Development of the combined chemical-mechanical approach to polymeric materials cutting

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Abstract. The analysis of the phenomena occurring during the interaction of polymeric materials with aggressive media is carried out. Scientifically substantiated is the chemical effect on workpieces made from polymeric materials before cutting. In this case, it is advisable to carry out the processing of polymers with an aggressive medium in such a way as to ensure cracking or loosening of the surface layer to a certain depth, without changing the chemical properties of a particular polymer. The results of experimental studies of samples in tension after appropriate chemical treatment are carried out. The research results analysis made it possible to establish the fact that the treatment of the studied polymeric materials with active media leads to a significant decrease in strength. Methods have been developed, the essence of which is a directed change in the properties of the processed material, by preliminary chemical treatment of the surface layer, in order to reduce the resistance to destruction of the surface layer of the workpiece during its subsequent interaction with the cutting tool.

The destruction of constructional materials such as polymers may occur under the action of aggressive media [1, 2]. The action of such media may simply change the structure and properties, without complete loss of integrity; for example, it may lead to cracking, crumbling, and swelling of the polymer surface to a certain depth. Therefore, analysis of the processes that accompany the interaction of a chemical medium with polymers is of practical interest and may serve as the basis for the development of chemomechanical cutting methods for polymer parts.

Depending on their interaction with polymers, aggressive media may be divided into two groups: physically active and chemically active media. Surfactants may belong to either group. The mechanism by which physically active media act involves diffusion into the polymer, with weakening of the intermolecular bonds and corresponding decrease in strength of the polymer’s surface layer.

On contact with polymers, chemically active media produce irreversible changes in the chemical structure of materials. The set of chemical processes leading to change in chemical structure and molecular mass of the polymer may be characterized as chemical destruction.

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When polymers interact with aggressive media, various physical and chemical processes may appear; the most important are as follows: adsorption of the components of the aggressive medium on the polymer surface; diffusion of the aggressive medium into the polymer; chemical reaction of the aggressive medium and a polymer with chemically unstable bonds; diffusion of the destruction products to the polymer surface; desorption of the destruction products from the polymer surface [2].

The influence of physically active aggressive media on the strength of polymers, determining their resistance to disintegration, may extend throughout the volume (swelling) or be confined to the surface (adsorption, surface diffusion). In the case of adsorption, only the surface sections of the body participate in the process; the chemical potential of the solid is unchanged. The surface of the solid is understood here to mean not only the external surface but a region around individual groups of molecules, as well as the surface of individual molecules. Obviously, this effective surface of the solid depends on the supermolecular structure and also on the characteristics such as the size and shape of its molecules. Adsorption may occur at the internal sections of the solid, which have cavities and pores for the accumulation of the diffusing molecules. In swelling of the polymer in physically active media, the strength of the polymer is usually reduced, but its elasticity is increased [1, 2]. Two factors may be responsible for the decrease in polymer strength on swelling.

First, internal (local) stress arises on account of the nonuniform swelling of the polymer. In the sorption of solvents by polymers, sharply defined regions with different degrees of swelling are often observed [2].

This is especially notable for glassy polymers. It may be explained by the direct dependence of the diffusion coefficient on the concentration of the diffusing component in the system and also by the specifics of polymer interaction with this component. In this system, on account of the unequal mobility of molecules of the absorbed material and the polymer segments, no steady stress appears; this stress is often very large. The swelling regions of the polymer experience compressive stress from the more rigid adjacent regions, in which tensile stress acts. As a result of the nonuniformity of swelling and the appearance of heterogeneous internal stress in the material, microcracks and internal micro defects are formed. The local stress may be sufficient for rupture of the C–C bonds.

Second, the strength of the material may change on account of change in the molecular interaction on polymer swelling.

However, as already noted, swelling tends to increase the elasticity of the polymer, i.e., to increase the flexibility of its molecular chains and hence reduce the vitrification temperature. Greater flexibility of the molecular chains facilitates orientation of the polymer macromolecules under the action of a mechanical load, in machining of the polymer by a cutting tool. Thus, strain hardening of the material occurs. The strength of the material increases at exactly the moment when decrease in strength would be expedient. Therefore, in terms of machining efficiency, the swelling of polymers under the action of aggressive media is undesirable. Machining processes accompanied by cracking or crumbling of the surface layer to the required depth, without change in chemical properties of the polymers, would be more expedient.

The adsorption process has internal (mechanical) and external (energy) components. The internal component is associated with adsorption of active materials on the surface of defects such as cracks, which hinder spreading of the materials. As a result, the defects become deeper and broader. Consequently, the solid becomes weaker and more brittle. The external component is associated with decrease in the yield point and hardening coefficient of the material at its surface. Characteristics such as the plastic strain, the resistance to creep, and the fatigue strength depend on the state of the surface. The strength of solids is proportional to their surface energy. Hence, with decrease in the free surface energy, i.e.,
with decrease in the work of formation of new surfaces, the strength of the material declines. Therefore, with decrease in surface energy as a result of adsorption, crack nucleation and development is observed; the strength of the material declines. This is also observed when surfactants are used.

Rebinder has studied the effect of surfactants on the physical properties of stressed bodies. This effect is seen in many materials, including polymers. It is found that liquids such as water and acetic acid considerably reduce the effectiveness of cutting for many materials, while ethyl alcohol does not [3]. This may be explained in terms of adsorption. The weakening of a polymer by surfactants is due to microcracks appearing at its surface during the production process. The surfactant is adsorbed at the surface and enters the defects. As a result, a large pressure develops in the capillaries:

$$\Delta P = \frac{2\gamma \cos \theta}{r}$$

where $\Delta P$ is the pressure in the meniscus cross section; $\gamma$ is the free surface energy; $\theta$ is the contact angle characterizing the degree of wetting; $r$ is the pore radius.

In complete wetting ($\cos \theta = 1$), $\Delta P_{\text{max}} = 2\gamma / r$. With small $r$, $\Delta P$ may be very large.

On account of the difficulties in experimental determination of the surface energy, the influence of various media is estimated by means of Young’s formula

$$\gamma = \gamma_{s,g} - \gamma_{l,g} \cos \theta,$$

where $\gamma_{s,g}$ is the surface energy of the material; $\gamma_{l,g}$ is the surface tension of the liquid; $\theta$ is the limiting wetting angle.

Since $\gamma_{s,g}$ is constant, depends on the surface tension of the liquid at complete wetting. With decrease in $\gamma$, the strength of the polymer should also decline. In incomplete wetting, with increase in $\gamma$, variation in may be associated with either rise or fall in $\gamma$. It is found that, below the vitrification temperature, the crystalline regions are physically inaccessible to most sorbed materials [4–6]. Analysis of data for various samples indicates that the solubility $S$ is directly proportional to the volume of amorphous phase [1]

$$S = S_a \varphi a$$

where $S_a$ is the solubility of the sorbed material in completely amorphous polymer; the coefficient $\varphi$ takes account of the proportion of amorphous material (by volume) within the whole material; the constant $a$ takes account of the properties of the specific material.

In crystalline polymers, the action of the solvent is localized mainly along the boundaries of the spherulites and sometimes also within the spherulites between the rays. This is because crystallization is associated with the ordering of units of identical structure within the spherulites, for example, linear molecules within linear polymers. In this case, any molecules containing branches and foreign groups that appear as a result of oxidation or other processes are automatically expelled from the crystals and form an amorphous or less ordered phase between the spherulites. Thus, ordered phase appears between the spherulites. Consequently, there is an increase in concentration of defects at which disintegration may begin.

Under the action of aggressive chemical media, chemical destruction of the polymers also occurs. Analysis of research data shows that three types of polymer destruction in aggressive media may be distinguished, depending on the ratio of the diffusion rate of the aggressive medium and the reaction rate [1, 2]:

- internal diffusional–kinetic destruction: destruction occurs within a reaction zone that expands over time and ultimately extends throughout the polymer;
- Internal kinetic destruction: destruction occurs at the same rate within the accessible polymer volume;
- External diffusional-kinetic destruction: destruction occurs within a thin surface layer of constant size, which may be a polymer monolayer.

Under the action of aggressive media in polymer composites (getinaks, textolite, etc.), destruction begins at the polymer–filler interface on account of deterioration in the adhesive properties and the weakening and cleavage of the bonds across the interface. The aggressive media may also help to wash away the polymer binder. These processes disrupt the structure of the composite. To determine the influence of the parameters of treatment by active media on the state of the polymer under the action of a mechanical load, samples are subjected to tensile tests after the corresponding chemical treatment.

Parts made from reactive plastics and thermoplastic polymers (caprolon, getinaks, and textolite), which are widely used in industry, are subjected to tests in constant conditions; the manufacturing technology for the samples remains the same, along with the temperature, the moisture content, and the uniaxial tensile load (State Standard GOST 11262-80). The samples are held for 5 and 15 hours at room temperature in toluene [6]. Then they are subjected to extension (speed of the loading-machine clamps 12 000 mm/h).

The tests show that treating such polymers with active media considerably reduces their strength, as indicated by the decrease in the limit of forced elasticity \( \sigma_{fe} \) for caprolon and the destructive stress \( \sigma_d \) for textolite and getinaks. Thus, in treating caprolon with toluene, \( \sigma_{fe} \) declines from 85 to 62 MPa after 5-hours holding and to 54 MPa after 15-hours holding; for getinaks, \( \sigma_d \) falls from 118 to 52 MPa after 5-hours holding and to 40 MPa after 15-hours holding; for textolite, the drop is from 102 to 53 and 48 MPa, respectively.

In addition, analysis of Figs. 1–3 indicates that, in treatment with active medium, the destruction time of reactive polymers is reduced. The curves of the forced elasticity limit are less steep, with no clear extremum. This is explained by the change in structure, which is accompanied by decline in strength of the material. The behavior of the \( \sigma_{fe} \) curves for caprolon may be explained by the decline in flexibility of the polymer chains due to the formation of enlarged kinetic units (conglomerates) under the action of active media. The presence of conglomerates accelerates destruction, which proceeds along the weak points of the polymer structure, i.e., along the bonds between conglomerates.

In cyclic deformation of the polymers and their contact with moving surfaces, considerable stress arises; this probably also introduces changes in the destruction process. However, there has been no study of these changes in polymers in the presence of aggressive media. There are only a few data for rubber, which is widely used in components subjected to cyclic deformation in aggressive media [1, 2].

Thus, in machining polymer blanks, preliminary treatment to improve the cutting efficiency is expedient. The cutting process may be regarded as the destruction of polymers with a major crack and the formation of two new surfaces. We may assume that surfactant adsorption reduces the resistance of the polymer to cutting and loosens the surface layers. The formation of prefailure zones facilitates the deformation of the cut layer of material, which in turns increases the cutting rate and improves the quality of the cut surface [3].

Physically active media are desirable for polymer treatment. When using chemically aggressive media, the treatment parameters must be regulated so as to ensure external diffusional–kinetic destruction.

On the basis of experimental data, the corresponding treatment method for polymer parts had been developed [7]. This method is based on directed change in the polymer properties
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**Fig. 1.** Variation in the limit of forced elasticity of caprolon samples with no chemical treatment (1) and after treatment in toluene for 5 (2) and 15 hours (3).

**Fig. 2.** Variation in the limit of forced elasticity of getinaks samples with no chemical treatment (1) and after treatment in toluene for 15 (2) and 5 hours (3).

**Fig. 3.** Variation in the limit of forced elasticity of textolite samples with no chemical treatment (1) and after treatment in toluene for 15 (2) and 5 hours (3).
by preliminary chemical treatment of the surface layer so as to reduce its resistance in the cutting zone.

The preliminary treatment produces a structure in which some of the chemical and intermolecular bonds are ruptured and the remainders are placed under stress. Thus, there is local embrittlement of a portion of the surface. The part is then subjected to machining for example, turning. In that case, the chip formation is considerable changed: the removal of cut material is primarily due to brittle failure, since the deformation forces are reduced by the embrittlement. As we know, the energy of brittle failure is considerable less than the energy required for plastic failure [3, 6]. Various defects in the vicinity of the leading deformations are formed at considerably lower stress, which promotes the nucleation of plastic shear and more stable propagation of major cracks ahead of the cutting edge along the line of action. The decrease in stress also tends to reduce the temperature in the cutting zone, which helps to reduce the roughness of the cut surface and increase the cutting speed for plastic blanks.

On the basis of this technical solution, a more advanced chemical-mechanical method [8] has been developed for turning workpieces from polymer materials. The effect of preliminary treatment with chemical reagents may be enhanced if depressions of identical size are first made in the polymer surface. The depth of the depressions must not exceed the thickness of the layer removed in cutting; the distance between the depressions, which will depend on the reagent employed and the density of the blank, must be the same over the cut surface and must ensure overlapping of the active zones of the chemical reagent, so that the reagent distribution is uniform. Such treatment results in embrittlement of the surface layer to the required depth. The duration of chemical treatment is

$$t = \frac{\rho \delta}{V},$$

where $\rho$ is the density of the material; $\delta$ is the thickness of the cut layer in one pass; $V$ is the rate of action of the reagent (determined experimentally); $K$ is the integrity coefficient of the blank’s surface.

The presence of a surface layer of constant depth and embrittlement permits improvement in quality of the cut surface, since it ensures stable propagation of the major crack ahead of the tool’s cutting edge.

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