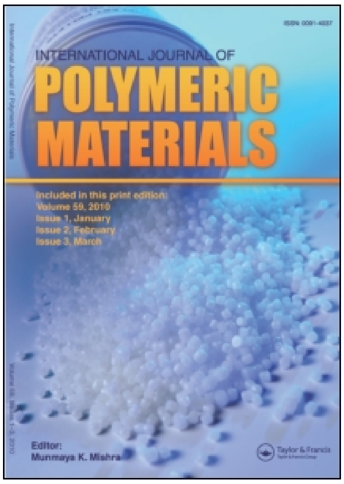

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Temperature Dependence of the Mechanisms of Crazing and Shear in Amorphous Glassy Polymers: A Current Review and a New Approach

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The critical review is presented of modern models of plastic deformation of amorphous polymers, with the emphasis on concepts of temperature dependencies of the mechanisms of crazing and shear. It was shown that these models cannot satisfactorily explain the experimental data. A new approach is proposed based on the cluster model of structure of amorphous polymers developed by authors. This model gives an alternative explanation of the changes in deformation mechanism with changing temperature and agrees well with experimental data.

Keywords: Amorphous polymers; cluster model; entanglements; crazing; plasticity yield stress

INTRODUCTION

1. Current Theories of Crazing in Amorphous Polymers

It is very well known (1) that in amorphous glassy polymer there are two main mechanisms of plastic deformation; shear and crazing. The ratio of these two mechanisms determines the plasticity of the polymer. As a rule, the increasing tendency to crazing means increase in

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the brittleness of polymer, whereas the increasing tendency to shear increases its plasticity (2). A great deal of works are dedicated to the investigation of these mechanisms, their concurrence and, in particular, the dependence of their intensity on the temperature of testing.

Wellinghoff and Baer [3] have studied the mechanism of the plastic deformation of various polymers. They have found that for poly (phenylene oxide) (PPO) and polycarbonate (PC) there is a transition from shear to crazing when the testing temperature approaches the glass transition temperature T_G. Such a transition was observed at 373–398 K and 413 K for PC and PPO correspondingly (3). The glass transition for PC and PPO are correspondingly at 418 and 473 K. It is worth noting that authors (3) have discovered similar behavior of the PC specimens with various molecular masses $1.1 \cdot 10^4$ and $3.0 \cdot 10^4$ g/mol. Donald and Kramer [4–6] have proposed a micromechanical model of crazing in amorphous polymers where the possibility of realization of one or another mechanism of plastic deformation is determined by the structure of the polymer- by the density V_E of the network of macromolecular entanglements. In the framework of this model it was shown that increasing V_E leads to the more intense occurring of the mechanism of crazing. Kramer [7] has proposed the following equation for the effective surface energy Γ:

$$\Gamma = Y + \frac{1}{4} d\, V_E\, U_B \tag{1}$$

where Y is van-der-Waals surface energy, d is the distance between the junctions of the entanglement network and U_B is the energy of the destruction of chemical bond in the main chain.

Increasing V_E at other similar conditions determines the growth of Γ, this, in its turn, initiates the increasing tension of fibrilization and, therefore, prevents the craze formation. Henkee and Kramer [8] have shown also that the formation of the craze fibrils needs some "geometric loss" of entanglements that may be realized in two ways: either by destruction of the macromolecules, or by their slipping and going out of the entanglement. The advantages of the Donald Kramer model are evident: it connects the craze structure with such an important parameter of the polymer in bulk as the density of the network of macromolecular entanglements. At the same time, the shortcoming of the model is also evident. It is known (9) that value V_E is estimated from the measurements of mechanical properties of polymers above T_G and is assumed to be equal to this values throughout the whole temperature interval of the glass state, i.e. even at $T \ll T_G$. Besides, this variant does not take into account the effect of the heat treatment on the polymer structure. In terms of this model it was supposed that "geometric" loss of entanglements is realized at the relatively low temperatures by the scission of macromolecule, whereas at more high temperatures- by their splitting. To explain the high temperature crazing-shear transition Donald [9] proposed the model based on the temperature dependence of the stresses corresponding to the yield stress and crazing. Figure 1 shows schematically the temperature dependencies of the shear stress corresponding to the yield point and to crazing. For high molecular weight polymers, the splitting of macromolecule is difficult and because of it the crazing stress σ_C diminishes slower with temperature as compared with low molecular weight polymer. If the yield stress σ_y is higher than σ_C, then the dominating process is crazing and vice versa. It is supposed (9) that σ_y does not depend on the molecular mass of a polymer, because the draw ratio λ_C of craze fibrils depends on molecular mass M_E of the chain segment between two entanglements, to explain the growth of λ_t with temperature the concept of the splitting macromolecule with increasing

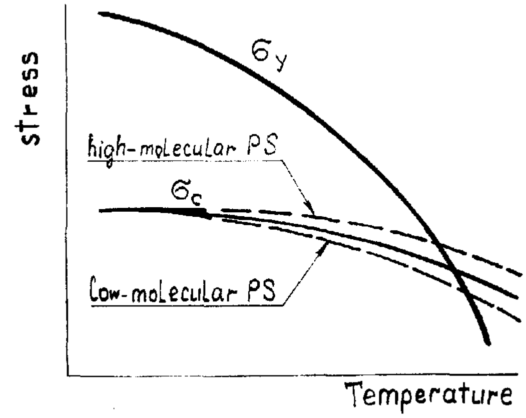

FIGURE 1 Schematic representation of the temperature dependencies of the plasticity yield stress σ_y and crazing σ_C for PC according to Donald [9].

temperature was proposed [9–11]. This concepts implies that at comparatively low temperatures the friction coefficient ξ_0 of macromolecule is high enough to allow the realization of the macromolecule scission under the action of applied force. The increasing temperature leads to diminishing ξ_0 and the load that is necessary for molecule to slip, becomes, less than the strength of the chemical bond. The sliding of macromolecule in the "entanglement tube" initiates the splitting or diminishing V_E and, therefore, diminishing σ_C.

We believe that the concept discussed above suffers from many weaknesses that need to be considered.

2. Critics of the Modern Concepts of Crazing

It is well known (12) that the crazing stress σ_C is the function of temperature and monotonously increases with diminishing temperature. For PC diminishing temperature from 300 K to 100 K (12) increases σ_C three times. If the "geometric loss" of entanglements even at the room temperature is realized exclusively through the mechanism of macromolecule scission, the reason of increase in σ_C becomes unclear.

The slipping of macromolecules in the "tube" under the action of loading and their escaping from the entanglements can hardly be considered a one-directional process. For polymer melt the three-stage model was proposed to describe this phenomenon that accounts for the establishing of the local equilibrium without any slipping, the extension of a chain and recovery of the conformation of a statistical coil due to micro-Brownian motion. For the glassy-state, Donald [9] considers only the first two stages. One should not, however, forget that only an active zone at the interface craze-polymer is considered, where higher molecular mobility may take place due to closeness of the free surface and/or mechanical deglassification of a polymer.

At last, one of the most important reasons for revision of the concepts discussed above, is the discrepancy between experimental data [13–15] and Donald model [9]. Authors [13–15] have obtained the empirical linear correlations between the crazing parameters (crazing deformation ε_C, the greatest main stress σ_{yy} and stress of hydrostatic extension P) and main characteristics of the polymers (T_G, cohesive energy density W_C), σ_y and elasticity modulus

E) in the following form:

$$\varepsilon_C \propto \frac{W_C(T_G - T)}{E} \tag{2}$$

$$\varepsilon_C \propto \frac{W_C(T_G - T)}{\sigma_y} \tag{3}$$

$$\sigma_{yy} \propto W_C(T_G - T) \tag{4}$$

$$P \propto W_C(T_G - T) \tag{5}$$

The correlations between E and W_C [16], E and σ_y [17] and W_C and T_G [18] are well known.

The equations 2–5 reflect as a first approximation the dependence of ε_C or (σ_{yy} and P) on $\Delta T = T_G - T$, on the degree of approaching the testing temperature to T_G. This approximation is proved by the correlations $\varepsilon_C = f(\Delta T)$ and $P = f(\Delta P)$ presented in Figure 2 that were calculated from published data [14, 15]. Despite rather high scattering, the data clearly show the increase of ε_C and P with increasing ΔT. The reasons of scattering are explained by the deviation of correlations $E = f(W_C)$ and $T_G = f(W_C)$ from the straight line) that were considered in some works [16, 18]. It is evident that the increasing parameters ε_C and σ_{yy} and P reflect the progressing hindrances for crazing. However, it is also evident, that at equal values of ΔT all polymers should have equal probability of the craze formation. In the framework of the model [4–7] this condition should be the result of different V_E values. It was noted before that the entanglement network in the whole temperature range of the existence of glassy state is "frozen" and V_E is constant. Therefore, to explain this disparity, the concept was introduced [9–11] of slipping the chains and their disentanglements with increasing T.

3. New Approach to the Crazing Mechanism

In the present work we propose an alternative concept of the temperature dependence of crazing mechanism, that seems to be more simple

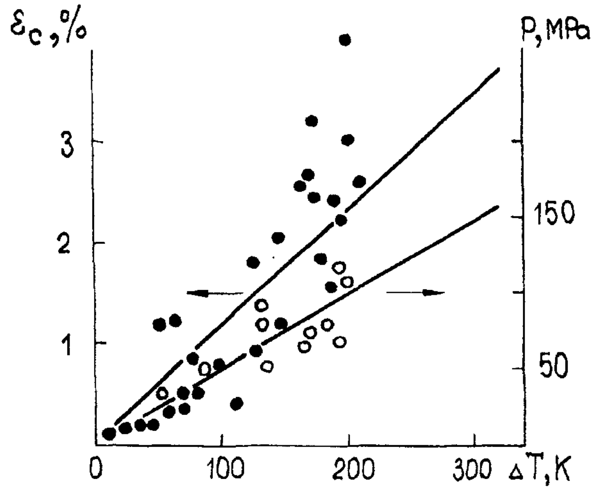

FIGURE 2 Dependencies of the crazing deformation ε_c (1) and hydrostatic extension pressure P (2) on Δ T plotted according to the data [14, 15].

and natural. This concept accepts all the main positions discussed before [4–6], it however does not deal with the simple entanglement network, but with cluster network of macromolecular entanglements [19]. The junction points (knots) of such a network are supposed to be clusters formed by some colinear segments of different chains (by analogy with crystallites with extended chains). To determine the density of the cluster network the equations are used analogous to the equations of the theory of kinetic rubber elasticity.

The density of the cluster network V_e^C may by found by means of mechanical testing and is defined as

$$V_e^C = \frac{\rho N_A}{M_e^C} \tag{6}$$

$$M_e^C = \frac{\rho R T}{K} \tag{7}$$

where ρ is the polymer density, N_A is Avogadro number, M_e^C is the molecular mass of the chain segment between two clusters, R is gas constant K is a constant, that may be found from the Money-Rivlin equation [20]

$$\sigma_t = K(\lambda^2 - \lambda^{-1}) \tag{8}$$

where σ_t is the fracture stress measured in the region of glass plastic yielding and λ is the drawing ratio,

$$\lambda = 1 + \varepsilon \tag{9}$$

where ε is relative elongation. The criterium of the applicability of this approach is the linearity of the experimental dependence (eq. 8).

EXPERIMENTAL

The following polymers have been used as films: polycarbonate (PC)$T_g = 423$ K), polysulfon (PSF) ($T_G = 458$ K), polyarylate (PA), ($T_G = 478$ K) and polyblock copolymer of polyarylate sulfon (PASF) ($T_G = 473$ K) based on the dichloroanhydride of iso- and terephthalic acids and *bis*-phenols of various structure. The films were obtained by casting from 5% solutions in chloroform onto the glass support. For PASF films were prepared from solutions in dimethylformamide, tetrahydrofuran, methylene chloride and tetrachloroethane. Using different solvents allowed us to change the film structure. Some part of films was subjected to thermal ageing in air at 400 K during 20 days.

Mechanical testing of the films was performed using the specimens in the shape of double-sided blade cut-off from the films of 0.08 mm thickness with the working width of 5 mm and basic length of 40 mm. The stress-strain curves diagrams were obtained at 293 K and deformation rate of approx. 10^{-3} sec^{-1}. From PASF films the specimens were cut with the width of 11 mm and basic length of 25 mm. In the centre of the film a one-side incision of 1 mm length was made. The specimens were stepwise elongated (with interval 0, 75%) using a special device mounted on the polarization microscope. The loading was measured using a dynamometer. After each experiment, the region of the specimen including incision was photographed.

RESULTS AND DISCUSSION

It is known [21, 22] that the behavior of amorphous and partly crystalline polymers in the plateau region of plastic yielding is described rather well in the framework of the rubber elasticity theory. According to the Gaussian statistics, in this case the segment of a chain between junction points should contain no less than 20 repeating units [23]. However, the calculated data show the value M_e^C are usually 250–400 g/mol. This apparent discrepancy may be eliminated in the following way [19]. The cluster functionality (the number of chains coming out of it), $F \approx 10$–40, i.e. the number of chains in a cluster is 5–20. For multifunctional knots the following expression is valid [24]:

$$V_e = \frac{\mu_e F}{2} \tag{10}$$

where μ_e is the number of clusters. From eq. 8 follows that increasing F leads to diminishing μ_e and increasing distance between clusters. As a result, M_e should be $F/2$ times greater than that determined by the rubber elasticity theory. Under this condition, the elasticity theory is working.

For various amorphous glassy polymers the dependencies $V_e^C = f(T)$ are similar: increasing T monotonously decreases V_e^C, especially by approaching T_G [19].

The change of the slopes of curves $V_e^C = f(T)$ takes place at the temperature approx. 50 K below T_G. This feature is explained in the framework of cluster model by a deglassification process proceeding in two stages: loosely packed regions of amorphous polymers (intercluster regions) have the glass transition temperature about $T'_{G'} = T_G - 50$ K [25]. The temperature T'_G corresponds to the temperature of transition from shear to crazing in PC and PFO [3]. As follows from the Donald-Kramer model [4–6], sharp decrease V_e^C at $T > T_G$ enhances craze formation.

The general regularity of the dependencies of $V_e^C = f(T)$ allows the principle of the temperature superposition to be applied to various polymers. Figure 3 shows that dependencies V_e^C (ΔT) for PC, PA, PASF, PSF are described by one curve. In such a way, the crazing parameters (ε_c and P) and V_e^C are determined by the ΔT. The limiting ratio λ of polymers, as well as the value of λ for craze fibrils [21] is

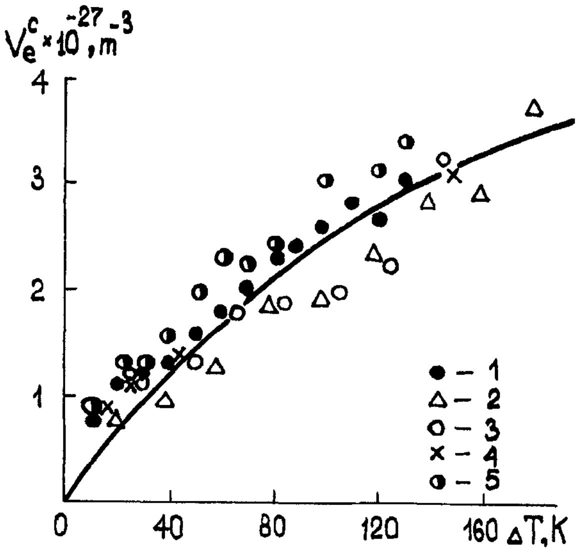

FIGURE 3 Dependence of the density V_e^C of cluster network on ΔT for PC (1), PA (2), PSF (3), PASF (4) and heat-treated PC (5).

determined by the length l_e of the chain segment between the junction points of the network of macromolecular entanglements [26]. Increasing M_e^C increases λ. Deformation ε in crazes or zones of shear deformation may be calculated by [27]:

$$\varepsilon = \ln \frac{r_p + \delta_C}{r_p - \delta_C} \tag{11}$$

where r_p is the craze length (or deformation zone), δ_C is the craze opening (or deformation zone). Having measured r_p and δ_C immediately before sample breaking, from equations 9 and 11 it is easy to estimate the maximum draw ratio in the deformation zone λ_D. Figure 4 shows that the dependence of λ_D on M_e^C follows the conclusions of [26]: i.e. λ_D increases with M_e^C.

Plummer and Donald [11] have measured the drawing ratio λ_c for crazes and λ_D for deformation zones in PC (Fig. 5, curves 1 and 2) and shown that λ_c begins to increase sharply at 385 K (i.e. at $T \sim T_G'$), whereas λ_D stays approximately constant. The theoretic estimation of

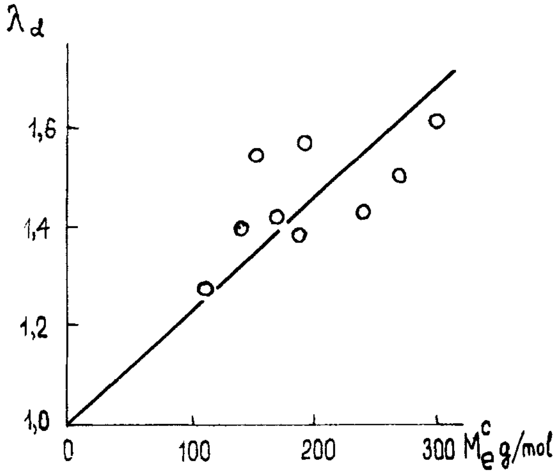

FIGURE 4 Correlation between maximum draw ratio λ_d in deformation zone sand molecular mass M_e^c between cluster network junction points for PASF films, obtained using various solvents.

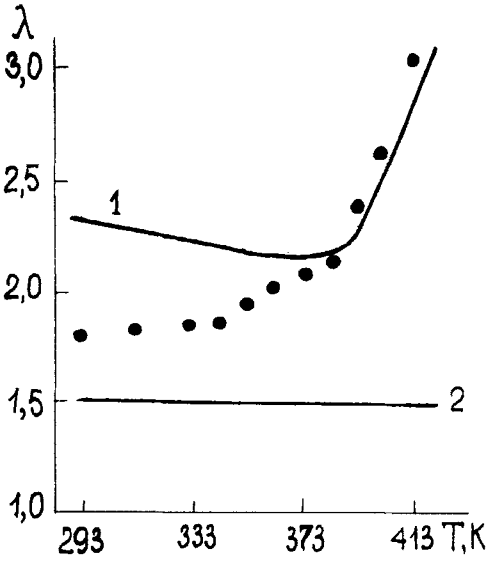

FIGURE 5 Experimental (1, 2) [11] and calculated according equation 12 (points) dependencies of maximum draw ratio in craze (1) and deformation zone (2) on temperature for PC.

the draw ratio in craze, or in deformation zones, may be done using the relationship proposed by Donald and Kramer [4, 5]

$$\lambda = \frac{l_C}{d} \tag{12}$$

In the framework of the cluster model l_e may be found from the known values of M_C^C using the relationship between molecular mass and chain volume [28] and cross-section area of macromolecule [29], $d = \sqrt{\mu_e}$. The results of such calculations of λ_c and λ_D for PC are presented in Figure 5 by points. Their comparison with the experimental data obtained by Plummer and Donald [11] shows that in the crazing region the values of λ_c are in a good agreement, despite the use of PC of different origin. In the region of the deformation zone realization ($T \ll 343$ K)) a rather good concordance of λ_D is also observed in both the temperature dependence and absolute values. The comparison of the theory and experiment in the transition region from deformation zones to crazes (333–373 K) shows that the diminishing V_e^C, that is necessary for such transition, and therefore, increase in λ, is determined by the destruction of clusters through thermal fluctuation with increasing T. It is known [30] that annealing of PC is accompanied by the increasing tendency of a polymer to crazing as compared with shear. From Figure 3 follows that value V_e^C for annealed PC is higher than that of the initial polymer. It is worth noting that increasing of the local ordering of amorphous polymers by annealing was proposed earlier [31], on the basis of the corresponding increase of σ_y for annealed PC. It was discovered [32] that by annealing PC the stress values that control the crazing process (σ_{yy} and P) do not change, whereas the tendency to crazing is determined by the relative increase in σ_y. In such a way, the cluster concept may explain the annealing behavior as well.

The results presented above indicate that in the case of amorphous polymers, the cluster model allows an alternative explanation for the change of the mechanism of nonelastic deformation and of controlling parameters with temperature change. A good quantitative accordance with the data of other authors is observed. We believe that this new approach to the crazing mechanism has some advantages because of its simplicity and the possibility in a quantitative way to estimate the parameters of the structure of amorphous polymers.

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