

Process-Morphology-Property-Relationships of Titania-filled Polypropylene Nanocomposites

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Abstract—Although the research and development of nanocomposites for almost a decade focused on structural properties, these properties remained until today far below expectations, which were forecast at the beginning of the new millennium. However, even if it is well known that the processing history has a major impact on the structure and properties of final components, this aspect was not subject of intensive research in the past. The talk focuses on the role of the manufacturing sequence on the morphology and properties of polypropylene based nanocomposites. In general it can be stated that the incorporation of nano-sized TiO₂-fillers improves the some mechanical properties of the resulting nanocomposites as long as the production enables a good dispersion and distribution of the nanofiller agglomerates. However, with increasing filler loading, the morphology of injection molded parts changes: The size of the spherulites and the degree of crystallinity decreases while the crystallization/solidification proceeds faster. Simultaneously a slight improvement in the mechanical performance up to a certain filler loading can be found. However, improved mechanical properties of the nanocomposites in the final component cannot be exploited if its production in a subsequent welding step is required. The reason for the decrease in the mechanical properties is the decrease in the viscosity by the addition of the fillers, and thereby caused extreme flow processes and subsequent orientation of the fillers as well as the weakening of the filler/matrix-interphase in the welding zone. In summary, it can be observed that nanocomposites increasingly offer great opportunities for applications where single-component materials reach their limits. The key to success is the processing. Therefore it is of crucial importance that the total manufacturing history is understood and controlled. Only then it is possible to sustainably exploit the potential of polymer nanocomposites in the application.

Keywords—Polymer nanocomposites; processing history; morphology and properties

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I. Introduction

Polymer nanocomposites (PNC) achieved more and more attentions in the last decade. The extremely high surface areas of nanoparticles can result in a great amount of interphase in the composite and thereby a strong interaction between filler and matrix is created [1, 2]. The incorporation of inorganic nanoparticles into polymer matrices has been proved to be one of the effective ways for improving the mechanical properties of pure polymers [3-7]. The improvement of the properties is dependent on the type, geometry and location (distribution) of particles and the properties of the matrix material itself.

However, it is one thing to produce outstanding material properties in optimal laboratory samples. In reality, the manufacture of plastic components, temperature and flow gradients in part determine the morphology locally and hence the user properties of the component.

Therefore, it is of great interest to check whether or not the materials properties are affected by extreme processing conditions.

In our study, polypropylene based nanocomposites were produced due to injection molding and the molten plates were used as the welding parts in addition, in order to examine the relationship between extreme processing conditions on the morphology and the morphology and mechanical behavior of the resulting joints.

II. Experimental

A. Materials: Polymer and filler

Commercial polypropylene homo-polymer (HD120MO) was provided by the Borealis group. The melt flow rate and the density of this product are 8 g/10 min (230 °C/2.16 kg) and 0.908 g/cm³, respectively. Hombitec RM 130 F was used as nanofiller, which was supplied by Sachtleben Chemie GmbH. This type of TiO₂-nanoparticles exhibits an acicular form and has due to the supplier a mean diameter of about 15 nm. All of the materials were used as received.

B. Processing

Polypropylene nanocomposites with 5 vol.% content of TiO₂ particles were first extruded by a Theysohn co-rotating twin-screw extruder under the screw speed of 160 rpm. The temperatures were set from 190 °C near the hopper to 210 °C at the die. The obtained PP/TiO₂ nanocomposites were then

diluted to 0.5, 1 and 4 vol.% TiO₂ particle content using the same extruder under the identical conditions.

Then neat PP and PP/TiO₂ nanocomposites were injection molded to 50x50x4 mm³ sheets, which were used as welding components in the vibration welding experiments. [8]

The welding experiments were performed on a fully automatic Branson Ultraschall Lab.-Vibration welding machine M112H. The friction force, amplitude and penetration of the parts were recorded during the whole welding process. The welding pressure was chosen 0.4 MPa, the welding time 8 s while the amplitude and frequency of vibration were kept at constant values of 0.7 mm and 240 Hz, respectively.

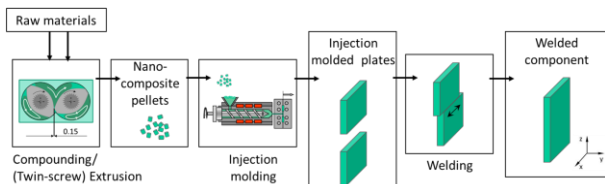


Figure 1: Manufacturing sequence

C. Morphology investigations

In order to study the morphology of bulk-crystallized samples, the center part of injection molded sheet was cut into rectangular cuboids. From these cuboid thin sections of 10 μm thickness were taken with a microtome (Hyrax M25, Carl Zeiss AG, Germany). The basic part of the cuboided, the microtomed bulk specimen, was cleaned with distilled water followed by etching with a permanganic etchant. The etchant was prepared according to a procedure described by Basset and Olley [9] and Shahn et. al [10]. The whole procedure is described in detail in [11].

The morphology of the nanocomposites was analyzed on a light microscope (Zeiss AxioSkop A1. M, Carl Zeiss AG, Germany) using the etched specimens and in parallel microtomed thin sections.

A Field Emission Scanning Electron Microscope (FESEM) of a FEI Altura 875 Dualbeam FIB (Focused Ion Beam) operating with 5 kV acceleration voltage and a secondary electron in line detector, with working distance of 5 mm was used to observe the etched surfaces with higher magnification. All samples were sputter-coated with 10 nm of gold palladium prior to SEM analysis.

D. Mechanical Properties

The Charpy impact strength of the specimens (50x6x4 mm³) was tested according to DIN 53453 by using an impact pendulum (Resil 5.5, CEAST, Italy) at following conditions: room temperature, incident impact speed: 2.9 m/s, incident energy of the hammer: 4 J. Regarding the welding specimens, prior to the Charpy impact tests, the welding bead on the impact side was removed.

III. Results and Discussion

Figure 2 shows the morphology of etched specimens from the core area of each material.

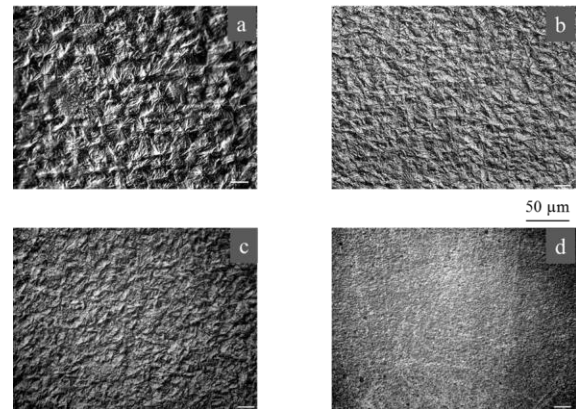


Figure 2: LM images of spherulitic structure of pure PP (a) and PP filled with 0.5 vol.% (b), 1 vol.% (c), and 4 vol.% of TiO₂ (d)

In the neat polypropylene the spherulitic morphology easily can be seen. As the filler loading increases the size of the spherulites decreases. A quantitative analysis on the spherulite size in the core area was carried out using the ASTM standard for grain size determination [13]. In total 240 spherulites for each specimen were measured to determine the size dependency on the filler loading. Figure 3 represents the mean spherulite diameter as a function of the filler loading. It is obvious that the addition of TiO₂ nanoparticles lead to slight decreases in the spherulite size from 23 μm in the neat polymer to 16 μm in the nanocomposite with 1 % filler loading, although they have no influence on the spherulitic shape of the PP matrix. At 4 vol.% filler loading some grain – like morphology in the range of 3-4 μm was identified. Actually at present we are not sure if these are spherulites.

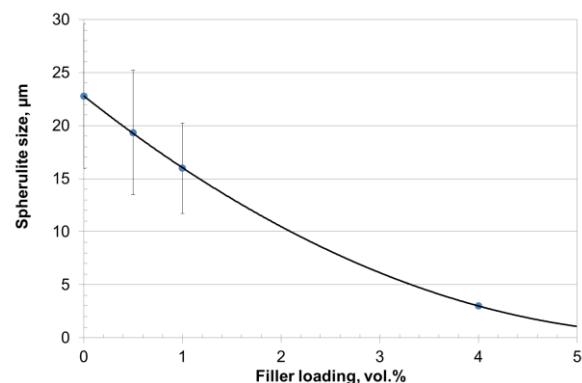


Figure 3: Spherulite diameter in the core of an injection molded plate made from polypropylene nanocomposites as a function of TiO₂ nanoparticles loading

We therefore assume that the particles act as nucleating agent which leads to an earlier onset of crystallization leading

finally to smaller spherulites. This hypothesis is confirmed by measurements of crystallization under the polarizing microscope. It clearly can be recognized that in non-isothermal experiments the crystallization at 123°C is largely complete, while in the unfilled polypropylene less than 30% of the area is covered with spherulites.

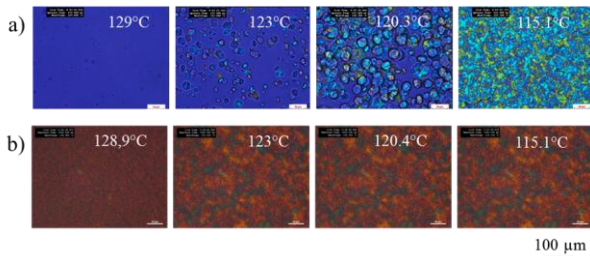


Figure 4: Progress of crystallization of a) pure PP and b) a PP/TiO₂ nanocomposite (4 vol.% filler loading) at different temperatures

The results of Charpy impact tests of non-welded (notched) and welded specimens are illustrated in Figure 5. With the non-welded specimens the data were collected by using notched specimens. The welded specimens exhibit the welding bead on the tension side acting as a geometric notch. For comparison purpose the data of each series are normalized on the value of the non-filled PP, which was $a_n = 5.2 \text{ kJ/m}^2$ for the notched injection molded specimens and $a = 27 \text{ kJ/m}^2$ for the (un-notched) welded specimens. Considering the Charpy-notched impact strengths of the injection molded plates (Figure 5, Not welded), one can recognize that the incorporation of nanoparticles into PP slightly improves the strength of the polypropylene. The maximum strength was obtained at about 1 vol.% TiO₂ filler, which is an improvement by approximately 10% compared to the neat polymer.

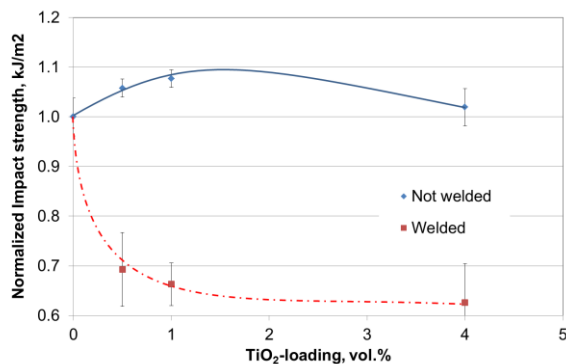


Figure 5: Impact strength of different materials: (a) non-welded materials, (b) vibration welded joints

By contrast, the nanoparticles decrease the Charpy impact strength of welds markedly as shown in Figure 5b. The unfilled polypropylene exhibits an outstanding impact strength value of about 27 kJ/m², which is in full compliance with earlier findings [14] under optimum welding conditions (low welding pressure). However, the impact strength is dramatically lower, already with a filler content of 0.5 vol.%.

At a TiO₂-loading of 4 vol.% the value drops down by 40% compared to the non-filled material.

High resolution SEM examination of fracture surfaces supplies more useful information about the fracture mechanisms of the joints. It is clearly to note that the fracture surfaces of the joints made of PP/nano-TiO₂ composites (Figure 6b and 6c) significantly differ from that of non-welded samples (Figure 6a). An obvious orientation of the nano-TiO₂ particle in the welding seam is noticed, which is parallel to the welding plane (xy-plane) and perpendicular to the load direction of mechanical tests (Figure 6b). This orientation of nanoparticles is more pronounced at higher filler loading and in this case the nanoparticles also appear to be aligned along lines parallel to the orientation axis rather than being distributed randomly. (Figure 6c). The orientation is attributed to the shear and elongation flows during welding process.

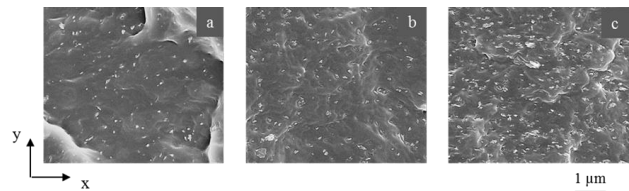


Figure 6: High resolution SEM fractographs of Charpy impact specimens: (a) notched PP/TiO₂ (1 vol.%); (b) PP/TiO₂ (1 vol.%) welded at 0.8 MPa, (c) PP/TiO₂ (4 vol.%) welded at 0.8 MPa (IFOS, Kaiserslautern)

In addition it clearly can be seen that in the non-welded specimen the filler seems to be perfectly embedded in the hosting PP, whereas in the welded specimens often gaps between filler and PP can be detected. As a consequence of filler orientation and interphase quality degradation, the mechanical properties of the welds were impaired.

IV. CONCLUSIONS

The addition of nanoparticles influences the morphology and properties of plastic parts considerably. The nature of the interference depends strongly on the local flow conditions and the local temperature conditions during the processing of plastic parts respectively the processing history. The prediction of properties and behavior of components manufactured out of nanocomposites from simple laboratory tests would therefore be clearly missing the point.

The studies presented here lead to the following conclusions in detail:

- The incorporation of Nano-TiO₂ particles into a polypropylene matrix slightly decreases the mean spherulite size of PP up to a filler loading of 1 vol.%.
- The fillers act as nucleation agent, facilitating a rapid solidification compared to the pure PP.
- The Nano-TiO₂ particles slightly increase the impact strength of injection molded bulk materials. However the maximum of improvement is achieved before the spherulitic morphology turns into a fine-grained structure.

- The impact strength of vibration welds significantly decreases with an addition of nanofillers.
- The reasons for the decrease of impact strength are related to the orientation of the TiO₂ into the direction of the relative movement of the joining parts, and probably the degradation of the interphase quality between the polymer matrix and the nanofiller.
- The incorporation of nano-sized fillers might be of interest from the point of view of processing: Reduced viscosity leads to better and faster mold filling, athermal crystallization and improved thermal conductivity to fast solidification.

In sum, with nanocomposites there is a great chance to outrun both faster cycle times and better properties in a polymer-based component. A vision for it pays to work.

Acknowledgment

The authors thank the German Research Foundation for the financial support according to the DFG-project SCHL 280/19-1 and the OPTIMAS/CARL ZEISS doctorate program. The authors are also grateful to Mr. V. Demchuk and Prof. Altstadt, Polymer Engineering, Hamburg and Mr. K.P. Schmitt and Prof. Arzt, INM, Saarbrücken, for the helpful cooperation. We also thank Mrs. A. Zeuner and Prof. Kopnarski, IFOS, Kaiserslautern, for the careful SEM measurements and the Borealis group and Sachtleben Chemie GmbH for kindly supplying experimental materials.

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