STRUCTURE-MICROHARDNESS CORRELATION OF POLYMERS AND BLENDS

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Abstract

Recent results concerning the microhardness (H) of polymers and blends relating to their structure are reviewed. The basic aspects of the microindentation mechanism are first introduced and the correlation between the microhardness and yield stress is highlighted. The hardness of polymer glasses is discussed and the relationship between H and the glass transition temperature is brought in. The development of structure during isothermal crystallization of glassy polymers as revealed by microhardness is highlighted and some examples are provided showing the capability of thermal H-analysis in providing evidence about physical transitions near T_g . Microhardness is shown to be capable of detecting polymorphic changes in polymers. The dependence of H on structural parameters, such as degree of crystallinity and lamellar thickness, is discussed and models to predict hardness of lamellar crystals are also reviewed. Finally, some applications to polymer blends are illustrated.

1. Introduction

The indentation test is one of the simplest ways to measure mechanical properties of a material. The micromechanical behaviour of polymers and the correlation with morphology and microstructure have been widely investigated over the past two decades [1,2]. Conventional microindentation instruments are based on the optical measurement of the residual impression produced by a sharp indenter penetrating the specimen surface under a given load at a known rate. Microhardness is obtained by dividing the peak load by the contact area of impression. While hardness defined in this way, is an indicator of the reversible plastic deformation processes, information about elastic release of the

indentation depth is mostly lost. The need to characterize the surface of very thin films and near surfaces has led to the development of ultra- and nano-indentation testers [3,4,5]. Continuous load-displacement monitoring, as the indenter is driven into and withdrawn from the film, substitutes the imaging method used in conventional microindenters. Smaller loads can be applied leading to indentation depths within the sub-micron scale. The compliance method opens up the possibility of investigating the mechanical properties of polymers at the near surface [6,7,8]. In addition, the elastic recovery of the indentation upon load removal can be studied.

This lecture attempts to summarize some of the relevant issues concerning the microhardness studies of polymers that are of interest because they might lead to further development in the subject. It also intends to provide some examples showing how successful the microhardness technique is in providing direct evidence about structure changes in polymers and blends.

2. Basic aspects of indentation

Fig.1 shows schematically the contact geometry for a pyramid indenter. This is the most common geometry in indentation tests because of the geometrical similarity of the residual impressions. The contact pressure is independent of indent size, and thus affords a convenient measure of the hardness [9]. It has been shown that indentation causes a change in the surface level of the specimen near the indenter [9,10]. According to Marsh [11], the material under the indenter consists of a zone of plastic deformation (a few times the penetration distance h) surrounded by a larger outer zone of elastic deformation. The strain boundaries below the indenter for plastic deformation have been shown to depend on the morphology of the polymer material (crystal size and perfection, degree of crystallinity, etc) [1]. Typical loads of 50 mN, using a square based diamond (Vickers) of $\sim 200\ \mu\text{m}$ in height, when applied onto the surface of a conventional polymer like PET, produce penetration depths, h , of about $1\text{--}4\ \mu\text{m}$ (see Fig.2, ref. 12). With this technique we, thus, can plastically deform stacks of a few hundreds of crystals [13]. In other words, we probe the surface of the polymer sample "quasi" non-destructively within a small volume element.

During an indentation cycle the following effects can be distinguished: a) An elastic recovery of the material beneath the indentation upon removal of the load [14]. However, the elastic recovery of the diagonal of the impression appears to be negligible [14]. b) A permanent plastic deformation (measure of hardness) [1]. c) A time dependent contribution during loading (creep) [15]. d) A long delayed recovery of indentation after load removal (viscoelastic relaxation) [14]. Since elastic effects are negligible, hardness is measured at

Figure 1. Contact geometry for a pyramid indenter at zero load (left), maximum load (center) and complete unload (right). The residual penetration depth after load removal is given by h_{residual}

Figure 2. Stress distribution (MPa) in amorphous PET at an indentation depth $h = 2$ μm. c : depth of plastic zone. Stresses larger than 78 MPa are elastic. [12]

very short loading times (few seconds) to minimize creep; immediately after the load is removed (to minimize viscoelastic relaxation).

3. Correlation of Microhardness to Macroscopic Mechanical Properties

From a macroscopic point of view, hardness is directly correlated to the yield stress σ_y of the material, *i.e.* the minimum stress at which permanent strain is produced when the stress is subsequently removed [16]. In many cases, such as a tensile test, yield coincides with the observation of a maximum load in the load-elongation curve. It is noteworthy that for low hardening materials the yield stress and the flow stress are close. According to Tabor [17] a stress analysis of the region under the indenter shows that almost 2/3 of the mean pressure is in the form of a hydrostatic component and, hence, plays no part in producing plastic flow. Thus, as a first approximation, the hardness, which is the equivalent of the average pressure under the indenter, is directly correlated to σ_y in compression, through the expression

$$H \approx 3\sigma_y \quad (1)$$

Equation 1 is well substantiated for amorphous and semicrystalline unoriented polymers when creep is minimized and when σ_y is the yield stress in tension [1]. However, when σ_y is measured in compression, $H/\sigma_y \sim 2$, because σ_y in compression is larger than σ_y in tension. This difference has been ascribed to the effect of the hydrostatic component of compressive stress on polymers [18]. Darlix et al [19] have developed a method based on Marsh's indentation model to derive σ_y and the elastic modulus of polymers from H measurements.

4. Hardness calculations

Hardness is intimately related to the critical stress required to plastically deform the polymer crystal. The applied compressive force, thus, has to separate adjacent molecules and, consequently, has to overcome the cohesive forces between said molecules. When the value of the intermolecular force reaches a critical value (critical stress), an irreversible separation of the molecules is produced. The intermolecular force is equal to the derivative of the interaction energy with respect to the separation distance between molecules. Hence, one may attempt to derive the ideal shear stress S_0 of the Van der Waals solid normal to the chain axis from the value of the lateral surface free energy, σ , of the polymer crystal [1]. If one assumes that a displacement between adjacent chain molecules by δl is sufficient for lattice destruction, then, the ultimate stress per chain will be given by $S_0 = \sigma/\delta l$.

Table 1 shows the so obtained values for various polymers. In practice, the polymer material is far from perfect and contains a combination of disordered (amorphous) and crystalline phases which may account for deviations between experimental and calculated values [1].

TABLE 1. Comparison of calculated ultimate shear stress S_0 and typical microhardness values for various polymers

Polymer	σ (erg/cm ²)	$S_0 = \sigma/\delta l$ MPa	H MPa
Polyethylene	17.3	170	50-125
Nylon 6,6	16.1	158	80-120
Nylon 6	11.6	113	90
Poly(methylene oxide)	16.2	159	170
Polypropylene (α -phase)	14.6	143	111
i-Polystyrene	9.6	94	129-170
Poly(ethylene oxide)	9.5	93	70
Trans- 1-4 polyisoprene	8.9	87	--

5. Microhardness of Polymer Glasses

In the glassy state the critical stress required to plastically deform the amorphous solid (microhardness) involves displacements of bundles of chain segments against the local restraints of secondary bond forces and internal rotations [20]. Yield mechanisms in glassy polymers have been reviewed by Crist [21]. The intrinsic stiffness of these rigid polymers below T_g leads to microhardness values which may even be 2-3 times larger than those obtained for typical flexible polymers. At the glass transition the onset of liquid like motions, involving longer segments, takes place. These motions of larger bundles, above T_g , require more free volume and lead to a fast decrease of microhardness with temperature. The dependence of microhardness on T_g for some amorphous glassy polymers is presented in Fig. 3 [22]. One can see the fairly good relationship existing between H and T_g , in the interval between 300 and 500 K, which can be expressed as:

$$H = k T_g + C \quad (2)$$

where $C = -548$ MPa and $k = 1.88$ MPa/K. The C-value is physically meaningless. It only reflects that polymers characterized by T_g -values below room

temperature do not have a measurable microhardness at room temperature. To measure H in these systems one has to decrease the temperature below T_g .

TABLE 2. Glass transition temperature T_g and microhardness H of the polymers used in the plot of Fig. 3 [ref. 22]

Polymer	T_g (°C)	H(MPa)
Nylon 6	40	52
Poly(butylene terephthalate)(PBT)	52	54
Poly(ethylene terephthalate)(PET)	70	120
PET/PCHT copolymer (64/36) *	74	106
PET/PCHT copolymer (69/31)	76	111
PET/PC copolymer (70/30)	87	131
PET/PC copolymer (50/50)	93	138
PET/PC copolymer (30/70)	100	143
PET/PC copolymer (10/90)	113	149
Atactic polystyrene	10	190
poly(ethylene naphtalene-2,6-dicarboxylate)(PEN)	119	182
atactic poly(methyl metacrylate)(a-PMMA)	120	215
bisphenol-A-polycarbonate (PC)	128	152
dry gelatin	217	395

* PCHT: poly(1,4-cyclohexanediol terephthalate).

6. Development of Structure

Few studies on the variation of microhardness of glassy polymers depending on crystallization conditions are available [23,24]. In the course of isothermal crystallization of polymers one observes a sigmoidal rapid increase of the hardness followed by a very slow increase (Fig.4) [25]. The comparatively rapid H increase, during primary crystallization, is connected with the growth of polycrystalline aggregates (spherulites) (Fig.5a), until they impinge on each other, finally filling up the sample completely (Fig.5b). The much slower hardening process is denoted as secondary crystallization and is related with crystal thickening and formation of new crystals. We have shown that during

Figure 3. Relationship between room temperature measured H and T_g for amorphous polymers (see Table 2) [ref.22]

Figure 4. Variation of microhardness measured "in situ" for PET samples as a function of crystallization time for different crystallization temperatures. $T_c = 117^\circ\text{C}$ ($\blacktriangle$); $T_c = 110^\circ\text{C}$ ($\triangle$); $T_c = 105^\circ\text{C}$ ($\bullet$); $T_c = 100^\circ\text{C}$ ($\circ$) [ref.33]

primary crystallization H increases, depending of annealing time with the volume fraction of spherulites ϕ , according to

$$H = H_{\text{sph}} \phi + H_a (1 - \phi) \quad (3)$$

where H_{sph} and H_a are the hardness of spherulitic and inter-spherulitic ("amorphous") material respectively (for example, for PET, $H_a \sim 120$ MPa and $H_{\text{sph}} \sim 200\text{-}220$ MPa; for PEEK, $H_a = 135$ MPa and $H_{\text{sph}} = 210\text{-}250$ MPa) [23].

7. Detection of Physical Transitions

The crystallization of amorphous polymers like PET from the glassy state has been recently examined by measuring the microhardness in "real time" at different temperatures [25]. We wish to highlight the occurrence of some transitions near T_g which can be evidenced by means of microhardness measurements in situ.

Fig.6 shows the variation of H as function of temperature for glassy PET before and after physical aging [25]. The hardness values obtained below T_g depend on the physical aging of the samples. Physical aging below T_g is connected to local molecular motions. We have suggested that this pre-glass transition (slow nucleation mechanism) may involve ordering of PET benzene rings reducing segmental mobility and contributing to a hardening of the material. Above T_g the hardness shows a unique variation with a loss of memory of the previous aging (Fig 6). In the high-temperature region ($T > T_g$), in addition to the conspicuous softening range, there seems to emerge a faint H maximum at about 100°C . This transition could be related with the above molecular ordering phenomena below T_c [25].

Microhardness has been shown to be a promising technique to detect accurately the glass transition temperature in a variety of glassy polymers (PVAc, PMMA, PET, PEEK) [20].

8. Hardness of semicrystalline polymers

Melt crystallized polymers generally exhibit a spherulitic morphology in which ribbon-like lamellae are arranged radially in the polycrystalline aggregate [26]. An unoriented semicrystalline polymer can be considered as a two-phase composite of amorphous compliant regions sandwiched between hard crystalline lamellae (Fig.7 top). Crystal lamellae are normally $10\text{-}25$ nm thick (l_c) and have transverse dimensions of $0.1\text{-}1$ μm while the amorphous layer thickness l_a has dimensions of $5\text{-}10$ nm. Since the indentation process involves

Figure 5. Schematic representations of the development of spherulitic structure:
a) incompleted spherulitic growth, b) completed spherulitic crystallization.

Figure 6. Variation of microhardness for glassy PET as a function of temperature.
Open symbols: physically aged materials. Solids symbols: material immediately measured after quenching [ref.23].

Figure 7. Model of lamellar structure: before deformation (top); and after deformation under the stress field of the indenter (bottom) [ref.36]

Figure 8 Plot of reciprocal crystal hardness as a function of reciprocal crystal thickness for PEO with $M_n=13,000$ crystallized at various temperatures [ref. 37]

plastic yielding under the stress field of the indenter, microhardness is correlated to the modes of deformation of the semicrystalline polymer. These involve, at small strains, shearing motions of lamellae and lamellar separation [27]. Beyond the yield point, irreversible deformation processes take place, including lamellar fracture, microfibrillation, etc.

In dealing with the hardness of semicrystalline polymers it has long been recognized that the following general empirical relationship (parallel model) holds [1]:

$$H = \omega_c H_c + (1 - \omega_c) H_a \quad (4)$$

where H_c and H_a are the intrinsic hardness values of the crystalline and the amorphous phases and ω_c is the volume fraction of crystalline material. In the simple case of flexible polymers like polyethylene (PE) or polyethylene oxide (above T_g) with rubbery amorphous layers [1] (when indentation is done at $T_g < T < T_m$), $H_a \ll H_c$ we are led to

$$H \approx \omega_c H_c \quad (5)$$

This equation assumes that the semicrystalline polymer is a two-phase system and that hardness (yield) is due to plastic deformation taking place only in the crystalline regions. However, for stiff polymers like polyethylene terephthalate (PET) [23] or poly(ether-ether-ketone) (PEEK) [28], when $T_g > T$, $H_a \neq 0$.

9. Polymorphic Changes

The increasing variation of the unit cell dimensions of polymers (PE, PEEK) with temperature leads to a decrease of the microhardness [28,29]. For example, in linear polyethylene, H decreases from 90 to 70 MPa in the temperature range 20-70°C. The better packing of the chains and, therefore, the changes in cohesive energy seem to play a relevant role in determining the hardness value [29]. Since microhardness is related to the packing of the chains in the crystals one may expect that polymorphic changes may influence the strength of the intermolecular forces and, hence, the microhardness value. We wish to illustrate the influence of polymorphism on hardness in the case of polypropylene. Isotactic polypropylene can crystallize into several polymorphic forms. Microhardness measurements were carried out on samples prepared by the temperature gradient method of Fujiwara [30,31] which allows a distinct separation between the α (monoclinic) and β (hexagonal) phases within the sample. Results show that H decreases from 111 MPa to 90 MPa when passing from the α - to the β -phase [32]. The H decrease is partially connected with a

crystallinity decrease from 0.72 to 0.62. However, according to eq. 4 the microhardness of each phase depends not only on crystallinity but also on the crystal hardness H_c itself. Thus, we can write for both phases:

$$H^\alpha = \omega_c^\alpha H_c^\alpha + (1 - \omega_c^\alpha) H_a \quad (6)$$

$$H^\beta = \omega_c^\beta H_c^\beta + (1 - \omega_c^\beta) H_a \quad (7)$$

where ω_c^α and ω_c^β represent the degree of crystallinity of the α and β phases respectively.

If we take for the amorphous phase of isotactic polypropylene a value $H_a \approx 30$ MPa and solve eqs. 4 and 5, values of $H_c = 143$ MPa and $H_c = 119$ MPa are respectively obtained. The former value fits well with the ab-initio calculation for the α -phase [32]. In conclusion, microhardness is shown to be a technique capable of detecting polymorphic changes in polymers.

10. Hardness Predictions of Lamellar Crystals

From equation 4 it is clear that ω_c controls the microhardness value of a polymer. However, stacks of crystalline lamellae, as pointed out above, characterize the structure of the semicrystalline polymer. It was soon recognized the direct influence of crystal thickness l_c upon microhardness in case of chain-folded and chain-extended PE samples [1,33]. Popli and Mandelkern [34] and Crist et al [35] provided later independent evidence for the strong dependence of yield stress σ_y upon l_c . The above authors [34] found that spherulite size does not have direct influence upon yield in PE. On the basis of a heterogeneous deformation model involving the heat dissipated by the plastically deformed crystals, Baltá Calleja and Kilian [36] developed an approach to calculate the dependence of hardness on the average crystal thickness. Fig.7 shows the model of lamellar deformation under the indenter involving the generation of a number of shear planes ($\langle D_c \rangle$ and l_p in Fig.7 represent the average size of the crystallites normal to the chain axis, before and after plastic deformation [36]). The hardness of the crystals can then be described by

$$H_c = \frac{H_c^\infty}{1 + (b/l_c)} \quad (8)$$

where H_c^∞ is the hardness of an infinitely thick crystal (maximum possible value of dissipated energy through plastic deformation) and b is a parameter related to the surface free energy σ_c of the crystal and to the energy Δh required

for plastic deformation of the crystals through formation of a great number of shearing planes [36]. The b parameter is equal to

$$b = 2\sigma_e/\Delta h \quad (9)$$

Fig.8 illustrates, as an example, the plot of H_c as a function of l_c^{-1} for different polyethylene oxide samples crystallized from the melt at different temperatures [37]. The calculated continuous straight line was derived using for $b = 27$ nm and for $H_c^\infty = 150$ MPa. The constancy of the b -parameter is consistent with the constant σ_e -value obtained. Comparison of the b -mechanical parameter and the b -thermodynamical parameter, $b^* = 2\sigma_e/\Delta h_f$, shows that $\Delta h_f = 90 \Delta h$; i.e. the energy required for crystal fusion is about two orders of magnitude larger than that required for plastic deformation. Similar results have been obtained for PE [38].

Comparison of experimental and calculated H_c data in PE emphasizes the parallel increase in the b -parameter derived from mechanical data (14-26 nm) and σ_e determined thermodynamically (79-91 erg/cm²) for a series of samples with different molecular weights (56,000-307,000) [38]. This finding supports the view of an increasing number of molecular entanglements which are rejected into the crystal surface as molecular weight increases, thereby controlling the yield behaviour of the material.

Young [39] and Crist et al. [35] applied a different approach to describe the dependence of the 'crystal' yield stress, σ_y^o , with l_c in terms of the screw dislocation model for yield. The dependence of σ_y^o upon l_c is given by

$$\sigma_y^o \approx \frac{H_c}{3} = \frac{K}{2\pi e} \exp\left(-\frac{2\pi\Delta G^*}{K b^2 l_c}\right), \quad (10)$$

where K is a function of the shear modulus of the crystals (e is the base of natural logarithms), and b and ΔG^* are the Burgers vector and the activation energy respectively of the screw dislocation. Values of $\Delta G \approx (40-60)kT$ have been used [39]. Comparison of Baltá-Calleja and Kilian's approach [36] with Young's dislocation model for yield gives good agreement for oriented PE films [40]. However, although the absolute magnitude of σ_y^o is quite good, when using the yield dislocation model appreciable deviations between calculated and experimental values for isotropic melt-crystallized samples are observed (see Fig 9). We believe that this is so because the model was developed for the plastic deformation of crystals in a direction parallel to the molecular direction [40].

Figure 9. Dependence of yield stress σ_y^0 on crystal thickness l_c for crystals of linear polyethylene (■) and branched polyethylene (●). The continuous line is calculated from eq. 10. From Young [ref. 39].

Figure 10. Microhardness of ultrahigh molecular weight PE/iPP blended gel films vs. concentration (wt.) of PE. (1) Additivity behaviour (eq. 13) using ω_c values from individual polymers. (2) H - values from eq. 14 using ω_c^{PE} and ω_c^{PP} data for each blend. (3) Experimental (●); calculated data, eq.12 (▲) [29].

11. Generalized Tabor relation

An exponential law-type decrease with temperature has been found for the microhardness of various semicrystalline polymers (PE, nylon, PVF₂/F₃E copolymers) [1,41] and glasses [42,20]:

$$H = H_0 e^{-\beta(T-T_0)} \quad (11)$$

where β is the so-called coefficient of thermal softening of the polymer, T the absolute temperature and T_0 a reference temperature (usually room temperature). The thermal softening has been attributed to the thermal activation of the crystals [29]. By combining equation 1 with equations 8 and 11 we are led to:

$$\sigma_y = \frac{H}{3} = \left(\frac{\omega_c}{3} \right) \frac{H_c^\infty}{1 + \frac{b}{l_c}} e^{-\beta(T-T_0)} \quad (12)$$

Equation 12 offers a general expression for the microhardness (or yield stress) of semicrystalline polymers at a given temperature having a mean crystal thickness l_c and a crystallinity ω_c . Generally, a crystal size distribution within each lamellar stack occurs. According to equation 12, the yielding process entails the destruction of a large number of crystals so that H provides a measure of the average crystal size. Calculated data of H and σ_y for low density polyethylene at different temperatures using eq. 12, give satisfactory agreement with observation [43].

12. Polymer blends

Recent results show that hardness is a promising technique for the microstructural investigation of multicomponent blends of known composition and can provide information on the degree of interpenetration of the blend component [44]. The case of blends of low density (LD) and high density (HD) polyethylene is an example where the microhardness can be very well described in terms of an additive (parallel) system of two independent components, H_1 , (LD) and H_2 (HD) [45].

$$H_{\text{blend}} = H_1 \phi + H_2 (1 - \phi) \quad (13)$$

where ϕ is the weight fraction of the HDPE component. Equation 13 emphasizes the existence of distinct H values for the two phases owing to a molecular segregation at a crystal level.

In other systems like, for example, in PE and PP blends prepared by gelation from semi-dilute solution a conspicuous deviation from the additivity law given by equation 13 is detected [44]. Fig 10 illustrates the obtained variation of H as function of ϕ for the PE/PP dry gel blended films (curve 3). In this case equation 13 can be written as:

$$H = \phi \varpi_c^{PE} H_c^{PE} + (1 - \phi) \varpi_c^{PP} H_c^{PP} + (1 - \phi)(1 - \varpi_c^{PP}) H_a^{PP} \quad (14)$$

which describes the microhardness of the blended gel films in terms of the H values of the independent crystalline and amorphous components. One has shown that the iPP component hampers the crystallization capability of PE and therefore α_{PE} decreases with increasing iPP concentration [44]. On the other hand, the presence of PE crystals also inhibits the crystallinity of iPP. The crystallinity depression of PE and iPP is insufficient to account for the deviation of experimental values from the additivity law 1 in Fig.10, leading only to curve 2. It has been shown that the deviation of the experimental values from the additivity law is due to a decrease of the H_c^{PE} and H_c^{PP} values. The crystal hardness decrease is provided by an increase of the surface free energy (see equations 8 and 9) with composition which leads to curve 3. It has been suggested that the σ_e rise is a consequence of the increase in the level of surface defects including entanglements [44].

Other systems in which equations 13 and 14 provide an accurate description of the phase contribution and structural parameters on the microhardness value, include blends based on recycled polymer wastes [45], blends of non-crystallizable components [46,47], coreactive blends of condensed polymers [48], microfibrillar reinforced composites [49], etc.

13. Outlook

Microhardness (H) has been shown to be a bridging parameter between microstructure and macroscopic mechanical properties. When studying the temperature dependence of microhardness in glassy polymers several transitions can be distinguished: a) a preglass transition (physical aging), b) the glass transition (softening behaviour), c) a precrystallization transition (molecular ordering) and d) the spherulitic crystallization. Although physical aging has been the object of investigation during the last decade, the detailed molecular mechanisms are still open to interpretation [50]. One may expect that the microhardness technique can lead to future developments in the understanding and characterization of physical aging phenomena in glassy

polymers. In semicrystalline polymers H can be described on the basis of a composite consisting of hard lamellae intercalated by compliant disordered layers. A generalized Tabor relationship between H and σ_y accounting for the dependence of crystal thickness, crystallinity and temperature explains the correlation of mechanical properties with microstructure. We also expect that this technique will be of great value in the detection of other polymorphic transitions, like, for example, the recently detected ferro-to-paraelectric transition in ferroelectric copolymers of vinylidene fluoride and trifluoroethylene [41]. Microhardness offers, in addition, future possibilities for the mechanical characterization of specific parts of processed polymers on a micron scale (prepared by extrusion, injection molding, etc) [51]. So far we have only considered neat polymers. Work has been performed to examine the microindentation hardness of carbon fiber reinforced composites [52]. These materials represent a bridge in hardness between neat polymers and hard metals. The localized nature of the microhardness test will allow to obtain information regarding the heterogeneity of composites that is often not available with other analytical techniques. Several reports have appeared lately on the mechanical properties of polymer surfaces at nanometer resolution [6,7,8,53]. Nanoindentation techniques [54] for probing the mechanical behaviour of the top few tens of nanometers of bulk and thin polymer film specimens open up future possibilities to investigate the elastic and plastic flow properties of the near-surface region of polymer materials.

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