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SURVEY OF RELATIONS OF CHEMICAL CONSTITUENTS IN POLYMER-BASED MATERIALS WITH BRITTLINESS AND ITS ASSOCIATED PROPERTIES

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Abstract. The property of brittleness for polymers and polymer-based materials (PBMs) is an important factor in determining the potential uses of a material. Brittleness of polymers may also impact the ease and modes of polymer processing, thereby affecting economy of production. Brittleness of PBMs can be correlated with certain other properties and features of polymers; to name a few, connections to free volume, impact strength, and scratch recovery have been explored. A common thread among all such properties is their relationship to chemical composition and morphology. Through a survey of existing literature on polymer brittleness specifically combined with relevant reports that connect additional materials and properties to that of brittleness, it is possible to identify chemical features of PBMs that are connected with observable brittle behavior. Relations so identified between chemical composition and structure of PBMs and brittleness are described herein, advancing knowledge and improving the capacity to design new and to choose among existing polymers in order to obtain materials with particular property profiles.

Keywords: brittleness, scratch recovery, tensile toughness, impact strength, free volume.

1. Brittleness of Polymers

Brittleness, according to the general impression of the meaning of that term, has been observed in all types of polymer containing materials including bulk polymers, polymer composites, and polymer thin films and coatings. It is important to consider brittleness—even early on during the design process of new polymeric materials – as it can limit mechanical performance and be affected by

environmental conditions such as time, temperature, and humidity. Knowing the brittleness of a material can also help guide one in selection of materials.

The property of brittleness, denoted B , has been defined quantitatively in terms of other easily obtained mechanical properties [1]; the expression is:

$$B = \frac{1}{\epsilon_b \cdot E'} \quad (1)$$

where ϵ_b is the elongation at break determined from quasi-static tensile testing and E' is the storage modulus determined from dynamic mechanical analysis (DMA) at 1.0 Hz. Therefore, brittleness reflects a parameter that takes into account a large deformation of a material as well as a parameter that accounts for repetitive loading or fatigue.

We shall discuss connections of brittleness to free volume and molecular structures in Section 2, to tribological properties in Section 3, to mechanical properties of pure polymers in Section 4, then aging in Section 5, polymer blends in Section 6 and composites in Section 7.

2. Brittleness, Free Volume and Molecular Structures

From the inception of this quantitative description of brittleness, it was recognized that the structure of materials must also be connected with observed trends in brittleness. This has been demonstrated to some degree by experimentation that indicates a relation between free volume, viscoelasticity, and brittleness [1]. Free volume v^f

is defined in terms of the total specific volume v and the incompressible (hard core) volume v^* as follows [2]:

$$v^f = v - v^* \quad (2)$$

To calculate v^f from Eq. (2), we need to obtain v^* . One can imagine the hard core volume as the volume at 0 K after 'squeezing out' all empty spaces between molecules. To calculate v^* one obtains experimental values of specific volume v as a function of temperature T , in some cases also as a function of pressure P . One then uses an equation of state; we have been consistently using with good results the Hartman equation [3]:

$$P^{\sim} v^{\sim 5} = T^{\sim 3/2} - \ln v^{\sim} \quad (3)$$

$$v^{\sim} = v/v^*; T^{\sim} = T/T^*; P^{\sim} = PP^* \quad (4)$$

The idea of using reduced quantities can be seen in the Doctor of Science thesis of Johannes D. van der Waals already in 1873 [4]. Given a set of, say, N data in the $v(T, P)$ or $v(T)$ form, one solves an over-determined set of N equations of the form of our Eq. (3) for either three unknowns, v^* , T^* and P^* , or else in two unknowns, v^* and T^* .

In the following Section we shall consider sliding wear determination, which in fact led us to the definition Eq. (1) as well as connections of sliding wear results to free volume.

3. Tribological Properties and Brittleness

We shall now discuss tribological properties of polymers, beginning with sliding wear determination, before connecting those properties to brittleness.

Among tribological tests, which deal with contacts between moving interfaces, scratch testing provides valuable information about scratch resistance, wear, and viscoelasticity of polymeric materials. On a micro scratch tester equipped with a diamond (or other) indenter, one

can measure instantaneously the penetration depth R_p of the indenter as it scratches a specimen surface. In viscoelastic polymer-based materials (PBMs), some healing or recovery in the scratch groove typically takes place; this also can be measured and is recorded as the residual depth R_h . The percentage of viscoelastic recovery, f , is calculated from the equation defined in [5], namely:

$$f = \frac{R_p - R_h}{R_p} \cdot 100\% \quad (5)$$

To determine wear of a material, multiple scratches along the same groove can be imposed, all the while measuring both R_p and R_h for each pass of the indenter. Such multiple scratch tests are also referred to as sliding wear tests. Eq. (3) applies to multiple as well as to single scratch tests; thus the recovery f for, say, the 15th pass can be calculated and, used to compare different materials. An interesting phenomenon, referred to as strain hardening, has been observed for some polymers during sliding wear testing [6]. What occurs is that after about 10 scratches (the number is dependent on the force applied) the residual depth no longer increases but stays the same with each subsequent scratch along the groove. This strain hardening has been observed in a polyester (Fig. 1), polypropylene, TeflonTM, polycarbonate (Fig. 2) and polyethersulfone among others [1, 6, 7].

Actually, to date, polystyrene (PS) has been the only polymer or polymer composite tested that does not plainly exhibit strain hardening in sliding wear (Fig. 3). This is even more interesting when one considers the relation between free volume and viscoelastic recovery in sliding wear.

It has been shown for a set of six common engineering plastics – representing different classes of polymers – that the percentage recovery f increases linearly with the free volume for all the polymers except polystyrene [1]; see Fig. 4.

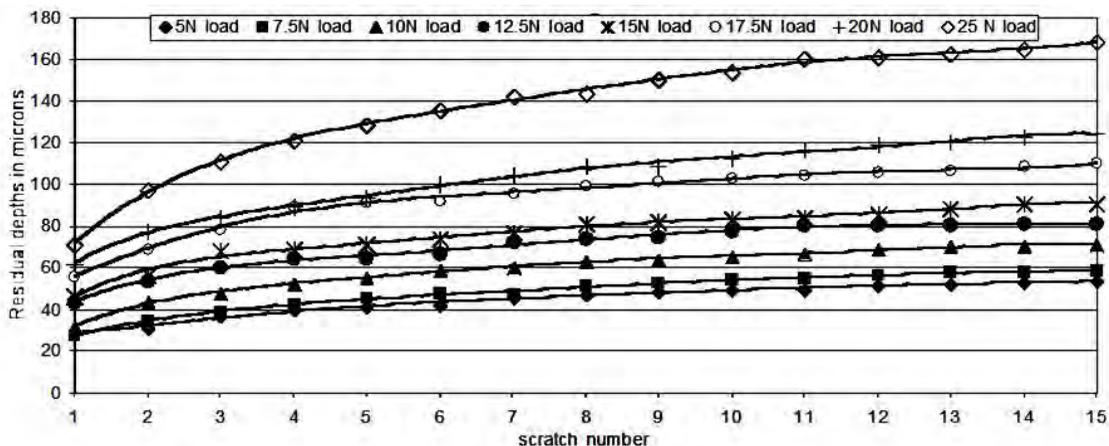


Fig. 1. Residual depth in sliding wear testing of a LB-18 polyester; from [6]

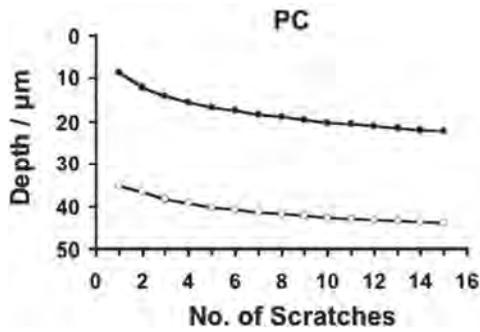


Fig. 2. Penetration depth (the curve with empty circles) and residual depth (the curve with filled circles) for polycarbonate; from [1]

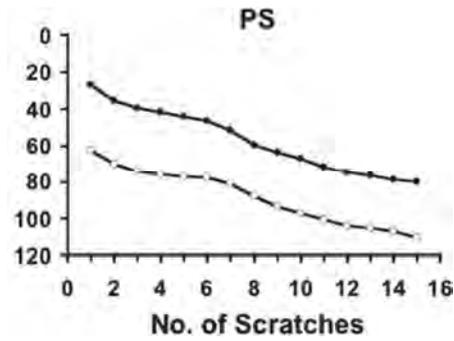


Fig. 3. Penetration depth (the curve with empty circles) and residual depth (the curve with filled circles) for polystyrene; from [1]

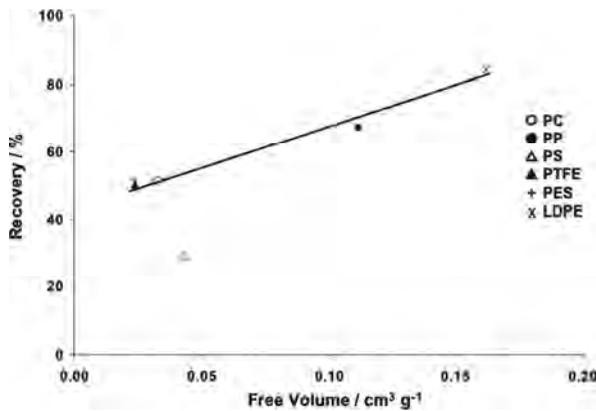


Fig. 4. Percentage recovery as defined by Eq. (3) vs. free volume; from [1]. Excluding polystyrene, $R^2 = 0.9779$ while $R^2 = 1$ pertains to a perfect fit

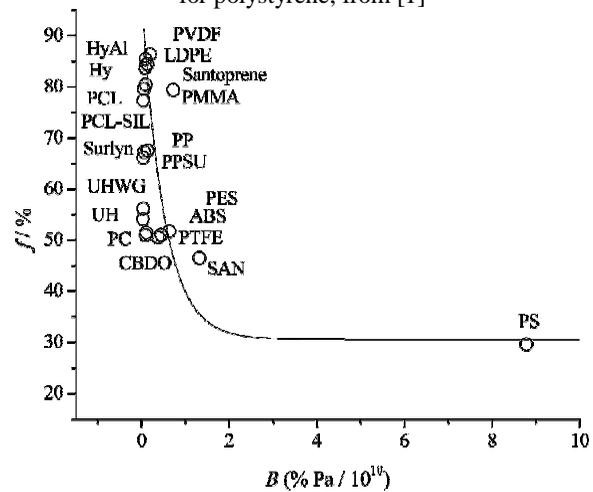


Fig. 5. Viscoelastic recovery f as a function of brittleness; from [6]. HyAl = Hytel (a synthetic elastomer) + aluminum; PCL-Sil = polycaprolactone + silica

PS is also notorious for its brittleness. Therefore, it is not surprising that there is a definite relation between B and f that has been shown to hold for as many as 20 different polymer-based materials [1, 7, 8]. That connection is in the form of exponential decay such that recovery decreases with increasing brittleness (Fig. 5). Notably, the comparison by Eq. (1) of brittleness for a wide range of polymer types having different chemical structures and components is not dependent upon their exhibiting the same type of fracture. The values of ϵ_b and E' do not have to be obtained within a specific temperature for either ductile or brittle fracture; rather the parameters can be measured for all the materials under the same conditions.

The curve shown in Fig. 5 corresponds to Eq. (6):

$$f = 30.6 + 67.1e^{-B/0.505} \quad (6)$$

Fig. 5 and Eq. (6) confirm the basic tenet of Materials Science and Engineering [9]: *all macroscopic properties are determined by structures and interactions at the atomic and molecular level.* Apparently it is on this basis that f , a tribological property, can be calculated from B , a mechanical property.

Chemical and spatial structures of materials affect their brittleness. Let us return now to Fig. 4 and the abnormal behavior of polystyrene seen there. The structure of PS includes a phenyl ring; the double bonds in that ring cause its rigidity. Moreover, polystyrene molecules can form stacks – also because of those rings. Stacking results in low values of free volume. Thus, we record two factors causing brittleness: *rigidity* and *low v^f* . We shall briefly return to tribology discussing multiphase polymer-based systems in Section 7.

4. Mechanical Properties and Brittleness

We now move on to mechanical properties of neat polymers. Possibly the most important is fracture. Wonderful thermophysical, tribological, electrical or other properties will not help if a given material undergoes fracture easily. When one speaks of fracture, it is natural to think of impact strength. A material's resistance to impact is usually measured in terms of the breaking energy per unit area (or thickness). The expectation that materials with the least brittleness will have the highest impact strength is borne out in defined relations between both Charpy and Izod impact strength and B [8]. For a number of polymers with a variety of chemical structures, the Charpy impact strength U_C is:

$$U_c = a_c + \frac{1}{\tanh(b_c B)} \quad (7)$$

where $a_c = 0.640$ and $b_c = 1.63$. This is represented in Fig. 6.

An equation of the same form defines the relation between the Izod impact strength U_I and brittleness of polymers, also with good results:

$$U_I = a_I + \frac{1}{\tanh(b_I B)} \quad (8)$$

where $a_I = 0.660$ and $b_I = 2.29$.

Toughness is another important and related property, although clouded by the fact that there multiple methods used for its determination. However, for the present purpose, the definition with parameters obtained from tensile testing serves well. Accordingly, toughness τ is expressed as the area under the curve of engineering stress σ vs. engineering strain ε [9, 10], namely:

$$t = \int_0^{\varepsilon_b} \sigma d\varepsilon \quad (9)$$

Toughness is thought of as the energy required to crack a material. Since many chemical modifications to

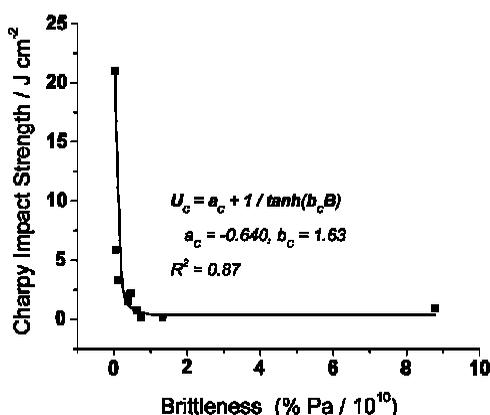


Fig. 6. Charpy impact strength as a function of brittleness for polymers. The continuous line is calculated from Eq. (7)

polymers are applied in order to increase toughness, a connection between τ and B is significant [11]; it is shown graphically in Fig. 7. The respective equation is:

$$t = \frac{b_t + c_t B}{1 + a_t B} \quad (10)$$

where $a_t = -111$; $b_t = -1.41 \cdot 10^4$ and $c_t = -1640$.

We have seen in Fig. 5 that polystyrene has a value of B above 8 in the units chosen. Actually, PS fits in the same diagram, but we show here the central part of the diagram to avoid 'crowding' of points. Aluminum also fits in the same diagram, but it has a value of B even lower than steel and polycaprolactone. Thus, while our aim was to obtain a 'universal' relationship for polymers, *apparently the use of that relationship is even wider.*

There is an opinion still appearing in some quarters that "brittleness is the inverse of toughness"; possibly that opinion was formulated before Eq. (1) was. Eq. (10) and its experimental verification in Fig. 7 tell us that there is indeed a connection, but not that simple.

5. Aging

We know that properties of glassy materials change with time as a result of *aging*; see for instance Chapter 5 in [9]. Since there are no fully crystalline polymers, all molten polymers on cooling go through the glass transition region, sometimes as wide as 20 K [12]. Below that region there is a slow process of densification, precisely aging, changing mechanical, tribological and other properties of the polymers and of polymer-based materials.

We consider here one example only. For Hypalon, a synthetic elastomer made from chlorinated and fluorinated polyethylene, aging causes a decrease of e_b faster than the simultaneous increase of E' [13]. Thus, brittleness of Hypalon increases with aging time.

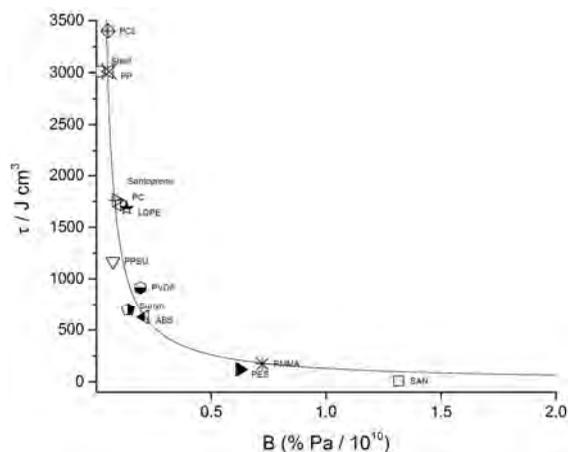


Fig. 7. Tensile toughness as a function of brittleness for a large variety of polymers plus steel. Continuous line calculated from Eq. (10)

6. Polymer Blends

We need to discuss at least briefly also polymer blends – called sometimes polymer alloys. Dorigato and his colleagues [14] created blends of linear low-density polyethylene (LLDPE) with a cycloolefin copolymer (COC). COC is rigid, hence it has a low elongation at break e_b . Addition of COC to LLDPE causes an increase of the tensile modulus – a desired effect. However, the decrease of e_b upon gradual addition of COC is *faster* than the increase of E . Consequently, brittleness increases along with addition of COC.

7. Polymer-Based Materials

Polymer-based materials are often multiphase composites. Thus, Chen and coworkers [15] have created 64 layer composites of propylene-ethylene copolymer (PPE) with ethylene 1-octene copolymer (POE). The composites were prepared by a microlayered coextrusion system. Increasing the concentration of elastomeric POE had a very small effect on the elongation at break e_b , while the dynamic storage modulus decreased. Thus, B went up – while original expectation was that more elastomer should bring B down. The Sichuan group, however, found an explanation: the B increase is a consequence of poorer adhesion between layers at higher POE contents. Thus, *adhesion between phases* has to be added to our list of factors affecting brittleness if there is more than one phase. We find that in multiphase materials B has one more role: it *reflects structural integrity of multiphase composites*.

Pedrazzoli and his colleagues [16] reinforced polypropylene (PP) with two kinds of silica nanoparticles, untreated and treated. Addition of these particles enhances the tensile modulus E , but the enhancement is complicated at higher filler concentrations by aggregation of the silica particles, particularly so for untreated ones. Gradual insertion of treated silica nanoparticles eventually leads to a plateau of E . The glass transition temperature, T_g , used to characterize the glass transition region, increases with addition of both kinds of nanoparticles, particularly so for treated ones. Tensile elongation at break e_b goes down, so that brittleness increases [16]. This is not unexpected – given the increase of T_g with addition of the nanoparticles. Pedrazzoli and his colleagues relate the increase in B to a change in polymer/filler interfacial interactions.

PP plus ethylene-propylene-diene (EPDM) rubber form a thermoplastic vulcanizate (TPV). 5 wt % of a thermal shock resistant ceramic (which ‘survives’ temperatures up to 1673 K) were added to the TVP [17]. TVP plus ceramic had higher B than TVP alone. However, when the filler was modified by three different kinds of organic molecules, all modifications had lower B than TPV. The lowest value of B was achieved for a coupling agent called Lica12; that agent not only improved the adhesion

between the TVP matrix and the filler but apparently also acted upon TVP similarly to a plasticizer.

Carbon nanotubes (CNTs) are used increasingly as a filler. Anna Szymczyk and her colleagues [18] functionalized multiwall CNTs (MWCNTs) and put them in poly(trimethylene terephthalate) (PTT). Glass transition and melting temperatures were not significantly affected by CNTs addition. However, all composites have lower B values than PTT. The diagram of B as a function of the filler composition exhibits a minimum at 0.3 wt % MWCNTs.

CNTs were also applied to a block copolymer of semicrystalline poly(butyl terephthalate) (PBT) with amorphous oxytetramethylene (PTMO), namely both single wall CNTs (SWCNTs) and MWCNTs [19]. For both SW and MW nanotubes, tensile modulus and strain at break e_b as a function of CNTs concentration (c_{CNT}) show maxima. This is explained by competition between two effects: reinforcement provided by the nanotubes and weakening of internal cohesion of the matrix. Elongation at break is enhanced by the nanotubes; this plasticizing effect is much stronger for SWCNTs. By contrast and as expected, MWCNTs provide more reinforcement. Sliding wear determination was also performed and the results fit the curve shown by us in Fig. 5.

Diagrams of B vs. c_{CNT} show minima [19], a reflection of the maxima of e_b and similar to the results of Szymczyk and her colleagues [18]. Volumetric wear was determined after abrasion on a pin-on-disk tribometer [19]. Minima are seen on the volumetric wear vs. c_{CNT} diagrams, *similar to those on the B vs. c_{CNT} diagrams*. Remembering our discussion of Fig. 5, we see here a *second* connection between B and a tribological property.

Along somewhat similar lines, Carrion and coauthors tested the effects of adding ionic-liquid-modified SWCNTs in PS, polymethylmethacrylate, and polycarbonate [20]. With respect to PS, as we know the most brittle of the three, they found that a reduction in wear rate up to 74 % could be achieved. This is largely attributed to “dispersion of the nanotubes in the polymer matrix, which increases their resistance to crack propagation and fracture, and to the surface modification of the nanotubes by the ionic liquid, which improves the lubricating ability of the additive” [20].

In agreement with the above results, Kopczynska and Ehrenstein [21] discuss the importance of polymer surfaces and interfaces for macroscopic properties. Keten and coworkers [22] report results of molecular dynamics computer simulations of b -sheet crystals in silk. There is a paradox here, namely silk has unusually high both e_b and E , while the dominant intermolecular interactions in these nanocrystals are hydrogen bonds which in spite of their name are not chemical bonds at all [9]. Nanocrystals with the sizes of a few nm are stronger than larger ones.

The simulations show the presence of *nanoconfinement* such that dissipative molecular stick slip

deformation mechanism makes an outstanding use of the hydrogen bonds for mechanical reinforcement.

8. General Discussion

By exploring relations between brittleness, tribology, free volume, mechanical properties, and polymer composition, we see how we can draw out much additional useful data that can inform our design and use of polymers. There is an increasing interest in 'green' polymers, obtainable from natural materials. Along these lines, Pourjavaheri and coworkers [23] derived keratin from chicken feathers. They argued that "Millions of tons of feathers are produced worldwide annually as a by-product of poultry-processing plants". They used chicken feather fibers (CFFs) to enhance thermo-mechanical properties of thermoplastic polyurethane (TPU) biocomposites. The storage modulus E' at 298 K has increased dramatically; for pure TPU is $E' = 0.1$ GPa, for 10 wt % CFFs is $E' = 1.0$ GPa while for 20 wt % CFFs the respective values is 1.6 GPa. While strain at break decreases with increasing CFF concentration, the increase of the storage modulus is faster. Thus, Pourjavaheri and colleagues [23] conclude that addition of CFFs lowers brittleness. Along our lines in this article, those authors state that addition of CFFs also increases free volume because of keratin functional groups – a fact reflected in some lowering of the glass transition temperature.

Speaking of connections between different properties, it might be worth noting that free volume is also the basis correspondence principles enabling prediction of long term behavior of polymers from short term tests [24].

Nature shows us in various ways it is capability to create materials structures with outstanding properties. Bouville and his colleagues [25] have created a ceramic composite from mineral constituents only, with outstanding mechanical properties up to 873 K, declaring that natural materials were their inspiration. Important for us is their statement that properties are determined by a *combination of mechanisms operating at different length scales*. An example of this is provided by a study of addition of Ni nanopowder to a thermoplastic elastomer [26]. Introduction of the nanopowder results in an increase of B ; the powder lowers the internal cohesion in the polymer. Crosslinking of the elastomer lowers e_b and thus also increases B . However, when both Ni powder is added and crosslinking performed, B decreases [26]. Apparently, metal nanoparticles go either into existing free volume pockets in the elastomer or else create new such pockets. Filling such pockets by Ni particles causes an enhancement of mechanical properties including E' . Creation of new free volume pockets increases e_b , thus also lowering B . Returning now to our Eq. (1), we infer that maneuverability of e_b can be achieved differently than that of E' .

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ДОСЛІДЖЕННЯ ВЗАЄМОЗВ'ЯЗКУ МІЖ ХІМІЧНИМИ КОМПОНЕНТАМИ НА ОСНОВІ ПОЛІМЕРНИХ МАТЕРІАЛІВ І КРИХКОСТІ ТА ПОВ'ЯЗАНИМИ З НЕЮ ВЛАСТИВОСТЯМИ

Анотація. Крихкість для полімерів і матеріалів на основі полімерів (МОП) є важливою властивістю при визначенні можливості використання матеріалу. Крихкість полімерів може також впливати на легкість і режим оброблення полімеру, впливаючи тим самим на економіку виробництва. Крім цього, крихкість МОП може бути пов'язана з деякими іншими властивостями полімерів. Встановлено взаємозв'язок між крихкістю і вільним об'ємом, ударною міцністю та стійкістю до подрятин. Загальним для таких властивостей є їх зв'язок з хімічним складом та морфологією. Зроблено аналіз відомих даних літератури відносно крихкості полімерів та щодо зв'язку між нею та хімічним складом й структурою МОП з метою створення матеріалів із заданими властивостями.

Ключові слова: крихкість, стійкість до подрятин, міцність на розривання, ударна в'язкість, вільний об'єм.