



# Physical state of the amorphous phase of polypropylene–influence on thermo-mechanical properties



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## ABSTRACT

Stable polypropylene, PP – low molecular weight modifier systems were prepared in order to analyze the influence of the physical state of the amorphous phase on thermo-mechanical properties. The modifier was introduced into solidified material by diffusion to the amorphous phase regions. The change of state of stress of the transmitters connecting adjacent crystals caused by substantial increase of interlamellar distance was observed. The new state of stress of the molecular network of the amorphous phase induced respective change of the stress state of the crystalline component. As the effect the tensile yield stress value was substantially reduced, also the stress caused a decrease of melting temperature of PP crystals. The above proposed mechanism served to explain the changes of thermo-mechanical properties of the blends with identical composition prepared by blending in a molten state. During the solidification of the blend, the modifier molecules were exuded out of the growing crystals. The physical state of the molecular network of the amorphous phase was changed in a similar way as for the systems with infused modifier into previously solidified polymer matrix. The changes of mechanical properties were additionally correlated with the observed change of the melting temperature of the crystals.

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## 1. Introduction

Intensive studies concerning semicrystalline polymers have been conducted for many years [1–7]. Growing interest in this class of materials results mainly because of their unique properties but also because of enormous possibilities for modification of properties. Most important for various applications of polymers are their mechanical properties including plastic behavior. Full description of plastic deformation of such materials requires considering the presence of lamellar crystals immersed in amorphous disordered regions and supermolecular structures that are formed during crystallization. In most of studies the influence of parameters of crystalline phase such as the degree of crystallinity, thickness of lamellae or orientation of crystals on the properties of semicrystalline polymers are analyzed and only few reports turn the attention to the role of the amorphous phase: its structure and physical state [8–16].

In the case of semicrystalline polymers the content of the amorphous phase, depending on the way of solidification process, may amount from 10 (crystallization under elevated pressure) up to 100% (ultra-fast cooling-quenching). The structure of the amorphous phase of semicrystalline polymers is complex. It includes areas of different packing density, different microconformation and content of chemical defects (branching) along chains or different connectivity between chains and crystals. Lack of homogeneity of the amorphous phase is caused also by the structure of the fragments of macromolecules, which are usually in its area. In the amorphous phase area there are the chain ends-cilia (it is believed that up to 90% of the chain ends is being pushed out during the crystallization process to the surfaces of the crystals into the amorphous phase area), folds, loops, macromolecules physically connecting adjacent crystals (tie-molecules) or whole molecules not physically connected with crystals. Furthermore, the macromolecules in the molten state create certain characteristic network of entanglements depending on a polymer (its chemical structure), molecular weight or its thermo-mechanical history. During the crystallization some of these entanglements are kept and are pushed out the area of a growing crystal into interlamellar regions. Complex, non-homogenous structure of the amorphous phase

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impedes the analysis of the influence of this component on thermo-mechanical properties of semicrystalline polymers.

The difficulty related to the analysis of the amorphous phase arises also from the lack of a proper method of modification of the polymer matrix that would enable the creation of a sequence of samples with identical structure of crystalline component (identical degree of crystallinity and thickness of the crystals) that differ only in the structure/physical state of disordered regions. The change of way of the solidification process or annealing of previously solidified samples affects the change of the amorphous phase structure but at the same time induces substantial changes in the crystalline component. Therefore, it makes impossible to estimate the influence of the amorphous component on the observed changes of thermo-mechanical properties of the analyzed material.

Generally, it is believed that the deformation of the amorphous phase in a rubber-like state occurs according to three basic mechanisms [3,6]: interlamellar slips (shear) [17–19], interlamellar separation (change of distance between the adjacent lamellae) [17,19–22] and rotation of lamellae (rotation of stacks of lamellae) [19,23]. Activation of the above mentioned mechanisms of the amorphous phase deformation occur in different zones of spherulites, depending on the direction of applied tensile stress. However, it is commonly believed that during uniaxial stretching of semicrystalline polymers the role of the amorphous phase, above its glass transition temperature, is relatively small and limited to transferring the stress between adjacent crystals [24]. Transferring the stress between crystals is possible by chains physically (directly) connecting adjacent crystals (tie-molecules). Also a network of entanglements and knots can effectively transfer the stress during uniaxial stretching. Proper sequence of the already mentioned chain fragments in a normal direction to the surface of lamellae may effectively participate in the transferring of generated tensile stress. Physical connection of crystalline and amorphous areas has additional implications. It may be expected that each substantial change of the distribution of stress along the fragments of macromolecules located in disordered areas directly or indirectly (through the network of entanglements) connecting adjacent crystals will also affect the physical state of the crystals. In such a case the value of yield stress as one of the mechanical parameters determined mainly by the structure of crystals (their physical state) should be subject to a substantial change. Change of the state of stress of chains located in the amorphous phase area may occur for example as a result of the sorption of water in hydrophilic polymers at high humidity (the modification of physical state of the amorphous phase of the polymer with already created crystalline skeleton). The solidification of miscible or partially miscible polymer blends is usually accompanied by pushing out non-cocrystallizing component into the amorphous phase area (modification of the physical state of the polymer amorphous phase during the formation of the crystalline structure). There are several questions concerning probable effects of modified amorphous regions in several other cases. In blends: does the additives and low fraction of the second component entering the interlamellar regions affect the physical state of the amorphous phase and the properties of lamellar crystals? Does the reduction of the yield stress of miscible or partially miscible polymer blends observed in many cases [25–29] is partially a result of changing the physical state of amorphous regions and hence crystals?

Recently we have presented a way of modification of amorphous regions by infusing low molecular weight modifiers (depending on a polymer: hexane, chloroform or water) into solidified polymer [30–32]. For example, in case of polypropylene/hexane system we showed that introducing the molecules of a modifier leads to a significant change of the physical state of the amorphous phase without detectable changes in the crystalline phase area. At the

same time we confirmed that such modification substantially affects the intensity of cavitation – one of the phenomena accompanying deformation of most of semicrystalline polymers and having negative impact on thermo-mechanical properties of polymeric materials [33]. It appeared that it is due to lowering of the content of free volume of the amorphous phase. Additionally, we observed a measurable influence of a modifier in the amorphous phase regions on the intensity of lamellae fragmentation. The amount of heat generated during drawing of the polymer/modifier system in relation to the reference material was also reduced [34]. We proved also that the change of stress state of molecular network physically connecting adjacent crystals by increasing interlamellar distance may result in changing of the value of the yield stress [30,31,35]. However, the studied systems were not stable over time because the modifiers were highly volatile.

In this paper stable polypropylene/low molecular weight modifier systems have been prepared. A modifier was introduced in two ways: by infusion into ready-made samples or by blending prior the solidification. The proposed mechanism of filling the free volume of amorphous intercrystalline layers and their expansion due to swelling are used to explain the changes of thermo-mechanical properties of such systems.

## 2. Experimental

### 2.1. Materials

Polypropylene Moplen HP 456H (PP) of melt flow index MFI = 1.8 g/10 min (at 190 °C, 2.16 kg according to ISO 1133), by Lyondell Basell was used. A paraffin wax (m.p. 58 °C), by Loba Chemie and nonadecane 99% (m.p. 30–34 °C, b.p. 330 °C,  $d = 0.786$  g/mL), by Sigma–Aldrich were used as liquid low molecular weight modifiers.

### 2.2. Modification

*Modification in solid state (SS).* The process of modification was performed by immersion of polypropylene samples (obtained by compression moulding and cooled between metal plates) in a modifier bath placed in an oven at 70 °C for 7 days in order to obtain full penetration of the amorphous phase of the material with a low molecular weight modifier (polypropylene/nonadecane (SSn) or wax (SSw)). The reference samples had the same thermal history. *Modification in the molten state (MS).* The process of modification was melt blending using Brabender batch mixer (Duisburg, Germany) operating at 190 °C for 5 min at 60 rpm. Neat PP was also processed under the same conditions to obtain a reference material. The samples for proper measurements were cut out from 1 mm thick polymer films, obtained by compression moulding and cooled between metal plates.

### 2.3. Thermogravimetry (TGA)

The content of modifiers in samples was estimated by means of thermogravimetry (TGA). A thermogravimetric analyzer Hi-Res TGA 2950 by TA Instruments was used with the heating rate of 20 °C/min in an air environment.

### 2.4. Supercritical CO<sub>2</sub> extraction

The content of modifiers in samples modified in the molten state was verified by means of supercritical CO<sub>2</sub> extraction. The extraction was performed in a batch manner. The samples were loaded into the 50-ml extraction vessel of supercritical fluid extractor (SFT-110, Supercritical Fluid Technologies, Inc., Newark,

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