglements the rheological time sweep test was performed using Ares rheometer (TA Instruments). The 1 mm thick compressed samples were tested in plate-plate configuration, at 185 °C, 1 % of strain, and frequency of 10 rad/s.

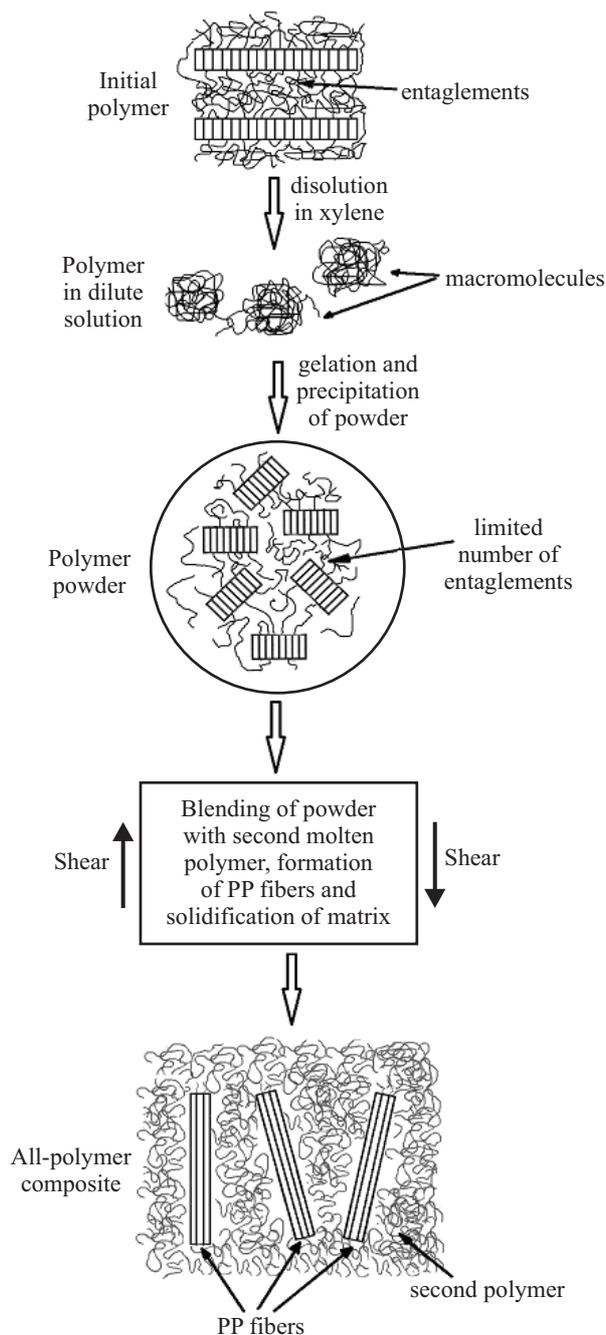


Fig. 1. Scheme showing the steps of composite preparation and the changes of structural elements during processing

The morphology of the resulting material was examined using scanning electron microscopy (SEM). The objective was to confirm the presence of fibers, and therefore the possibility to produce composite by blending. A sample of compounded material was frozen fractured at liquid nitrogen temperature. The exposed surface after coating with gold was examined in the Jeol JSM 6010LA scanning electron microscope.

## RESULTS AND DISCUSSION

PP powder obtained by controlled precipitation from xylene solution and initial PP have been characterized

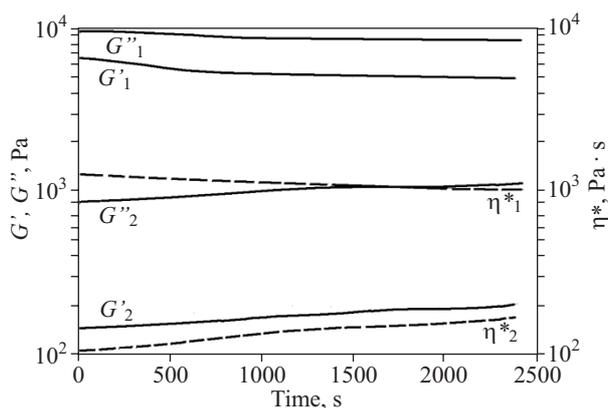


Fig. 2. Changes of complex viscosity ( $\eta^*$ ), storage modulus ( $G'$ ) and loss modulus ( $G''$ ) in time for initial PP (index 1) and for the PP powder (index 2)

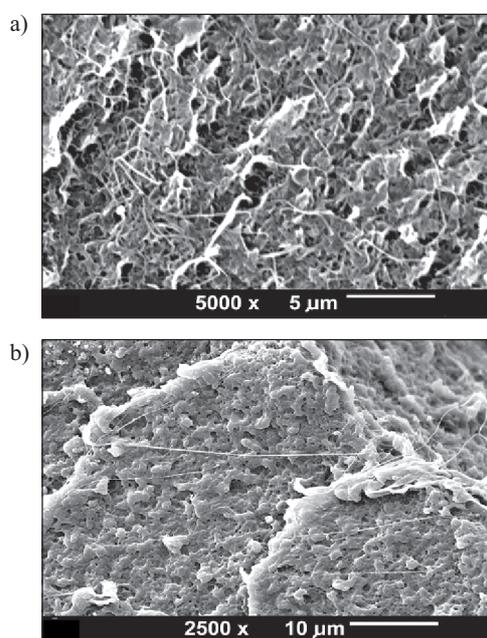


Fig 3. Morphologies of the composite showing PP fibers dispersed in PE-UHMW matrix with magnification: a) 5000 $\times$ , b) 2500 $\times$

using rheological measurements. The results of time sweep tests are shown in Fig. 2. The complex viscosity ( $\eta^*$ ), storage and loss moduli ( $G'$  and  $G''$ , respectively) were significantly lower for PP powder precipitated after dissolving than for the original material. We attributed those differences to the reduction of entanglement density. As the time sweep was prolonged, the initial polymer showed slow decrease in values of parameters, associated with limited degradation. In the case of PP powder the increase in values of those parameters was observed, which resulted from reconstitution of entanglements as time elapsed. However, the parameters for disentangled powder did not reach the values for the initial PP. A probable reason for that was the lower concentration of original antioxidants because most of them percolated

through the filter and remained in the filtrate. The accelerated degradation gave the opposite effect on the values of rheological parameters than an increase in entanglements.

The examples of morphologies of the frozen fractured composite are presented in Fig. 3. The presented samples contained 6 wt % of PP deformed grains. The PP fibers created in PE-UHMW matrix due to shear stresses during compounding are clearly visible. On the photographs fibers having diameters between 60 and 300 nm can be distinguished. In principle the fibers are not oriented, because they were prepared by mixing using the internal mixer. However, in Fig. 3b, under the lower magnification, it can be seen another region of the sample in which most of the fibers are straight and oriented horizontally. At the tips of some fibers small balls are visible that are rather the result of melting of the tips of fibers than the residue of grains from which the fibers were formed.

## CONCLUSIONS

Polypropylene with lowered number of entanglements in the amorphous phase was obtained by preparing a dilute solution and controlled precipitation. It was able to deform to large strains under action of shear stresses during blending with a second polymer. Partially disentangled PP solid grains were used to prepare the nanocomposite by blending with molten PE-UHMW. The selected temperature of mixing ensured on one hand that PP grains were not melted and entangled again, on the other hand it facilitated easier plastic deformation of PP crystals. The shear and elongation forces acting during melt blending on the PP powder particles caused the transformation of lamellar PP crystals in grains into fibers, typically having the diameter of approx. 100 nm. After solidification a nanocomposite was obtained composed of PE-UHMW matrix and randomly oriented PP nanofibers.

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