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Flory Prize Lecture: Cavitation during Drawing of Crystalline Polymers

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Summary: Cavitation in low molecular weight liquids under tension and in crystalline polymers during tensile drawing was recapitulated. The review indicated that the amorphous phase of crystalline polymers at temperature above its glass transition temperature differs markedly from low molecular weight liquids. Cavitation in polymers seemingly is not of a heterogeneous character, unlike in unpurified low molecular weight liquids. The most probable reasons are: confinements of amorphous layers between crystalline lamellae and macromolecular chain entanglements, the factors that are absent in low molecular weight liquids.

Keywords: cavitation; crystalline polymers; lamellae; tensile drawing; yielding

Introduction

In the simplest kind of deformation, tensile drawing, deformation of most crystalline materials is accompanied by a strong whitening of the material, occurring shortly before or just after reaching macroscopic yield point. Studies conducted in order to explain reasons for the observed differences showed that a source of strong scattering of light in such deformed material are cavities and crazes which appeared in the amorphous phase during deformation.

The first model to deal with the phenomenon of formation of cavities in a crystalline polymer during its deformation was a ''micronecking'' model proposed by Peterlin.[1–3] Even though the model explained many phenomena taking place during plastic deformation of polymers, it contained significant inconsistencies. Further research allowed to examine and better understand the mechanisms of plastic deformation of crystalline polymers.[4–8] However, the phenomenon of cavitation was only treated as a side effect, related to distribution of stresses, a result of operation of other deformation mechanisms. Moreover, cavitation was frequently treated as a phenomenon which not only does not influence the course of deformation, but even masks the true mechanisms activated. Pawlak et al.[9] demonstrated that cavitation of the crystalline polymers is not only responsible of material whitening, but also influences mechanical parameters such as yield stress.

For years the term ''cavitation'' only referred to the process of ruptures and discontinuities occurring in low molecular weight liquids. In 1662 Huygens[10] carried out first experimental observations of negative pressure in water, which is the source of cavitation in liquids. Huygens experiment was repeated many times for water, mercury and other liquids by other researchers,[11–14] but these were the studies by Reynolds[12,13,15] at the turn of 19thand 20th century which allowed to better understand the nature of the phenomenon. Until present, a coherent theory describing the phenomenon, one that would include all the parameters and properties of liquids has not been developed, however, many studies published so far allowed to thoroughly examine and understand the process of cavitation in liquids. The results, present among others in papers,[16,17] demonstrate that cavitation is influenced by the following factors: (i) generation of tensile stresses in the liquid, (ii) physical and thermodynamic

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parameters of the liquid and (iii) presence of cavitation nuclei in the form of vapour or gas bubbles and of solid impurities.

Understanding the mechanisms responsible for cavitation in liquids can eliminate or reduce its intensity when it has a negative impact on the durability of materials or functioning of devices, and to intensify the phenomenon when the presence of cavitation is desired.

If a deformation of a crystalline polymer is accompanied by cavitation, it is localized in the amorphous phase of the material. In some aspects the properties of the amorphous phase (such as folds, chain ends, dangling chains, macromolecules connecting at least two different lamellae and numerous chains not connected with crystals in a permanent way) present between lamellae and localized on the interspherulitic boundaries, are similar to the properties of low molecular weight liquids at the temperature above its glass transition temperature. A significant difference is the presence of physical constraints in the amorphous phase structure, reversible chain entanglements and fragments of macromolecules spanning interfacial boundaries of crystallites, which markedly decrease the mobility of macromolecules. Extensive research on cavitation in low molecular weight liquids, over the years, allowed to learn many aspects accompanying the phenomenon. Thorough analysis of achievements in this field seems vital for proper understanding of the nature of cavitation accompanying deformation of crystalline polymers. Therefore, the state of knowledge concerning negative pressure and the phenomenon of cavitation in low molecular weight liquids will be discussed, together with the results of studies on cavitation occurring during deformation of crystalline polymers obtained so far.

Cavitation in Low Molecular Weight Liquids

Any two parameters, e.g. pressure and volume determine equilibrium of a body, and the third parameter, in this case temperature, can be determined on the basis of an equation of state.

In the case of real substances most commonly used is the van der Waals equation in the form:

$$(p + a^2/V_m^2)(V_m\text{-}b) = RT \qquad (1)$$

where p is pressure, V volume, T absolute temperature, R a universal gas constant, the coefficient a is a parameter taking into account interaction between molecules and the coefficient b is characterized by the finite size of particles. The parameters of state bound by the van der Waals equation, are interrelated. For the selected temperatures one obtains relations between pressure and volume as shown in Figure 1a.

If the liquid is chemically homogeneous, free of cavitation nuclei, lowering the pressure below zero is possible and the liquid is then called "liquid under tension". The difference in pressures between ambient pressure and achievable negative

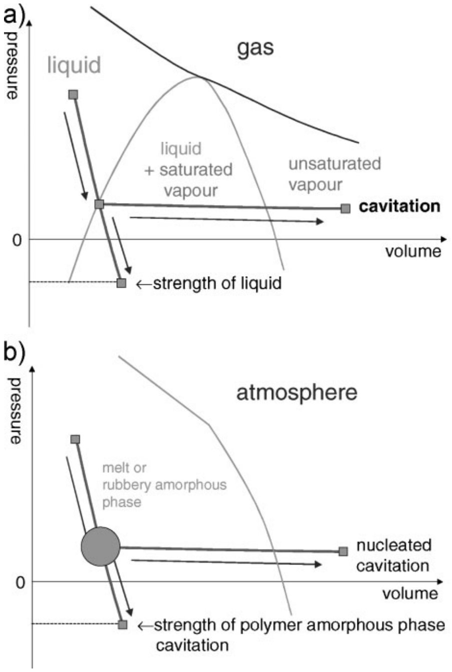

Figure 1.
Van der Waals isotherms of: (1a) liquid, (1b) amorphous phase of a polymer.

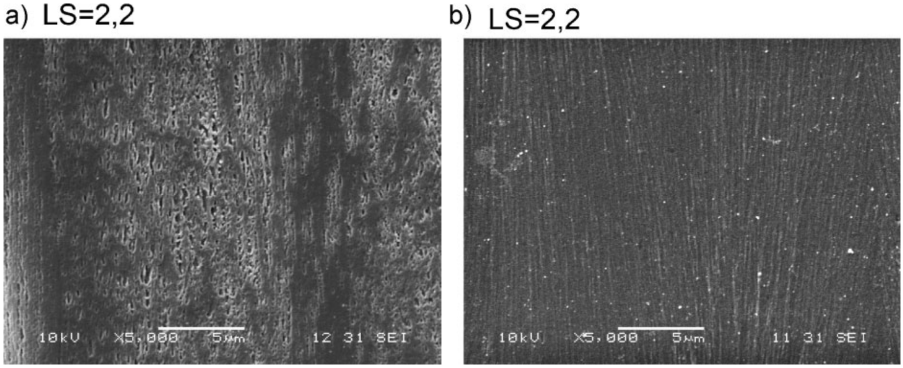

Figure 2.
SEM images of etched interior of compression molded polypropylene samples deformed to the local strain of 2.2 with the same strain rate of 15%/min, a) poly(propylene) cavitating, b) poly(propylene) non-cavitating.

pressure is equal to the strength of the liquid. If the liquid subjected to tensile stress is a homogenous substance, then cavitation would be virtually impossible, since it would require an application of stress reaching up to hundreds of MPa. For such liquids a source of cavitation could only be voids between molecules of the liquid, transiently generated as a result of thermal fluctuations. Cavitation occurring under such conditions is defined as homogeneously nucleated. Fundamentals of the theory of homogeneous nucleation of cavitation were developed by Frenkel.[18] The strength of water determined basing on the theory of homogeneous nucleation should reach the value of −140 MPa.[18] Surface tension σ occurs as a result of intermolecular interactions, which prevents formation of voids. Pressure in the liquid, p, outside the bubble of radius R, is connected with pressure inside the bubble, p_B, through the following relation:

$$p_B - p = 2\sigma/R \tag{2}$$

In order for a bubble to remain stable the pressure in the liquid must be lower than the pressure within a bubble. If the pressure in the liquid remains constant, less than p_B $-2\sigma/R$, the bubble after reaching the critical size, will grow, finally leading to rupture of liquid. In this case, the strength of the liquid is determined by negative pressure at which cavitation occurs:

$$\Delta p_C = 2\sigma/R_C \tag{3}$$

An important parameter is also energy cost connected with formation of a bubble of radius R.[19,20] Assuming that a bubble is in the state of thermodynamic equilibrium with the surrounding liquid, energy cost is composed of two factors: generating a surface of the bubble of radius R ($4\pi R^2\sigma$) in the liquid and formation of free volume ($4/3(\pi R^3\Delta p)$). Thus, the minimum work necessary to create a vapour bubble is defined by a following equation:

$$W = 4\pi R^2\sigma - 4/3(\pi R^3\Delta p) \tag{4}$$

For a given critical radius $R = R_C$ (Figure 3) the value of energy is highest:

$$W_C = 16\pi\sigma^3/3(\Delta p_C)^2 \tag{5}$$

Bubbles of a radius smaller than the critical radius require additional free energy for further growth, whereas others can grow freely. Bubbles can be formed in a homogenous liquid as a result of local fluctuations of temperature or entropy. In order for a bubble of critical size to be formed in a liquid, a whole series of "beneficial" fluctuations are required at the local level; such a situation occurs very rarely. The theory of homogenous

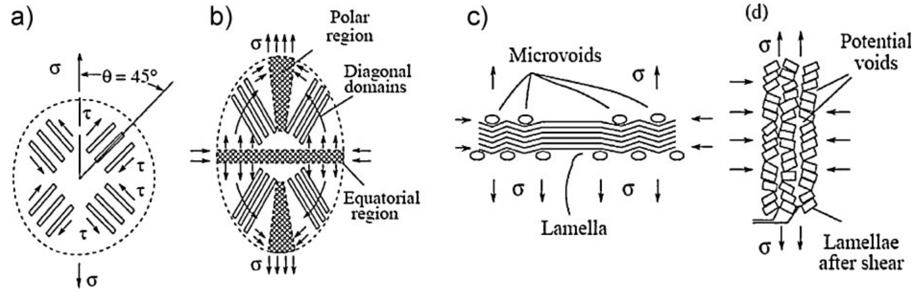

Figure 3.
Stages in the formation of cavities in the spherulite structure during uniaxial deformation [redrawn after 60]: a) crystallites of the diagonal region; b) lamellar rotation in the diagonal region resulting from an increase in tensile and compressive stresses in the equatorial region of a spherulite c) kinking of lamellae due to shear instability in the amorphous matrix in equatorial region; d) shear instability due to chain slip in lamellae in polar regions.

nucleation connects W_C with the kinetic energy of molecules leading to the negative pressure at which rupture of liquid will occur in a period of time t:

$$p = -\{(16\pi/3)\sigma^3/[\mathrm{kTln(NKTt/h)}-\Delta f^*]\}^{1/2} \tag{6}$$

where k is the Boltzman constant, N is the Avogadro number and Δf^* symbolizes activation energy of molecule movement. Attempts were also made to relate the nucleation rate with the critical energy.[17]

It is known, however, that liquids not subjected to purification contain a huge number of cavitation nuclei, in the form of vapour or gas microbubbles and all kinds of solid impurities whose presence substantially decreases the liquid's ability to transfer tensile stresses. For such liquids, subjected to negative pressure, the process of cavitation is of heterogenous nature.

Stress necessary for generating cavitation in a liquid is equal to its tensile strength.

Cavitation in Polymers

In the case of macromolecular materials the phenomenon of cavitation has been observed during melt crystallization of selected crystalline polymers[21–30] and tensile Drawing[31–43] of given materials. As in the case of liquids of low molecular weight, the driving force of the phenomenon is negative pressure generated in the material. During crystallization negative pressure is generated in the areas tightly surrounded by the growing spherulites and this is where cavitation bubbles are mainly observed.

During deformation of the material cavities can also be generated in the interspherulitic regions, although in the interlamellar regions, inside the spherulites, the phenomenon is more intense and is initiated at a much earlier stage of deformation. The phase diagram of a polymer subjected to negative pressure is presented in Figure 1b. The main difference is that polymers do not have vapours and melting rarely occurs when changing pressure.

Despite numerous studies [e.g. 44–48], the mechanisms of plastic deformation of crystalline polymers due to complex, hierarchical architecture of such materials still require a more detailed research. Deformation of a crystalline polymer is a process which include the crystalline lamellae as well as amorphous layers. If the deformation of a polymer is accompanied by cavitation, it is in the amorphous phase of the material where cavities are being formed. Understanding the phenomena taking place in the early stages of deformation in the interlamellar layers of spherulites seems vital for understanding the nature of formation of cavities in polymers. It is currently believed that deformation of amorphous phase takes place according to three basic mechanisms, interlamellar slip, lamellae stack rotation and interlamellar separation.[46,48]

The interlamellar separation is the deformation of amorphous regions, particularly important for the phenomenon of cavitation.[49–53] The mechanism of interlamellar separation involving a change of distance between the adjacent lamellae, when the direction of stress is perpendicular to their surface, satisfactorily explains the changes observed. 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 intense process of formation of cavities. Due to limitations resulting from neighbouring lamellae and their large lateral dimensions the first type of contraction seems unlikely since it would require a massive rapture of tie molecules.[54] However, much more frequently, especially for materials such as polypropylene, high density polyethylene or polyoxymethylene, 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 –cavities (compare Figure 2a and 2b). Macroscopic effect of this type of response is a strong whitening accompanying uniaxial stretching. Spherulites consist of radially arranged lamellae and amorphous regions. Considering a typical architecture of a spherulite one should take into account three characteristic regions differing in relative arrangement of lamellae, whose mechanical response under the influence of the applied stress significantly differs.

- Polar region: most macromolecules are arranged perpendicularly to the direction of deformation. A consequence of such chain arrangement is orientation of lamellar surfaces parallel to the direction of the applied stress. Two most important processes accompanying deformation of this spherulite region is micronecking (taking place according to the mechanism proposed by Peterlin) and formation of microcavities.[55,56] Consequently, this spherulite region exhibits the highest plastic deformation resistance during uniaxial tension.
- Equatorial region: lamellae are arranged almost perpendicularly to the direction of deformation. Results presented in the papers[46,47,57] show that it is the equatorial region that deformation first appears in, which is explained by the presence of easily activated deformation mechanisms of amorphous phase such as lamellar separation and rotation. It was shown[58] that for single large polybutene spherulites deformation initiated in the centre of a spherulite (according to theory it is in the centre of a spherulite that stress reaches the highest value[60]) spreads over the equator along the radius.
- Diagonal region: material deformation takes place intermediately to the above mentioned limiting cases. The process of lamellar separation is observed accompanied by shear of interlamellar amorphous layers. The result of the complex processes taking place in this deformation region is lamellar rotation in the direction of the applied stress and a macroscopic change in the spherulite’s shape: sphere-ellipse.

Complex changes taking place in the spherulite structure, including changes in the distribution of stress in individual regions and the phenomenon of cavitation accompanying deformation process were presented in a paper by Galeski et al..[60]

Although formation of stresses inside a spherulite is a complex phenomenon, it has been observed on the basis of transmission electron micrographs combined with the process of contrasting samples, that a number of interrelated processes occur preferentially in the selected areas of different lamellar arrangement (Figure 3). Under the influence of the applied stress the lamellae oriented at an angle of approximately 45° to the direction of deformation (diagonal region of a spherulite) are brought to rotation because of intra-and interlamellar slips (Figure 3a). This type of deformation and change in the spherulite shape results from formation of additional tensile and compressive stress in equatorial and polar regions (Figure 3b). Under the action of these stresses selected mechanisms of crystal deformation in the equatorial region are blocked due to the specific orientation of packets of lamellae with respect to stresses. As a result, lamellae undergo kinking, which leads to formation of cavities in this spherulite region (Figure 3c). Analogous processes should also take place in the polar region of spherulite. Specific arrangement of crystallites prevents deformation of the amorphous phase. Lamellar deformation, analogous to crystallites in the equatorial region, takes place as a result of their limited crystallographic slips and local break-up. Lack of proper contraction of the amorphous phase leads to formation of regions of lower density, whose consequence in further stages of deformation of the polar region of spherulite is formation of cavities (Figure 3d).

Results presented in a previous paper[61] and the schematic representation (Figure 3) show that first discontinuities in the material appear just before or shortly after reaching the macroscopic yield point. Initially the cavities of ellipsoidal shape are oriented with the long axis perpendicular to the direction of deformation. This shape of cavities is forced by lamellar structure of the material. The presence of such objects is confirmed by a strong signal on a diffractogram in the meridional region as a result of significant difference in the electron density of the material and the generated cavities. Change of interlamellar distances and fragmentation of lamellae force a change in the shape of cavities. The phenomenon observed on a small angle scattering pattern manifests itself in the fading signal in the meridional region and appearance of strong scattering in the equatorial zone. Further deformation of the material is accompanied by strong extension and thinning of cavities, which show as a long, narrow diffraction signal in the equatorial region of a scattering pattern.

The mechanisms of deformation of crystalline polymers appearing during tensile stretching are related to a number of factors such as deformation rate,[62–64] temperature,[64,65] molecular weight,[42,63,66–68] thermal history[41,61,63,66–68] and lamellae orientation.[64] It turns out that cavitation of the material also is a phenomenon sensitive to the aforementioned factors. Furthermore, cavitation is a process simultaneously determined by several of the mentioned parameters, therefore, depending on the characteristics of the material and conditions under which deformation takes place, each of the factors plays a more or less important role. Certain factors are so important that they determine the presence or absence of cavitation, others only influence the scope of the phenomenon.

It was clearly demonstrated[40] that during plastic deformation there is a kind of ''rivalry'' between activation of deformation mechanisms of the crystalline phase and cavitation occurring in amorphous regions. Deformation of materials with large, strong, well-developed crystals, such as polypropylene (PP), high density polyethylene (HDPE) or polyoxymethylene (POM), is accompanied by cavity formation. In the case of materials of small, strongly defected crystallites, however, such as low density polyethylene (LDPE), ethylene copolymers, deformation takes place without cavitation. That is because the plastic deformation of crystals is initiated before the stress reaches the resilience of the amorphous phase. On the basis of surface tension and thickness of amorphous regions the authors of the mentioned paper estimated negative pressure necessary to generate stable cavitations, equivalent to strength of amorphous phase, in the following materials: PP (−13.7 MPa), POM (−35.8 MPa), HDPE (−15.1 MPa) and LDPE (−17.6 MPa). Negative pressure occurring locally at the yield point in PP (−20.7 MPa), POM (−42 MPa), HDPE (−15.3 MPa) and LDPE (−4.7 MPa) have also been determined. In cases where the resistance of the amorphous phase is lower than the negative pressure at the yield point (PP, HDPE, POM), the applied stress will cause cavitation of amorphous phase prior to activation of deformation mechanisms of crystalline phase. In materials of thinner and softer crystals (like LDPE) deformation of crystals will be initiated before stress exceeds the strength of the amorphous phase.

Even in the case of the aforementioned polymers, thanks to changes at the level of material structure caused by differences in thermal history during crystallization and after solidification, one can influence the intensity of cavity formation.[41] Running the crystallization process at a higher temperature or at a lower cooling rate one obtains materials with thicker crystals, exhibiting higher mechanical strength. Analogous effect can be achieved by annealing of already solidified materials, which results in thickening of crystallites and increase in their strength. In materials with higher strength of the crystalline phase the cavitation process is more intense because it requires less stress.

As has already been mentioned, occurrence of cavitation during deformation of a crystalline polymer is first observed in the equatorial region of spherulites. Specific arrangement of lamellae in that region, whose surfaces are oriented perpendicularly to direction of deformation, facilitates their separation. An important factor influencing the phenomenon of cavitation is thus orientation of the material's lamellar structure. The role of this parameter in the process of cavitation has been illustrated in the paper by Pawlak.[41] The subject of study were HDPE injection molded samples. On the surface of such samples, in contrast to their core, the arrangement of lamellae is the same as in the spherulite's equatorial region. When deformation takes place perpendicular to lamellar surfaces, arranged parallel to one another, cavitation in the amorphous layer occurs already with deformation from about 0.15%, which is much below the value at which cavitation is observed in isotropic samples, and stress of 2 MPa (first cavities in isotropic samples appear at approximately 10 times higher stress). Specific lamellar arrangement in the material, perpendicular to the direction of deformation, by favouring this type of material response is thus beneficial to the phenomenon of cavitation.

Another factor influencing the intensity of cavitation during deformation of the material is the molecular weight of a polymer. Results presented in papers[42,61] showed that increasing molecular weight of a polymer leads to a decrease of the intensity of cavitation. The authors explained this effect by a higher molow number of strongly entangled macromolecules, which form the amorphous phase. Macromolecules in the unordered regions of a polymer of a higher molar mass form a more durable entanglement network, more resistant to tensile stresses.

Apart from parameters related to the material structure, cavitation is also affected by the deformation rate and temperature under which deformation of the material is conducted. The authors of papers[42,69] proved a strong dependence of cavitation on the deformation rate – an increase in the deformation rate caused an increase in the intensity of cavity formation in the material. The influence of a sample's deformation rate on cavitation is accounted for by changes in the stress values at yield point with a change in deformation rate. An increase in stress initiating plastic deformation of crystals leads to initiation of cavitation, as an easier phenomenon, when the strength of amorphous phase is exceeded.

Temperature of deformation is also an important parameter. Studies presented in papers[63,69,70] show that by performing deformation at elevated temperature one can completely eliminate the phenomenon of cavitation. A material cavitating at room temperature deforms without cavitation when the temperature is increased. It is believed that the reason for such an effect is lowering stress initiating deformation of crystalline phase by crystallographic slips that are thermally activated. Before stress exceeds the strength of the amorphous phase, deformation mechanisms of crystalline phase will be activated as easier ones.

Conclusion

The above presented review indicates that the amorphous phase of crystalline polymers at temperature above its glass transition temperature differs markedly from low molecular weight liquids. Polymers are not specially purified, in addition they contain additives such as stabilizers, antioxidants, residue of catalysts, low molecular weight fractions, lubricants, light stabilizer etc. Despite of impurities and additives amorphous phase of crystalline polymers exhibit amazingly high strength in terms of cavitation stress, at the level of 10–20 MPa. It is even more astonishing when considering that all those substances and additives are concentrated in amorphous layers during polymer crystallization. Cavitation in polymers seemingly is not of a heterogeneous nature, unlike in unpurified low molecular weight liquids. The most probable reasons are: confinements of amorphous layers between crystalline lamellae and macromolecular chain entanglements, factors that are absent in low molecular weight liquids.

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