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Modification of amorphous phase of semicrystalline polymers

Summary — Routes of amorphous phase modification of several semicrystalline polymers, such as polypropylene, high density polyethylene and polyamide 6 were described. It appeared that amorphous phase alteration leads in each case to changes in tensile deformation of those polymers, especially cavitation. The reason is the modification of amorphous phase free volume: increase or decrease of the average size of free volume pores. The modification of the free volume of amorphous phase by introducing penetrants has been developed that affects the initiation and intensity of cavitation. Furthermore, the reasons for the yield stress decrease as a result of introducing low-molecular weight penetrator into pores of free volume of the amorphous phase were also described.

Keywords: semicrystalline polymers, amorphous phase, cavitation, yield stress, purification, swelling.

MODYFIKACJA FAZY AMORFICZNEJ POLIMERÓW CZĘŚCIOWO KRYSTALICZNYCH

Streszczenie — Opierając się na doniesieniach literaturowych oraz badaniach własnych zaprezentowano sposoby modyfikacji fazy amorficznej polimerów częściowo krystalicznych, takich jak polipropylen, polietylen wysokiej gęstości oraz poliamid 6, wpływające na proces ich deformacji podczas rozciągania jednoosiowego. Przedstawiono sposób modyfikacji swobodnej objętości fazy amorficznej i wpływ zmiany, zwiększenia oraz zmniejszenia, średniej wielkości porów, swobodnej objętości na inicjowanie oraz intensywność procesu powstawania kawitacji. Opisano także przyczyny obniżenia naprężenia na granicy plastyczności w efekcie wprowadzenia w obszar fazy amorficznej molekuł małocząsteczkowego penetratora.

Słowa kluczowe: polimery częściowo krystaliczne, faza amorficzna, kawitacja, naprężenie na granicy plastyczności, oczyszczanie, spęcznianie.

Semicrystalline polymers, like polypropylene, polyethylene or polyamide 6 are widely used class of the materials. Knowing and understanding basic mechanisms of plastic deformation of such materials is essential to fully exploit the possibilities offered by those macromolecular materials. In the case of amorphous polymers, due to a relatively simple structure of such materials, research conducted in the last three decades allowed to understand a number of aspects accompanying their deformation. However, despite numerous studies being carried out [*e.g.* 1—5], the mechanisms of plastic deformation of crystalline polymers still require a more detailed research due to their complex, hierarchical architecture.

ROLE OF AMORPHOUS COMPONENT IN PLASTIC DEFORMATION OF SEMICRYSTALLINE POLYMERS

Deformation of a crystalline polymer is a process which should include the presence of crystalline lamellae as well as amorphous phase. It is assumed that at temperatures at which amorphous phase exhibits rubber-like properties, it is in the interlamellar regions that the initial stage of polymer deformation takes place. This result, from data presented in the paper [6], whose authors demonstrated that stress required to initiate deformation of amorphous phase constitutes from 2 to 10 % of the value of stress needed to activate the mechanisms of crystalline phase deformation. Studies conducted by Bartczak *at al.* [7—9] also confirm the observed dependencies.

It is currently believed that deformation of amorphous phase takes place according to three basic mechanisms, schematically presented in Figure 1 [3, 5].

Interlamellar slips (Fig. 1a) [10—12] are realized as a result of simple shear of amorphous layers between lamellae taking place parallel to lamellar surfaces. This deformation mechanism is believed to be relatively easily activated in the early stages of deformation when amorphous phase exhibits rubber-like properties [5]. The

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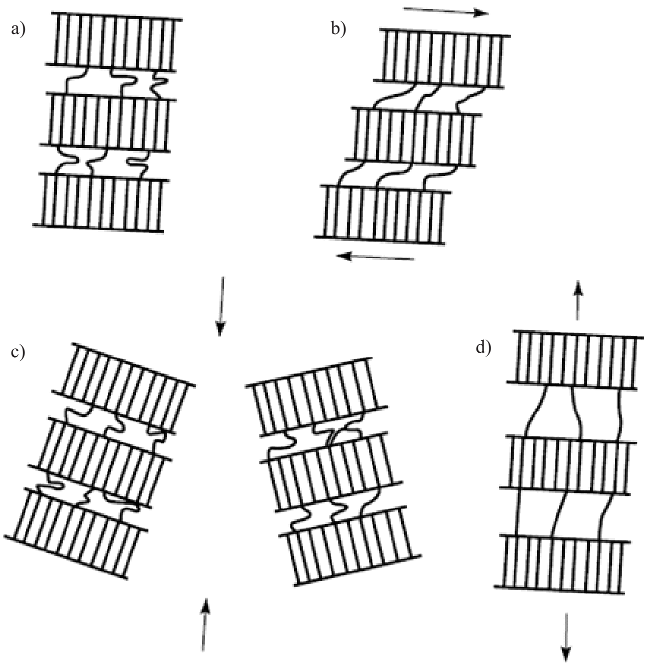

Fig. 1. Models of deformation in amorphous regions according to [5]: a) undeformed, b) interlamellar slips, c) lamella-stack rotation, d) interlamellar separation

mechanism is inactive when deformation takes place below glass transition temperature (T_g) of amorphous phase. Lack of interlamellar slips, accounts, among others, for a high increase in the elastic modulus of the deformed material below T_g of the material. Almost complete reversibility of this type of deformation has been observed, which was explained by elastic properties of amorphous phase or significant residual stresses in the undeformed material [10, 11]. The author of the paper [13] observed a complete reversibility of interlamellar slips up to true strain 0.6. According to Pope and Keller [10] some irreversibility of interlamellar slips can be attributed to the processes of breaking of chains (which reduce residual stress), or pulling out macromolecules from lamellae (increasing frictional forces between surfaces of the moving lamellae).

The second mechanism accompanying deformation of amorphous phase, schematically presented in Fig. 1b, is lamella-stack rotation. This type of deformation activated through shear of the material requires cooperative movements of amorphous phase and crystallites. In order for such a mechanism to be activated stack of lamellae have to be surrounded by a relatively easily deformable amorphous phase. Such deformation mechanism was first observed by Groves and Hirsch [14]. The results of small-angle X-ray scattering in combination with the data obtained for wide-angle X-ray diffraction presented in the paper [12] allowed to distinguish this mechanism from others accompanying the process of material deformation. The author of paper [15] proved that stacks of lamellae, consisting of three to ten crystallites, move cooperatively under the influence of stress.

The last type of deformation of amorphous phase is interlamellar separation (Fig. 1c) [10, 12, 16—18]. This type of deformation and the ability to activate this mechanism strongly depend on the material structure, particularly on the number and the distribution of active, taut tie molecules between the lamellae and the lateral dimension of the lamellar crystals. Lamellar separation in the volume of a sample must be accompanied by either „flowing in" of the material into the opening gaps between lamellae or an intensive process of a decrease in density of the deformed material, *e.g.* occurrence of cavities. Much more frequently, especially for materials such as polypropylene, high density polyethylene or poly(methylene oxide), that is materials characterized by a relatively high modulus and also capable of substantial plastic deformation, the separation process is accompanied by local changes in density of a sample, whose final result is formation of the material discontinuity — a cavity. Macroscopic effect of this type of contraction is a strong whitening accompanying deformation (uniaxial stretching) of the aforementioned materials.

Cavitation, usually occurring on early stages of deformation as a result of the increase in the interlamellar distances and lack of „flowing in" new batches of the material into the opening gaps, accompanying the deformation of most of the semicrystalline materials, was considered by many researchers as an artifact not affecting mechanical parameters and responsible only for changes in the material's density and whitening. The results of studies published in recent years shed some new light on that issue [19—27]. For it appears that the mechanical properties of the cavitated material are much worse than the properties obtained during the deformation of the same material in non-cavitation conditions (for example during channel die compression) [19]. The results presented in that paper indicate substantially higher recorded value of the yield stress in the non-cavitated sample (during channel die compression) than in the cavitated sample (during tensile drawing); in case of polypropylene the value is higher even by 75 %, for polyethylene it is about 55 % or for poly(methylene oxide) about 70 %.

It is commonly accepted that the above mentioned mechanisms of the deformation of the amorphous phase relatively quickly become exhausted in early stages of deformation. In further stages of deformation, the amorphous phase has been claimed to have the relatively small role, limited to transferring the stress between adjacent crystals [28]. In light of the literature data, the mechanical parameters of the material such as the yield stress were determined by the changes occurring in the area of the crystalline phase (dislocation nucleation, multiplication and their termination [29—31]). Therefore, the macroscopic mechanical properties of the semicrystalline polymer were determined by the material factors such as the thickness of crystals obtained during solidification of the material [32, 33] but also dependent on the temperature and the deformation rate (since the deformation of the crystalline polymers is a thermally activated process).

Meanwhile, the authors of papers [24, 27, 34—37] observed the effect of decreasing of the yield stress of the materials swollen with a low-molecular weight modifier, introduced into the amorphous phase area after its solidification. The presence of the modifier molecules located only in the amorphous phase area affected the material parameters, which, according to current knowledge, should be determined by the crystalline component. At the same time it was impossible to explain the observed phenomena based on the material plastification effect as a result of infusing the amorphous phase (reducing glass transition temperature of the amorphous phase). A typical example of such system is polyamide 6, which exhibits a natural tendency to absorb water in typical use conditions. However, the analogous effect, the decrease of the yield stress as a result of introducing of molecules of low-molecular weight liquid into the amorphous phase area of the polymer material, was observed also in other systems *i.e.* polypropylene-xylene [34] and polypropylene-chloroform, polypropylene-hexane or polyethylene-chloroform [24, 27].

Therefore, the mechanisms activated inside the amorphous phase due to its swelling contribute to the complex system of mechanisms activated during the plastic deformation of semicrystalline polymers and can affect the certain mechanisms in crystalline regions. The cavitation phenomenon, or rather its presence or absence, determining the mechanical properties is initiated in the amorphous phase of the material. Therefore, the cavitation process should be sensitive to any changes occurring in the amorphous phase. The physicochemical condition of the amorphous phase may substantially affect the macroscopic mechanical properties of the material and at the same time may determine its potential application, like in case of the polyamid 6-water system, or other systems of semicrystalline polymer-low-molecular weight modifier. The importance of the amorphous phase in plastic deformation of semicrystalline polymers seems to be more fundamental than it is expected in the current theory. The modification of the amorphous phase of semicrystalline polymers, as a valuable tool for modifying macroscopic properties of the material, will be the subject of this paper.

INFLUENCE OF MODIFICATION OF AMORPHOUS PHASE ON CAVITATION PHENOMENON

Increase of size of free volume pores of amorphous phase

For years the term „cavitation" only referred to the process of ruptures and discontinuities occurring in low-molecular weight liquids. The phenomenon of cavitation was observed already at the end of 19th century during examination of propellers, which bore clear signs of erosion caused by implosion of cavitation bubbles. Long before, that is in 1662 Huygens carried out first experimental observations of negative pressure present in water, which as we know, is the source of cavitation in liquids [38]. The results, present among others in papers [39, 40], demonstrate that cavitation is influenced by the following factors:

— formation of tensile stresses in the liquid (regions of lowered/negative pressure),

— physical and thermodynamic parameters of the liquid,

— presence of cavitation nuclei in the form of vapour or gas bubbles and all kinds of solid impurities in the liquid.

All kinds of impurities deteriorating the properties of the liquid constitute a particularly important factor affecting the intensity of the cavitation phenomenon in case of low-molecular weight liquids. For example, according to the theory of homogeneous nucleation of cavitation, chemically pure water should transfer tensile stresses up to 140 MPa — the strength of water on such level was determined experimentally by testing micro-inclusions of ultrapure water in quartz crystals [41].

Stabilizers present in the polymer material (added by manufacturers to improve thermal parameters and material processing) and low-molecular weight fractions — oligomers (result of an imperfect process of synthesis) can act as impurities, that is substances that affect the intensity of the cavitation process. Since, in some aspects the properties of the amorphous phase (consisting of folds, chain ends, dangling chains, macromolecules connecting at least two different lamellae and numerous chains not connected with crystals in a permanent way) present in the interlamellar regions inside the spherulites and localized on the interspherulitic boundaries, are (at the temperature above its glass transition temperature) similar to the properties of a liquid. Rozanski *et al.* [25] decided to evaluate the influence of „impurities" (stabilizers and low-molecular weight fractions) present in the amorphous phase on initiation and intensity of cavitation phenomenon during tensile drawing of polypropylene. The additives were extracted from compression molded samples by critical CO_2 and also by a mixture of non-solvents (hexane/chloroform/ethanol 4/1/1, v/v/v) in Soxhlet apparatus. The extract was an oily liquid composed of antioxidant, processing stabilizer, and a spectrum of low-molecular weight fractions of polypropylene. Deformation process of reference (with impurities) and purified samples allowed to estimate the influence of additives on the intensity of the cavitation phenomenon. Figure 2 presents small-angle X-ray scattering (SAXS) patterns recorded for the reference (RS) and purified (PS) polypropylene deformed at a rate $3.3 \cdot 10^{-3}$ s^{-1}, up to the local strain of 4.5. The deformation of the reference and purified materials was accompanied by the cavitation process. The way how cavitation developed was similar for both samples:

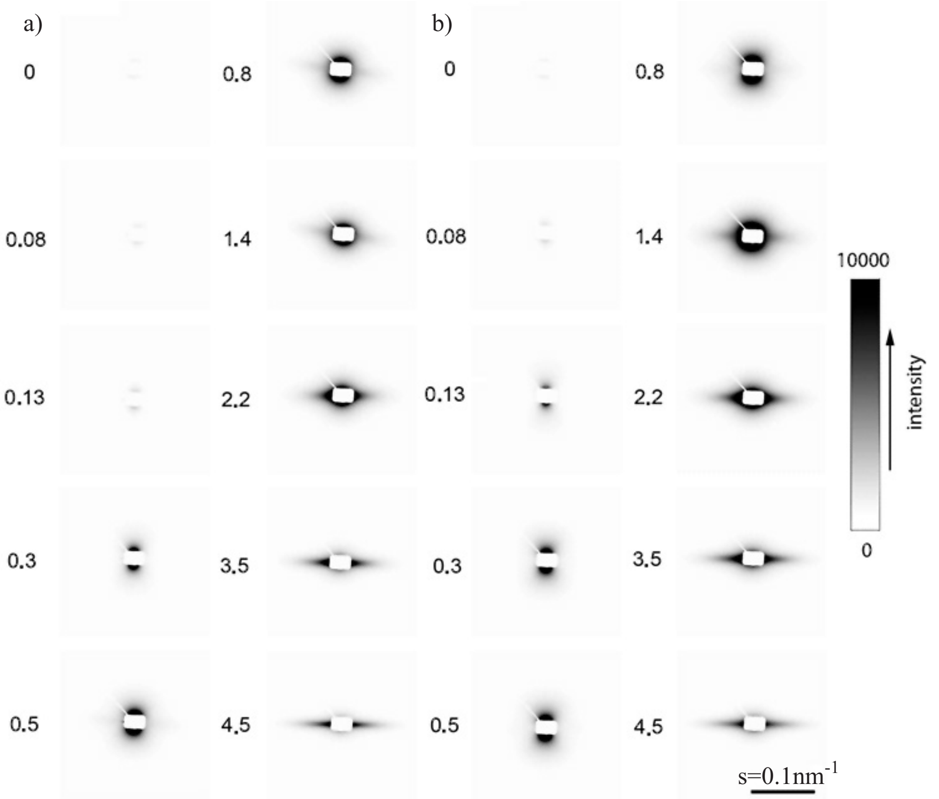

Fig. 2. SAXS patterns of a series of polypropylene samples: a) reference sample, b) purified sample; patterns correspond to the local strain of samples, deformation rate was 3.3 · 10^{-3} s^{-1} and direction of deformation was vertical (according to [24, 25])

— initiation of ellipsoidal, with long axes directed perpendicularly to deformation direction, cavities at the local strain amounting to 0.13,

— intensification of the cavitation phenomenon in further stages of deformation,

— reorganization of the shape of cavities, along the deformation direction of the sample at the local strain amounting to 0.8,

— decrease of the intensity of the signals originating from cavitaties as a result of the increase of average size of cavities beyond the detection range of the SAXS method.

A significant difference concerned the intensity of scattering signals coming from cavities at subsequent stages of deformation. The presented scattering patterns indicated that the intensity of the cavitation process was significantly increased in the purified material. The extraction process, which resulted in the removal of substances capable of nucleating cavitation, not only did not decrease the intensity of cavitation (like in case of low-molecular weight liquids) but produced a reverse effect, an increase in the number and sizes of cavitation pores formed during deformation of the material.

The authors of the paper drew analogous conclusions while analyzing volume strain measurements performed for the examined material prior to and after the purification process (increase in volume of around 75 % in case of reference sample and up to around 95 % in case of purified sample).

The process of material purification did not lead to any detectable changes in the crystalline phase of the material that is why the authors of the paper focused on the amorphous phase. Using the positron annihilation lifetime spectroscopy (PALS) method, they estimated the changes in the amorphous phase area, induced by removing the above mentioned impurities. Figure 3 presents relative size distributions of free volume pores of the amorphous phase of reference (RS) and purified polypropylene (PS).

The presented data clearly indicated an increase in the mean size and number of the free volume regions in the purified material. Removal, by extraction, of stabilizers,

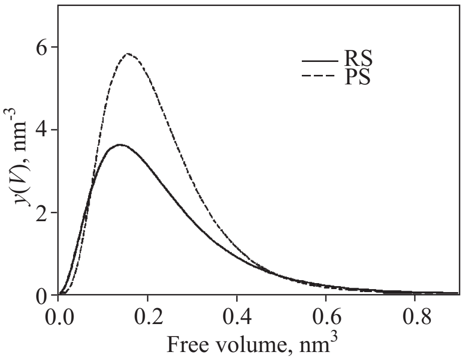

Fig. 3. Relative size distributions of free volume pores [y(V)] of the amorphous phase of reference (RS) and purified polypropylene (PS) according to [25]

other additives, and low-molecular weight fractions filling the amorphous part of the material led to changes in the interlamellar regions, resulted in the increase of sizes and number of free volume pores constituting an integral part of the amorphous phase. The nuclei of cavitation during the deformation of the material are the pores of the free volume of amorphous phase. Their sizes, depending on their filling (by additives and oligomers) determine the intensity of cavitation process. The cavitation initiated during the deformation of reference and purified polypropylenes indicates a homogeneous nucleation by the free volume pores that are an integral part of the amorphous phase of every semicrystalline polymer.

Decrease of size of free volume pores of amorphous phase

In the previous chapter the effect of the size of the free volume pores on the cavitation effect was described. Increasing the average size of free volume pores of the amorphous phase lead to intensification of the cavities forming process in the material during its deformation. In the paper [27] the results of the studies related to such materials as polypropylene, high density polyethylene and polyamide 6 were described, in which the generated effect was opposite. By introducing molecules of a low-molecular weight liquid into free volume pores of the amorphous phase the cavitation usually accompanying tensile drawing could be completely eliminated. The liquids used were carefully selected: size of liquid molecules should match the sizes of free volume pores and the liquid should not dissolve polymer crystals so, the parameters of polymer crystalline phase remained unchanged. Figure 4 demonstrates *in situ* SAXS patterns obtained during deformation of polypropylene samples: reference and chloroform-soaked using synchrotron radiation. Deformation of polypropylene penetrated with chloroform was not accompanied by formation of cavities. On the presented scattering patterns in Fig. 4 up to the local strain of 4.5 there is no indication of formation of discontinuities. There is a significant influence of low-molecular weight liquid present inside the free volume pores of amorphous phase on the phenomenon of cavity formation in polypropylene during its deformation. The authors confirmed complete elimination of the cavitation effect in the chloroform-soaked material also basing on scanning electron microscope (SEM) micrographs. In Figure 5 the micrographs of the polypropylene samples: reference and chloroform-soaked deformed up to the local strain of 2.2 are presented. SEM micrograph of the reference sample illustrates numerous cavities elongated in the direction of deformation. Meanwhile, up to

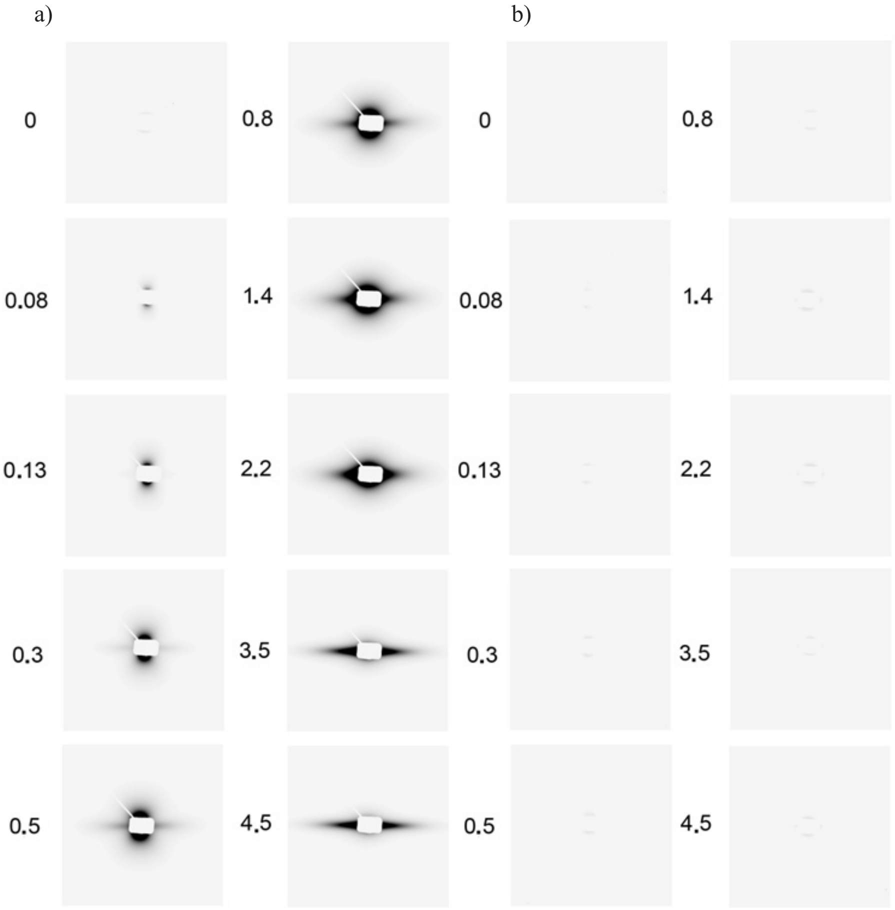

Fig. 4. SAXS patterns of a series of polypropylene samples: a) reference sample, b) chloroform-soaked sample; according to [27]

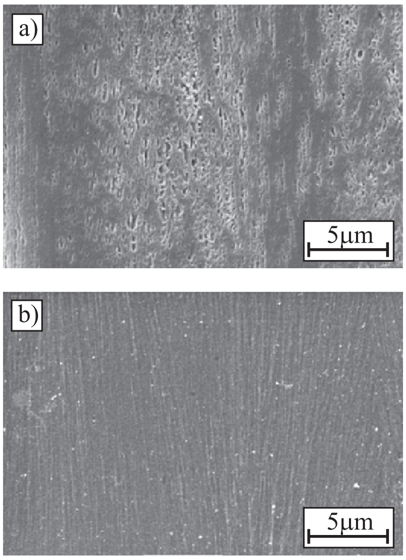

Fig. 5. SEM images of etched interior of compression molded polypropylene samples deformed to the local strain of 2.2 with the same strain rate of 3.3 · 10^{-3} s^{-1} and vertical direction of deformation: a) reference polypropylene, b) chloroform-soaked polypropylene; according to [26]

the local strain equal to 2.2 the formation of cavities was not observed in the chloroform-soaked polypropylene. Similar results of elimination of cavitation in the penetrant-soaked material, have been obtained by the authors of the paper [27] in case of the systems: polypropylene-hexane, polyethylene-chloroform and polyamide 6-water.

In case of polypropylene Rozanski *et al.* [27] observed similar effect — eliminating the cavitation process using liquids of substantially different physicochemical properties (chloroform and hexane) as a modifier. According to the authors' suggestions concerning elimination of the cavitation process in the deformed material, the type of liquid used in the amorphous phase modification is not relevant except that the used liquid must be able to penetrate the amorphous phase regions, its molecules should fit to free volume pores of a polymer and should not dissolve polymer crystals.

Since desorption of penetrants under laboratory conditions after removal of the materials from a conditioning vessel was a relatively quick process, it was not possible to record the PALS spectra for the soaked materials. The authors of the paper [27], based on the measurements of the samples' density proved that the penetrator molecules introduced into the amorphous phase area, fill partially the free volume pores — the volume of a low-molecular weight penetrant introduced during modification of the material was higher than the change in the volume of the sample as a result of saturation process. The authors of the paper [27] explained the elimination of the cavitation process in the analyzed materials with the decrease of the average size of the free volume pores of the amorphous phase filled with the molecules of low-molecular weight penetrant. The above presented data confirmed the hypothesis, described in the previous chapter, that cavitation during the deformation of semicrystalline polymers is activated by free volume pores and is of homogeneous nature.

INFLUENCE OF MODIFICATION OF AMORPHOUS PHASE ON YIELD STRESS

Introducing molecules of low-molecular weight liquid into amorphous phase of semicrystalline polymers leads to a reduction of the yield stress. Such effect was observed earlier in case of the polypropylene soaked with xylene [34] or polyamide 6 with water [35—37]. Recently, Rozanski *et al.* [24, 27, 42] have observed similar effect while analyzing the influence of the amorphous phase modification by introducing the molecules of low-molecular weight penetrant on the initiation the cavitation during tensile drawing of several semicrystalline poly-

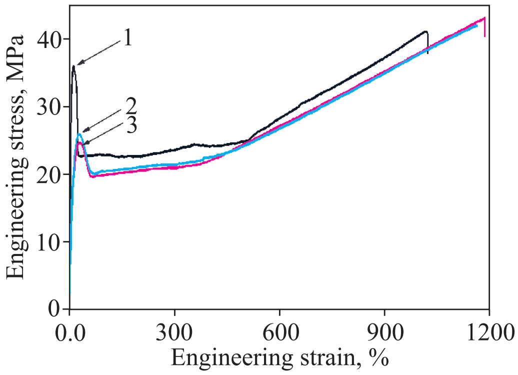

Fig. 6. Engineering stress versus engineering strain curves obtained with deformation rate of 3.3 · 10^{-3} s^{-1} for samples of unmodified polypropylene (1), saturated with modifiers: hexane (2) and chloroform (3); according to [27]

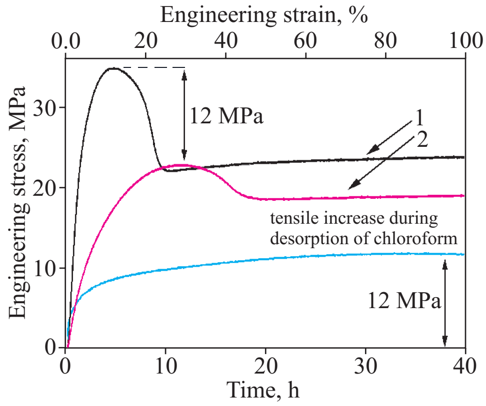

Fig. 7. Engineering stress versus engineering strain curves for reference (1) and chloroform-soaked (2) polypropylene samples obtained with deformation rate of 3.3 · 10^{-3} s^{-1} — the blue curve shows the stress build up on clamped swollen polypropylene sample during evaporation of chloroform; according to [24, 42]

mers. Figure 6 presents engineering strain-engineering stress curves for polypropylene samples: reference, chloroform-soaked and hexane-soaked, subjected to tensile drawing up to fracture.

The analysis of curves presented in Fig. 6 indicated strong dependence of the stress at yield point on the presence of a penetrant filling amorphous phase of polypropylene. The determined values were, respectively: 36.1 MPa for reference sample, 24.1 MPa for chloroform-soaked sample and 25.6 MPa for hexane-soaked sample. Introduction of penetrant molecules, therefore, leads to a decrease of the stress at yield point of the soaked material by 12 MPa and 10.5 MPa for chloroform and hexane soaked samples, respectively.

It is believed that the yield stress during the deformation of semicrystalline polymers is determined by the properties of crystalline phase. However, the data presented in the paper [27] indicated no detectable changes in crystalline phase as a result of introducing the penetrant. Therefore, the observed reduction of the yield stress must have been induced by the changes in amorphous interlamellar regions. Therefore, the authors of the paper [27] carried out the following experiment: a chloroform-soaked polypropylene sample, removed from a conditioning vessel, was immediately clamped in the tensile testing machine for measuring mechanical properties and stress build-up in the sample as a function of time of desorption of the penetrant was measured. Figure 7 presents the results of the experiment.

After approximately 40 hours since removal of the sample from the conditioning vessel stress build-up in the sample equaled to 12 MPa, which corresponds to the observed difference in stress at yield point between the reference and soaked samples. In the case of the hexane-soaked sample, in a similar test, the recorded stress build-up amounted to 10.5 MPa which is exactly the difference between the yield stresses of reference and hexane-soaked samples. According to the authors, the introduction of the modifier molecules, led to a strong swelling of the amorphous phase, which results in its significant deformation (no changes in the crystalline structure of the material, but a change in the values of long period). Highly swollen, hence deformed amorphous phase stretched the adjacent crystals with the force equal to the value of the observed difference in stresses at yield point. For penetrant-soaked samples lower stress was required to activate plastic deformations of the crystals, because crystals were already stretched by the stretched chains of the swollen amorphous phase.

The reduction of the yield stress, as a result of introducing the molecules of low-molecular weight penetrator has been observed by the authors of the work also in case of the high density polyethylene-chloroform system and polyamide 6-water system. In the first case the recorded stress in the test for stress build-up in the sample as a function of time of desorption of the penetrant, amounted to 4.9 MPa, corresponding perfectly to the recorded difference of the yield stresses between the reference and chloroform-soaked polyethylene samples. In the case of the polyamide 6-water system the reduction of the yield stress as a result of introducing the molecules of the penetrant (water) has been explained based on the experiment involving three water-soaked polyamide 6 samples. The samples were treated as follows: one sample was drawn in tensile testing machine, the second sample was conditioned in the lab for 65 h and drawn in tensile testing machine, and the third sample was clamped in tensile testing machine and the stress build-up was followed as water evaporated from the sample. The difference in stresses at yield and beyond the yield between wet and lab-conditioned samples amounted to 6.8 MPa. Nearly the same stress was generated in the sample that was allowed to dry with fixed ends during 65 h.

It is worth to mention that presented in the article explanation for the reduction of the yield stress of several semicrystalline polymers, as a result of the sorption of low-molecular weight penetrator, did not require any modification of the theory of the polymer crystals plasticity and leaves all its basic attributes unchanged *i.e.*: crystallographic slips and critical shear stress for their activation are determining the yield stress.

CONCLUSIONS

Proper modification of the amorphous phase of semicrystalline polymers may substantially affect the macroscopic properties of the analyzed materials. By removing „the impurities" (low-molecular weight additives or oligomers) from the amorphous phase regions, we can affect the cavitation phenomenon. Increasing the average size of the free volume pores, leads to the increase in the intensity of the cavitation in the material during its deformation. By increasing the average size of the cavities, we reduce the strength of the amorphous phase of purified samples, compared to the strength of the amorphous regions of the reference materials, which leads to an increase the intensity of cavitation.

On the other hand, introducing properly selected substances into the amorphous phase of crystalline polymers, we can eliminate completely the cavitation, often considered as undesirable, and we can also modify the mechanical properties of the material. Filling the free volume pores, it is reducing their average size, we increase the strength of the amorphous phase of the modified materials, compared to the reference material, which in turn impedes the process of forming the cavitation pores — higher stress is required to generate and stabilize such pores. At the same time, as a result of the penetrant sorption, the amorphous phase is subjected to swelling and hence, the deformation. Therefore, to activate the mechanisms of the crystalline phase plastic deformation a lower stress is required, reduced by the value generated in the material as a result of swelling. Above described phenomena are schematically illustrated in Figure 8.

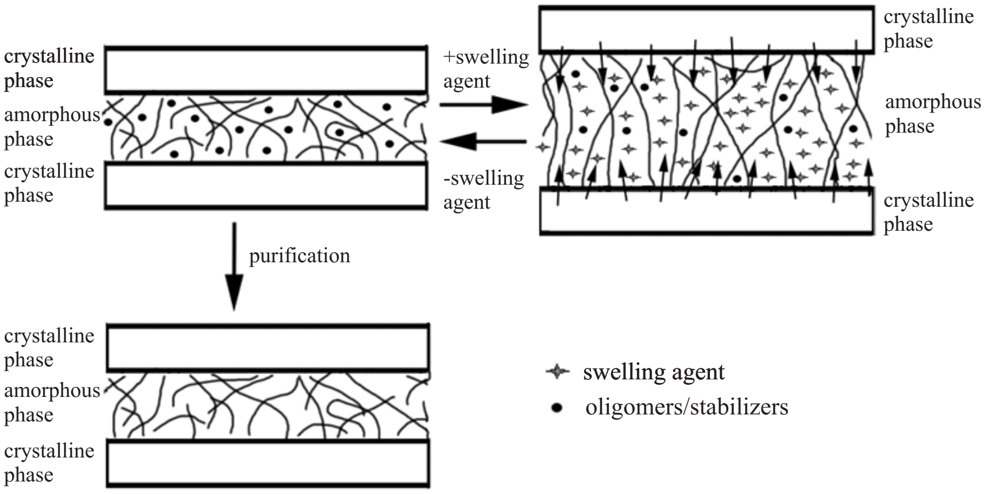

Fig. 8. The diagram shows schematically changes in the amorphous phase as a result of purification and sorption of molecules of low-molecular weight penetrant; according to [25, 42]

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