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Cavitation and Cavity-Free Deformation of Filled Crystalline Polymer Systems

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Summary: Main mechanisms of tough response of polymers are described. In heterogeneous polymer systems due to mechanical misfit between heterogeneities and the matrix a high negative pressure (tri-axial stress) is generated. The excessive negative pressure is the main reason of material cavitation. Cavitation appears to be another mechanism of tough response of the material to loading. Cavitation is a massive phenomenon in crystalline polymers and in all filled polymers. Cavitation itself does not consume much energy but allows for further toughening by activating other mechanisms. Examples of polypropylene filled with chalk modified by liquid, rubber and mineral filled polypropylene and syndiotactic polypropylene filled with chalk are described. Modes of deformation with significant compressive component of stress prevents for cavitation. Materials deformed in a cavity-free manner show much higher strength. It is pointed out that high polymer crystal anisotropy is necessary for the formation of a network of easy crystallographic slip in the unusual toughening of highly filled polymers observed recently. An example of syndiotactic polypropylene filled with submicro-chalk particles is presented.

Introduction

Polymer toughness, i.e. the ability of a polymer to plastic deformation and resistance to impact load without failure, is the most desired property of a material or product. Polymers are not always tough or brittle; their toughness depends on many parameters including temperature, pressure, load rate, shape of the item under load, type of load (e.g. shear, tension, compression, bending, twisting, tearing, etc), aside from the materials properties: as molecular weight, polydispersity, chain packing, chain entanglements, crystallinity, heterogeneity and several other parameters. Plastic deformation itself is a complex phenomenon and involves both crystalline as well as amorphous phases.

In filled systems only the polymer matrix is able to show a tough behaviour and undergo plastic deformation. The filler particles act as stress concentrators and the interfaces between filler particles and a polymer matrix play a significant role in mechanical response of the filled polymer. Below a short description of the mechanisms of deformation of polymers are presented, followed by the description of the role of interfaces and cavitation in mechanical properties of filled crystalline polymers.

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Main mechanisms of tough response of polymers

There are two main modes of polymer mechanical behavior: brittle, characterized by a linear dependence of load- deformation and ductile, characterized by plastic yielding. Brittle behavior is usually the result of highly concentrated *crazing*. Crazes themselves are highly localized zones of plastic dilatational deformation. Edges of crazes are spanned by highly drawn elongated fibrils called *tufts* usually having the diameter of several nanometers and confined to a small volume of the material. The tufts can carry the load applied to the material and preserve its integrity. In brittle materials crazes are initiated at the surfaces. Brittle fracture is usually caused by microcracks originating from broken crazes initiated at the surface. Localized crazes initiate, propagate and break down to give microcracks at the stress below that which is necessary to activate the shear yielding. Ductile deformation can be caused either by *multiple crazes* or by *shear yielding*. In the first case crazes have to be initiated in a relatively large volume of the material in order to contribute significantly to the overall deformation.

Shear yielding is the plastic flow without crazing. Crazing occurs in materials below glass transition temperature while shear yielding can be observed in a wide range of temperature but only if the critical shear stress for yielding is lower than the stress required to initiate and propagate crazes. Crazing was observed mostly in amorphous polymers although it has been noticed also in crystalline polymers in which crazes propagated through spherulite centers as well as through the material between spherulites [1,2].

Ductile deformation requires adequate flexibility of polymer chain segments in order to ensure plastic flow on the molecular level. If all other factors are equal the material will deform according to the most ductile mechanism.

Both massive crazing and shear yielding dissipate energy, however, shear yielding is often favored over crazing especially under uniaxial stress, elevated temperature or slow deformation. Shear yielding dissipates the energy more efficiently. Switching between crazing and shear yielding is not obvious as it depends also on additional factors such as shape of the article and presence of notches or scratches which produce local stress concentrations.

Many brittle polymer can be toughened by incorporation of rubbery particles. Depending on the character of a polymer, the temperature, the deformation rate and the deformation mode, the toughening occurs either via multiple crazing like in HIPS and ABS or by preferred shear yielding like in polypropylene or polyamide 6 modified with elastomers.

Cavitation

In heterogeneous polymer systems a high negative pressure (tri-axial stress) is quite often generated due to local stress concentrations. The main reason for the stress concentrations is the misfit between mechanical compliances of heterogeneous elements and the surrounding matrix. The excessive negative pressure is the main reason of material cavitation. Cavitation appears to be another mechanism of tough response of the material to loading.

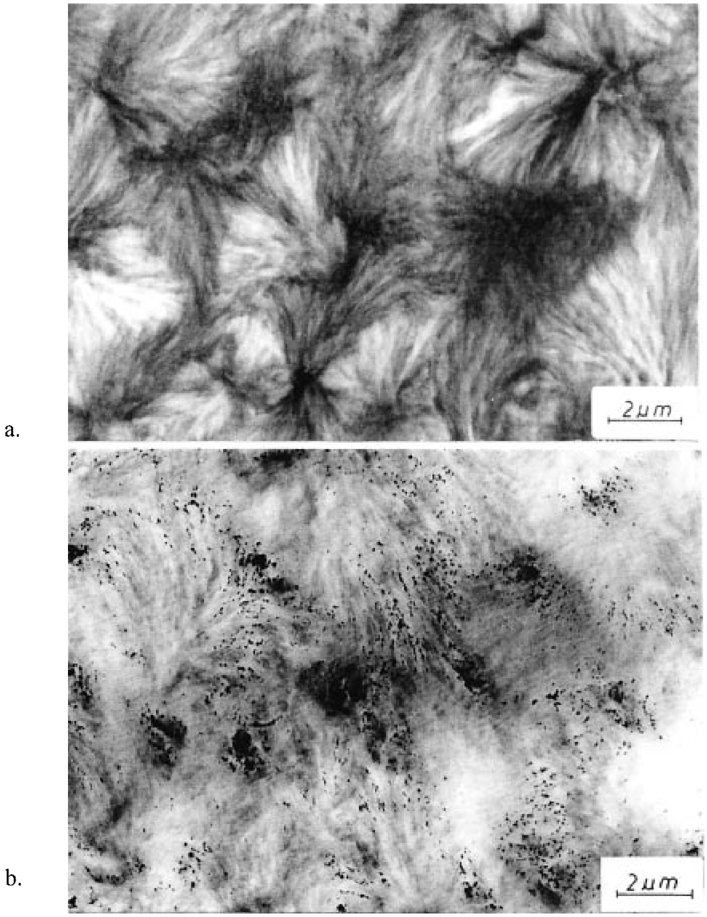

Fig.1 Transmission electron micrograph of ultra thin section of bulk polyamide 6 **a**.undeformed with clear spherulitic pattern and **b**. drawn 100% and then stained with OsO_4. Dark spots are the cavities formed during drawing. The faint spherulitic pattern can still be distinguished.

Although the cavitation dissipates not very large amount of energy, it enables the surrounding material to undergo further intensive crazing or shear yielding. Uncontrolled crazing and cavitation lead to microcracking and failure of the material while shear yielding is the beginning of plastic flow.

In semicrystalline polymers the crystallites act as stress concentrators increasing the stress on the local level much above the applied stress. An intense cavitation on the crystallite size level is observed. One of the sign of cavitation is a sudden polymer whitening near the yielding zone. Cavities formed in polyamide bulk during plastic deformation were visualized by transmission electron microscopy investigation of ultra thin sections by Galeski, Argon and Cohen [3] (see Fig.1). The samples were subjected to plastic deformation and immediately cooled below its glass transition temperature and followed by OsO_4 fixation. The cavities, which were formed, caused chain scission preferentially in places with mechanical mismatch of adjacent stacks of lamellae. In those places OsO_4 was chemically bonded to radicals producing strong contrast. (Formation of radicals during plastic deformation was first demonstrated by Peterlin with electron spin resonance [4].) The OsO_4 stained cavities were found in the form of rods with sizes reflecting the thickness and the width of polyamide lamellae. Cavitation associated with chain scission was found to be a massive phenomenon in the bulk of other types of polyamides

Haudin and Monasse [5] observed by light microscope of thin sections the formation of pores during drawing of polypropylene bulk sample. The pores were of sizes ranging up to few microns and most of them were generated in the yielding zone on both sides of the neck region.

The internal cavitation of the type observed in tension experiments has been referred to as "micro-necking" by Peterlin (see e.g. [6]). Such "micro-necking" had been considered for a long time to be essential for obtaining large-strain deformation of aggregates of chain folded crystals. It had been regarded that "micro-necking" removes kinematical constraints between lamellae and allow them to untangle. In the other papers of Peterlin [e.g.7], in which the micronecking model is defined and developed, cavitation is not consider explicitly. However, from the analysis of the picture of microfibrilar structure formation in crystalline samples as imagined by Peterlin in Refs.6 and 7 it follows that the drawing of crystalline polymers inherently involves cavitation as an essential feature.

Cavity-free deformation

While this picture is reasonable in tensile deformation, it is not correct for modes of deformation in which a compressive component of stress is developed. Compressive stress reduces the negative pressure developing at places of mechanical mismatch caused by heterogeneities and the cavitation is not produced. Such mode of deformation not producing cavitation is for example uniaxial compression or plane strain compression in a channel-die copmpression in which positive normal stress component prevents for the formation of cavities. By a series of such experiments it has been shown that "micro-necking" concept is inessential for understanding high deformation of crystalline polymers. On the other hand, in tensile experiments the associated cavitation obscures and disturbs to some extent the real crystallographic mechanisms of plastic deformation. The plane strain compression is kinematicly very similar to drawing of wide strips, however, the pressure component which arises due to compression prevents for cavitation. The WAXS, SAXS, TEM and light microscopy observations indicated that although some degree of inhomogeneous deformation in the form of localized shear bands occurs, the crystalline and associated amorphous regions of the material undergo a continuous series of shear induced morphological transformations without any cavitational process. The development of nearly perfect single crystal texture for several semicrystalline polymers is observed in high plane strain compression in a channel-die that result from cavity-free plastic deformation[8] .

Among other known methods of plastic deformation the rolling is one of the best ways of producing high preferred orientation. Due to a high pressure component the cavitation is usually not observed. Rolling is an attractive process of plastic deformation since it could be designed as a continuous process. However, for wider strips the force required to roll significantly the material increases sometimes unacceptably high while for narrow strips of polymeric materials there is an additional component of a transverse deformation which causes less sharp texture of the oriented material. The side effect of a transverse deformation is the formation of fissures, cracks and cavitation at edges of a rolled material.

A novel method of obtaining of highly oriented polymeric materials, developed in our laboratory being a combination of channel die and rolling, is by rolling with side constraints [9]. The process relies on rolling of a material inside a channel on the circumference of a roll with another roll having the thickness matching the width of the channel . The side constraints are produced by the side walls of the channel. The other roll plays a role similar to a plunger. The system of rolls with a channel produces conditions for plane strain compression of the rolled material. Plane strain compression is known to produce a single crystal texture (single component or twinned) of compressed materials. The advantage of rolls with side constraints is the possibility of compressing relatively wide, thick and long shapes in a continuous manner in a neck-free manner. The resulting rods or profiles may have considerably high cross-section area (few square centimetres).

Constraints enforce deformation with no or little volume increase:. the cavitation process is strongly inhibited and practically no cavities is formed during plastic deformation of polymeric materials in rolling with side constraints.

The presence of constraints changes completely the process of plastic deformation - different mechanisms are activated. There is no necking and although the yield stress remains at a similar level as in tension, further deformation of the polymer leads to built-up of dramatically higher loads than in tension. This is illustrated in Fig.2 where the true stress-strain curves for iPP (Malen P B200; PKN Orlen, Poland) deformed with constraints in a channel-die and for comparison in tension are plotted.

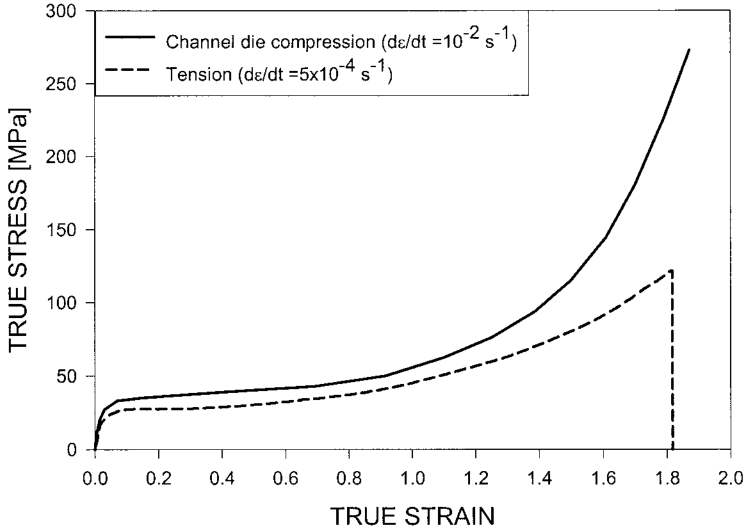

Fig.2 True stress-strain curves for isotactic polypropylene Malen P B200 : **a**. compressed in a chanel die and **b**. strained at the rate of 5 mm/min.

An intense cavitation during drawing of PP without constraints leads to an ultimate strength of merely 120 MPa , Fracture occurs in microfibrils one by one. Moreover, due to the presence of microfibrils the cavitated material has little transverse strength because of loose connection between microfibrils. However, the same material deformed in a channel die in a cavity-free manner responds with the stress of nearly 300 MPa at a similar deformation ratio (see Fig.2). From this experiment it is evident that cavitation reduces significantly the strength of the material and vice versa: high strength materials can be obtained if cavitation is inhibited during deformation process.

Toughness of filled crystalline polymers Several types of inert fillers, often called extenders, are used for polyolefins: chalk (calcium carbonate), talc and kaolin are are frequently used for this purpose. In polyolefins filled with calcium carbonate elastic modulus increases strongly with increasing content of a filler: at 60 wt.% of calcium carbonate in isotactic polypropylene (iPP) the elastic modulus increases 3 times as compared to plain iPP. At the same time the yield stress decreases with increasing content of a filler: at 60 wt.% of calcium carbonate the yield stress decreases 2.5 times [10]. This follows from the fact that extenders do not bear the load in the direction of tensile deformation and debond from the matrix [see e.g.11]. However, the most undesirable effect of introduction of extenders in polyolefins is the loss of toughness [12-16].

In recent years several methods of toughness recovery in filled polyolefins were elaborated [17-22]. A softening of a filler - polymer interface appears to be the best way of recovery of the toughness [e.g.23] The application of a more compliant rubber produces some toughening. The main reason for a tough response of rubber modified polyolefins is cavitation of rubber particles. Cavitation itself does not contribute much to the toughness but it enables the activation of other mechanisms of plastic deformation of the matrix, mainly of crystallographic nature.

An application of a liquid exhibiting excellent wetting properties towards a filler and a polymer is an extreme case [10,12-14,24]. Introductionb of an oligomer of ethylene oxide to interfaces between chalk and iPP results in an increases the strain at fracture from 0.2 for unmodified 60 wt.% chalk composition to 4-5 for liquid modified and Charpy impact strength from 3.1 to 6.4 kJ/m^2, respectively. The application of a proper liquid at interfaces toughens filled polyolefins via several simultaneous and synergistic phenomena [14, 25, 26]:

1. recovery of chain mobility of interfacial layers; the molecular mobility is a crucial factor for yield stress and plastic flow. This is illustrated in Figs.3a-c by dynamic mechanical properties of PP, PP filled with chalk and PP filled with liquid modified chalk. Chalk incorporated in PP produces two additional relaxation peaks denoted as α_1 and α_2 at temperature around 40 and 70°C, both are above its glass transition. Their origin is the friction at interfaces between loosely bonded PP and chalk particles. Lubrication of interfaces with a liquid removes both unwanted DMTA peaks and the drawability of the matrix is recovered.

2. formation of pores at interfaces PP-chalk particles is very easy because of the presence of the liquid which reduces adhesion force to the very low level. The micrograph in Fig.4 illustrates the easy detachment of polypropylene from chalk particles in polar regions leading to rhomboidal shape of cavities. Formation of pores releases the constraints which, in turn, allows for further deformation of PP. Pores contribute also to macroscopic strain of samples; e.g. at 60 wt.% of filling the pores increase the macroscopic strain by 1.5,

3. change in localization of plastic deformation zones; for unmodified compositions the cause of a premature fracture is a strong localization of plastic deformation of polymer around filler particles, while for modified compositions at filling of 40 wt.% a neck propagates gradually on the whole gauge length of the sample and above 40 wt.% the whole gauge length deforms almost uniformly,

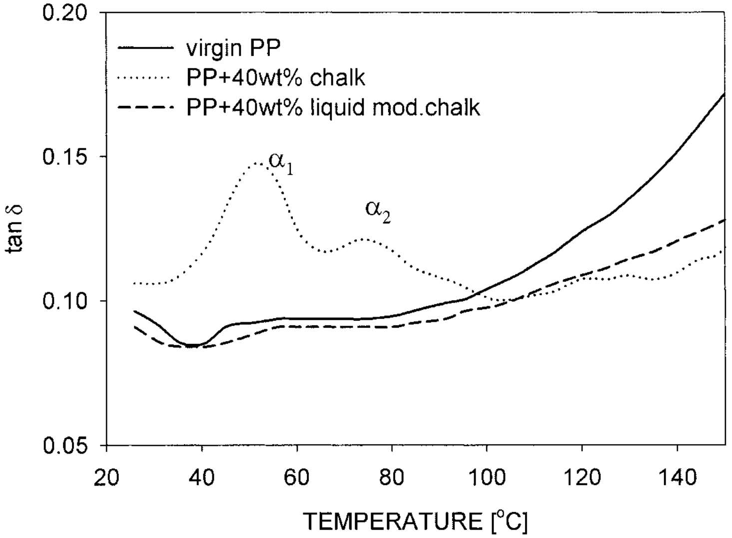

Fig.3 Dynamic mechanical loss tan δ for polypropylene, polypropylene filled with chalk and polypropylene filled with liquid modified chalk.

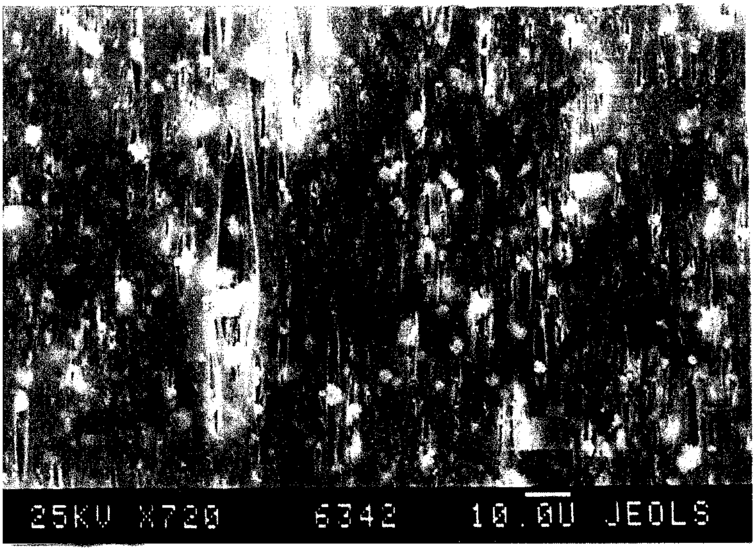

Fig.4 Scanning electron micrograph of drawn isotactic polypropylene film filled with 40wt% liquid modified chalk, drawing ratio 9x, surface for SEM observation exposed by peeling.

4. change in morphology of interfacial layers; application of a liquid modifier greatly reduces the nucleation activity of filler particles towards crystallization of a polymer,

5. fibrillation of pore walls; the reason for fibrillation is the transverse stress which arises because of rigidity of filler particles. The transverse component of stress increases the load bearing in a tensile experiment.

6. reorientation of anisotropic filler particles,

7. better subtraction of the heat produced during plastic deformation due to the presence of a liquid,

8. better physical contact of filler particles and a polymer through a liquid layer making the inner surface of caverns smooth and preventing premature cracks.

Toughened filled polyolefins containing high concentration of a filler, e.g. 40-60 wt.%, can be cold drawn to draw ratio of 5-7 or drawn at elevated temperature to much higher degree of deformation exceeding 20 times of the original length of a sample. Under certain conditions a continuous process of drawing of iPP filled with liquid modified chalk is possible which leads to a technology of a continuous process of film and tape extrusion and drawing. Chalk filled oriented porous straps and strings replace polypropylene in several products, such as woven agricultural bags, carpet bases, strings and ropes.

Toughening of highly filled polypropylene by means of a liquid modifier enables its stretching to a high ratio. Formation of pores during drawing is usual in such systems. Pore sizes and concentration can be controlled by the size of chalk particles and their concentration. Pores are elongated along drawing direction, mostly open and interconnected. The presence of large amount of pores in drawn toughened chalk filled isotactic polypropylene changes drastically its properties as compared to oriented plain polypropylene. High ability for fibrillation observed at high draw ratios adds more features to the characteristics of the material. Oriented toughened chalk filled polypropylene is a new material with interesting properties of high sorption of liquids, softness but simultaneously high modulus and tensile strength along orientation, roughness of surfaces, white color, easy fibrillation and overall similarities to paper or if in a fibrilled form similar to plant fibers. A technology for producing this material is in many ways similar to the production of oriented iPP films and iPP foil fibers.

Rubber toughened polymers Many polymers exhibit mechanical behavior ranging from very tough to brittle. There have been many solutions to restore to tough behavior of brittle polymers. Most of them are based of engineering experience and trials. Some successful and fairly well understood solutions, such as coupling craze plasticity with cavitation of incorporated rubber particles have been considered also effective in crystalline polymers. There are two cases of increasing tough response of the polymer with incorporated rubber particles:

1. The polymer is deformed in tension at the strain rate or at the temperature where the initial strength of unmodified polymer exceeds the stress of brittle fracture. When the mean normal stress exceeds the cavitation strength of the rubber, the rubber inclusions cavitate. Now, the effective stress in the matrix is increased by the factor corresponding to the volume concentration of the rubber. If it is still below the yielding stress the matter is brittle and further embrittlement occurs due to the reduction of brittle strength by the same factor corresponding to the rubber content. The resulting toughening came then from the changes in crack propagation by shielding the crack tip.

2. The polymer is deformed in tension and at certain stress rubber particles cavitate but this time the effective stress exceeds the yield strength. Under these conditions the critical energy for propagating crack increases sharply promoting yield and substantial toughening of the polymer.

Wu [27] has noted that the notch brittleness of nylon 66 is greatly improved by incorporation of fine grafted rubber. However, the improvement of toughness was neither correlated with the size of the inclusions nor with the concentration of rubber. The most relevant parameter was interparticle distance. Rubber toughened Nylon 66 exhibits brittle behavior if the interparticle distance exceeds 0.3 micron, but if this distance is less, it shows a dramatic jump in toughness. This effect that scales with the physical dimension must be a consequence of a specific material characteristics. In fact it is a consequence of the specific morphology of crystallization. Later similar effect was also observe in high density polyethylene and clearly explained [28].

Muratoglu, Argon and Cohen [29] postulated that in blending process the rubber first undergoes phase separation and subsequently nylon crystallizes preferentially with the low energy and low plastic resistance (001) crystallographic planes parallel to the rubber-nylon 66 interfaces. This results in specially oriented crystalline layers of the thickness around 0.15 micron adjacent to rubber particles. At certain concentration of inclusions the layers percolate over the whole material giving rise to a morphology of low plastic resistance. Similar feature was observed and evidenced by careful x-ray and TEM examination.

In the case of polyethylene (100) planes are found to orient parallel to the interfaces and the easiest slip system which sets in is (100)[001] at the low level of 7.2 MPa [30]. Moreover, it was demonstrated that similar, low plastic resistance morphology is obtained for other particles such as calcium carbonate provided their small sizes (0.7 micron). It was also shown in the case of mineral filler $CaCO_3$ that it is not necessary for cavitation to occur inside the particles but equally well effective is the cavitation at interfaces (debonding). One of conclusions drawn was that the compatibilization of the rubber and the polymer matrix with third-party polymers in the blending process is necessary not for direct modification of toughness but for obtaining fine dispersion of the rubber, which in turn influences toughness of the material. Cavitation may occur equally well at interfaces for tough response of the material.

The important point is that the toughening mechanism requires only modest level of adhesion between particles and the polymer. In the case of particles tightly bonded to the matrix the toughening mechanism can still operate as long as the rubber particles cavitate internally. Cavitation of rubber particles ceases below T_g of rubber and consequently the whole system became brittle. This is not the case for $CaCO_3$ particles with weak adhesion to the matrix. Such system retains ductile behavior up to the glass transition temperature of the polymer matrix.

All above observations of unusual toughening were made only for polyethylene and polyamides. Experiments with high filler loading of other polymers were not so successful: isotactic polypropylene showed only a moderate toughening while poly (methylene oxide) only retained its impact strength when loaded with 20vol% of 0.7 μm calcium carbonate [31]. However, it must be noticed that for polymers mentioned above only the crystals of polyethylene and alpha crystals of polyamide show high anisotropy for plastic deformation. Orthorhombic PE crystals have the easiest slip at 7.2 MPa and the others are at 12.2 and 15.6 MPa [32]. For alpha crystals of polyamide 6 the respective shear stresses for crystallographic slips are: 16.2, 23.0 and 23.2 MPa [33]. Crystals of isotactic polypropylene (monoclinic, (100)[001] and (010)[001] chain slips and (010)[100] transverse slip) [34] and poly(methylene oxide) (hexagonal unit cell) have a low difference between critical shear stresses for possible crystallographic slips. The difference or the lack of differences in shear stress for slips results from packing density in planes of possible slips. Usually, the crystal slips easily along the plane and in the direction of most dense packing. If the crystal has low packing anisotropy no preferred slip plane and direction exists. In such cases the mechanism of unusual toughening by the formation of easy slip network has little chance to operate within polymers producing crystals of inadequate anisotropy [35]. It is the reason of low toughening of iPP and poly(methylene oxide) filled with $CaCO_3$.

There is a range of polymers producing crystals with low anisotropy of packing; besides isotactic polypropylene and gamma crystals of polyamide 6 there are poly(tetrafluoroethylene) poly(propylene oxide) and many others. However, most interesting are polymers with crystals of high packing anisotropy: syndiotactic polypropylene, syndiotactic polystyrene (β form), poly(tetrahydrofurane), poly(oxybutylene), poly(vinyliden fluoride), poly(vinyl fluoride) and poly(vinyl alcohol) are among them.

In order to verify the concept of high crystal anisotropy as being necessary for the formation of an easy slip network we have used syndiotactic polypropylene (Fina, MFI=1 g/10min, having, however, a moderate tendency to crystallize at the level of 20-25% because of not very high syndiotacticity) which we filled with 17vol% of $CaCO_3$ having mean particle size diameter of 0.7 μm [35]. The Izod notched impact strength has increased from 10.1kJ/m^2 to average 33kJ/m^2. The fracture surface for unfilled sPP showed brittle behavior with plastic deformation only at the close vicinity of the notch while fracture of filled sPP was ductile. This is illustrated by SEM micrographs of fracture surfaces in Figs.5a-b. Also the stress-strain behavior suggests the formation of easy slip network: the yield stress is significantly reduced and the yielding occurs at 6-7% of elongation instead of 18-20% as it is for unfilled sPP.

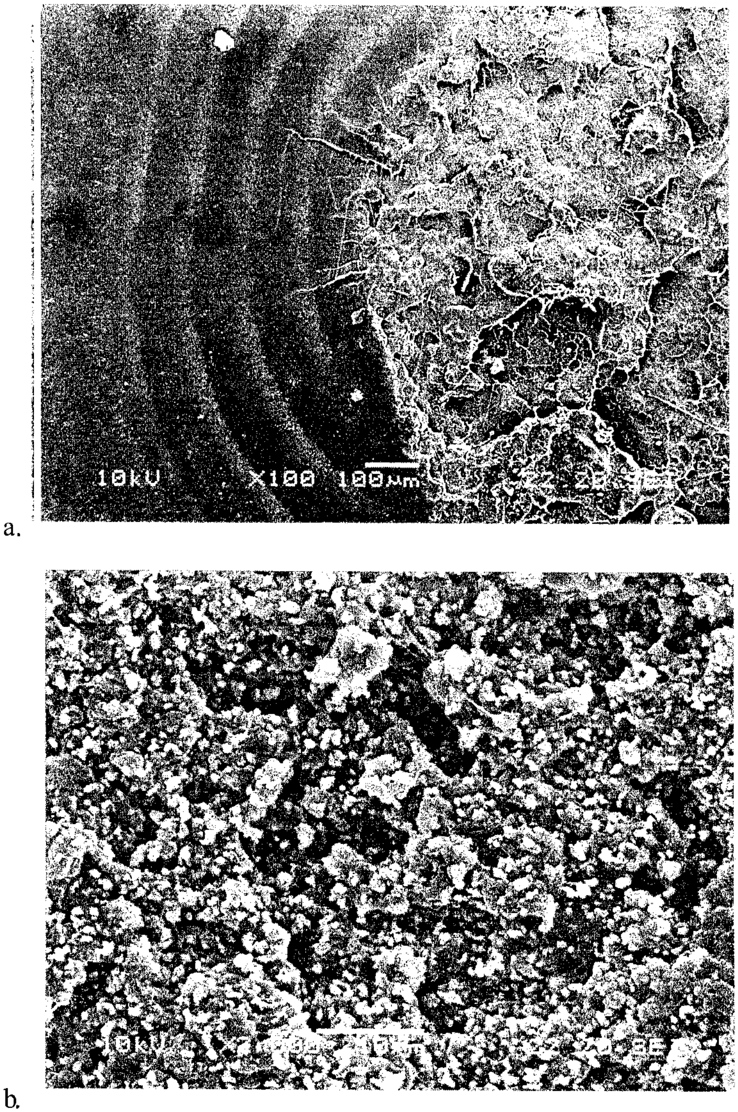

Fig.5 Scanning electron micrographs of fracture surfaces of notched Izod samples of a. syndiotactic PP, b. syndiotactic PP filled with 17vol% of 0.7µm chalk particles. Ultrasound was applied during compounding in order to obtain a better dispersion of chalk particles.

Rubber toughened filled polymers In most rubber toughened systems, apart from the network of low plastic resistance resulting from percolation of crystals oriented parallel with planes of lowest yield stress, further increase of toughness is attained by incorporating fine filler particles. Provided that some of filler particles prefer the rubber surrounding, they stimulate easier and earlier cavitation of the rubber. Resulting toughening ranges to lower temperature than for systems without filler and the impact strength reaches higher values. The success in blending depends on the material design: filler particles should be small enough as compared to rubber inclusions and their surface properties should motivate them to migrate toward rubber particles rather than stay in a polymer matrix during blending process. In Table I the properties of two such compositions based on polypropylene are listed [36].

Table I

Composition	Melt flow index [g/10min]	Izod impact strength at –30°C [kJ/m$^{2]}$	Elongation at break [%]	Yield stress [MPa]
PP+30% rubbers +5% talc	12.0	6.7	400	16.7
PP+30% rubbers +5%talc	8.0	8.0	350	17.4

It is worth to note that the high melt flow indices were achieved and simultaneously high ultimate draw ratio above 300% and high Izod impact strength above 6 kJ/m^2 at the temperature of -30°C were observed. In order to stimulate more the cavitation of rubbery inclusions, a mixture of two miscible elastomers were applied in these two polypropylene compositions. By incorporation of fine talc particles of a special type and application of a rubber blend the negative pressure necessary for cavitation of rubber particles was extremely reduced, which resulted in a very tough response of the material.

Conclusion

The toughening in most of polymer systems relies on the main mechanisms of promotion of energy dissipative processes that delay or entirely suppress fracture processes originating from imperfection of internal structure or scratches and notches. The advantage of occurrence of cavitation on loading is that it is the energy dissipative processes: crazing and shear yielding occur at reduced stress level. In crystalline polymer systems the tough response, besides cavitation and crazing, is crystallographic in nature. Crystallographic slips are the main plastic deformation mechanisms. These are controlled by generation and propagation of mobile crystallographic dislocations. Another toughening phenomenon in crystalline polymers is based on the idea of percolation of low plastic resistance material around filler inclusions.

In almost all cases cavitation either makes possible further toughening by activating other mechanisms or contributes itself to the plastic response of the polymer.

High polymer crystal anisotropy is necessary for the formation of a network of easy crystallographic slips in the unusual toughening of highly filled polymers observed recently for polyethylene and polyamides.

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