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Nanocomposites on the Basis of Crazed Polymers

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Abstract—Analysis of published data on the mechanism of structural rearrangements in solid polymers on their crazing in liquid media is presented. The experimental evidence characterize crazing not only as a kind of spontaneous polymer dispersion under joint action of a mechanical stress and an active liquid medium, but also as the method of colloidal dispersion of low-molecular substances in a polymer. In the process of crazing, active liquid fills the porous structure of crazes, thereby transporting various low-molecular substances to the polymer volume. Crazing is believed to open the ways for preparing various nanocomposites on the basis of a wide variety of glassy and crystalline polymers, on the one hand, and target additives on the basis of practically any low-molecular substances, on the other.

INTRODUCTION

One of most important and necessary steps in creating nanocomposites is the comminution of matter to the particle size about 1 to 50 nm. By Rusanov's definition, this process is "forcible" and, therefore, very intricate and labor-consuming [1]. The main reason for the arising difficulties is that one should work against surface forces. Moreover, if one manage to comminute matter to a given level, the problem of stabilization of the resulting system arises, since the excess of free surface always tends to initiate spontaneous coagulation and/or coalescence processes.

In this context, the process of polymer crazing in liquid media can be considered as a unique phenomenon allowing one to evade the above difficulties, or, in other words, as a universal method for creating a wide variety of composites where a glassy or crystalline polymer is one of the phases. The ability to crazing is a fundamental property of solid polymers. This property is very simple to realize. It is sufficient to subject a polymer to uniaxial strain deformation in a so-called adsorption-active liquid [2]. In fact, crazing is a specific manifestation of the Rehbinder effect in polymers [3] and leads to the dispersion of a solid polymer into smallest aggregates of oriented macromolecules (fibrils) separated with cavities of approximately the same size. It is important to note that the size of fibrils and separating microcavities is about 1–100 nm, i.e. fits the phase dimension range characteristic of nanocomposites. A fibrilar-porous structure can be created only if arising micropores are filled with the surrounding liquid medium in which the polymer deformation is carried out. This actually

means that crazing not only imparts a nanoporous structure to the polymer, but also makes possible filling this structure with the low-molecular component. As a result, the polymer and the low-molecular substance, being thermodynamically incompatible with each other, turn to be dispersed to the nanometric level and, importantly, form a highly dispersed and very uniform mixture. By convention, the creation of a nanocomposite can be divided into the following stages: preparation of a nanoporous polymeric matrix, filling the matrix with a second component, and stabilization of the resulting nanocomposite.

In accordance with this scheme, we will consider some peculiarities of the development of microscopic porosity in polymers in the process of their crazing in liquid media, the methods of filling this structure with the low-molecular component, as well as the structures and properties of nanocomposites on the basis of crazed polymers and some general principles of creating such systems.

1. SPECIFIC FEATURES OF DEVELOPMENT OF NANOPOROSITY IN POLYMERS SUBJECTED TO STRAIN IN LIQUID MEDIA

According to the IUPAC classification [4], pores smaller than 2 nm in size are called micropores, pores of size within the range 2 to 50 nm are called mesopores, and pores larger than 50 nm are called macropores. It happens that the realization of all the above categories of porosity in a polymer is possible with the aid of crazing in a liquid medium. One can get a foretaste of the structure of a polymer subjected to strain in a liquid medium from the microphotograph
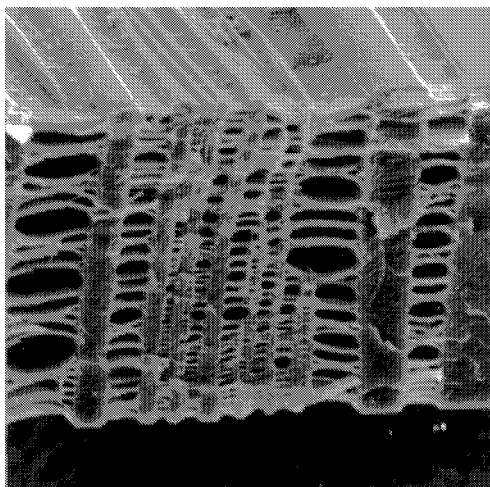
Fig. 1. SEM image of the sample of a glassy polymer strained in an adsorption-active medium. The polymer stretching axis is horizontal.

Fig. 2. Stretching curve for a polymer in an adsorption-active medium and schematic representation of individual stages of polymer crazing: (*I*) craze initiation, (*II*) craze growth, (*III*) craze widening, and (*IV*) craze collapse.

given in Fig. 1. As seen from Fig. 1, the polymer indeed acquires a porous structure. Let us consider the main features of formation of such kind of porosity.

As noted above, the phenomenon of polymer crazing is observed on mechanical loading of the polymer in special liquid media [2]. Such liquids should cause no polymer swelling (dissolution), but should effectively wet the polymer to decrease its surface energy. As a consequence, such liquids were termed adsorption-active media [5].

When a tensile stress is applied to a polymer in an adsorption-active medium, special zones of a plastically strained porous fibrilar material, crazes, arise and develop in the polymer. Due to the presence of microcavities in crazes, the whole process is easily registered and studied with the aid of direct microscopic methods [2]. Just in this way [6], the multistage nature of crazing was revealed and its relation to the mechanical response of the polymer strained. Figure 2 schematically represents the general picture of polymer crazing in a liquid medium and compares the picture obtained by direct microscopic observations with the corresponding strain curve. It is readily seen that a certain amount of crazes nucleate on the polymer surface on the first stages of polymer stretching (until the yield point, region *I* in the strain curve).

On further stretching, the crazes formed grow across the polymer strain axis and maintain their practically constant and rather small (fractions of micron) width (the stage of craze growth). This process continues until the growing crazes fill the sample cross section (region *II* in the strain curve). This moment corresponds to passing the strain curve
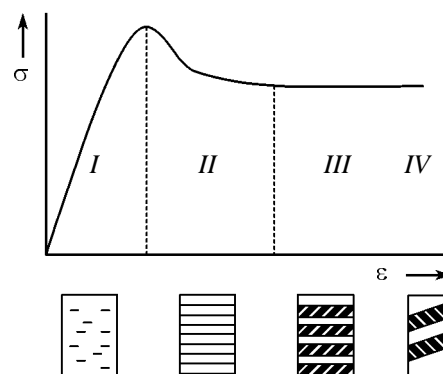
to a plateau (Fig. 2). After this, the next stage of polymer crazing in a liquid medium begins, craze widening, when the crazes, grown out over the whole polymer cross section, increase their dimensions along the polymer strain axis (region *III* in the strain curve). Herewith, obviously, there occurs the main transformation of the polymer to the oriented (fibrillar) nanoporous state.

There is one more stage of polymer crazing in an adsorption-active medium. When a considerable part of the polymer has passed to the oriented fibrillar state, collapse of the porous structure begins [7]. On this stage, the cross section of the sample strained characteristically decreases, which is accompanied by decreasing porosity [8], average pore size [9], and specific surface area [2]. In contrast with other crazing stages, this stage cannot be rigorously related to the strain curve, because its onset strain depends on the natural stretching of the polymer, as well as on the properties of the adsorption-active medium and on the geometry of the sample [10].

Let us consider the factors determining the main characteristics of the porous structure of a polymer (porosity, average pore diameter, specific surface area) on its crazing in liquid media. As follows from the aforesaid, crazing is a multistage process whose only driving force is mechanical stress. The process can be stopped on any stage by simple stress relief or, which is the same, by ceasing the strain process. As a consequence, there is a possibility of creating, in this way, an abundance of polymeric materials differing in their porous structure. Importantly, crazing endows a polymer not only with a porous structure, but also with a highly developed interface, since the structural
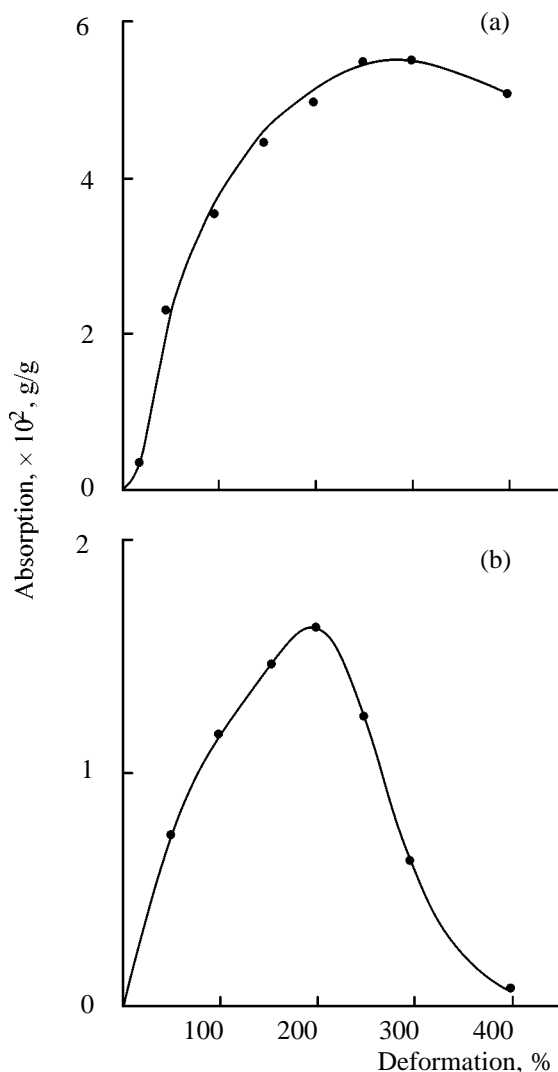
Fig. 3. Dependence of the adsorption of (a) iodine and (b) Rhodamine C from their aqueous solutions on the degree of stretching of polyethylene terephthalate in an adsorption-active medium.

units of crazes (fibrils) are of ten to hundred angstroms in diameter. Solids possessing a highly developed interface are adsorbents. Indeed, polymers subjected to stretching in an adsorption-active medium turn to be nonspecific porous adsorbents [11–13]. The fact of adsorption is in itself of undeniable interest, providing direct evidence to show that crazed polymers possess a developed interfacial area. It is still more important that adsorption enables one to characterize the porous structure of a polymer and to trace its evolution in the process of polymer stretching in an adsorption-active medium. For this purpose, in [11–13] we used sorbates with various molecular dimensions comparable with the dimen-

sions of arising pores. The results of these investigations are represented in Fig. 3 in the form of the strain dependences of the adsorption of each sorbate in polymeric samples stretched to various degrees in an adsorption-active medium. Actually, these data characterize the accessibility of the surface of pores arising on crazing for sorbate molecules of various dimensions. It is readily seen that the developing pores are accessible in the whole stretching range for the smallest of sorbates, iodine (molecular size ca. 5.4 Å). At low stretching degrees, adsorption increases with strain, since the polymer interfacial area increases in the process of crazing. Beginning with ca. 150% stretching, structure collapse begins, which is accompanied by decreasing interfacial area [2]. The collapse process influences adsorption, i.e. adsorption no longer increases with stretching. The increase in the molecular size of the sorbate to 17.5 Å (organic dye Rhodamine C) influences the dependence of adsorption on stretching degree. Beginning with ca. 150% stretching, the adsorption of Rhodamine C is seen to decrease practically to zero. Evidently, the decreasing adsorption is associated with the fact that the molecular size of the sorbate has become comparable with the pore size, and this prevents sorbate molecules from penetrating into the craze volume.

As follows from the above data, polymer crazing allows one to easily, smoothly, and widely vary the pore size, porosity, and specific surface area of the polymeric matrix. However, this not the only way of controlling the structure of polymeric matrices. Depending on the structure of the initial polymer [14], on the nature of the liquid medium [15], on the magnitude and rate of strain, and on the temperature [2], one can also easily and widely change the number and location of zones of plastically strained polymer. Moreover, nanoporosity can develop not only in local zones, crazes, but also over the whole polymer volume simultaneously (delocalized crazing [16–19]). The latter kind of crazing is characteristic of the deformation of crystalline polymers in active liquid media.

2. PREPARATION AND SOME PROPERTIES OF NANOCOMPOSITES BASED ON CRAZED POLYMERIC MATRICES

An important feature of crazing is effective filling of microcavities arising in the growing craze, with the surrounding liquid medium. In its turn, filling of the nanoporous craze structure with a low-molecular component means the comminution of the latter to colloidal dimensions. As a result, crazing allows mutual dispersion and uniform mixing of a polymer with an incompatible low- or high-molecular com-

ponent. This circumstance has the following implications in terms of creation of new types of nanocomposites.

Firstly, crazing makes possible in a simplest way (by stretching a polymer in a corresponding medium) incorporating a low-molecular substance, thermodynamically incompatible with the given polymer, into the polymer volume and comminuting the low-molecular substance to colloidal dimensions. This means that there is a new universal way to dispersion of low-molecular substances to the colloidal level, and thus a new possibility is open for investigating the properties of low-molecular substances in the highly dispersed colloidal state.

Secondly, crazing can be considered as a universal method of preparing new types of nanocomposites. Investigations into such highly dispersed polymer–low-molecular substance mixtures are an independent physicochemical problem. Investigations in this field not only facilitate understanding of many features of interaction of polymers and low-molecular components, poorly compatible with each other, but also, as will be shown below, provide additional information on the porous structure of crazes.

It is of note that crazing allows introduction of practically any low-molecular substances in polymeric structures. A necessary condition for this is a low melting point of the low-molecular component or its solubility in some adsorption-active medium. In the first case, the low-molecular compound itself can serve as an adsorption-active medium at elevated temperatures (but, evidently, not higher than the vitrifying (melting) point of the polymer strained). Stretching of the polymer in the melt of this substance results in crazing, and the porous polymer structure turns to be filled with the low-molecular component. Subsequent cooling leads to crystallization of the latter *in situ* and yields a polymeric nanocomposite with the low-molecular component crystallized in a highly dispersed state. In the second case, a substance dissolved in an adsorption-active medium is introduced to the craze volume. Subsequent evaporation of the volatile component also leads to *in situ* crystallization of the solute. In this case, evidently, low-molecular substances with practically any melting points can be introduces to the craze volume [20, 21].

Both of the above ways imply direct incorporation of low-molecular substances in the craze volume. Therefore, in what follows we lump them together as the direct method.

Evidently, there are also many substances that cannot be incorporated into a polymer by crazing by the above method. For example, such inorganic substances as metals, many their salts, oxides, etc. In this case, the above polymer–low-molecular substance mixtures are obtained via chemical reactions of corresponding precursors directly inside the porous structure of crazes (*in situ*). Hereinafter, we call this method of preparing nanocomposites the indirect method of incorporating low-molecular substances into the craze structure.

2.1. Direct Method of Preparing Nanocomposites by Polymer Crazing in Liquid Media

The first investigation on the incorporation of low-melting substances in polymers by crazing was performed on the example of the system amorphous polyethylene terephthalate–*n*-octadecane (mp 28°C) [22]. The polymer was stretched in the medium of liquid octadecane at 50°C and cooled in the clamps of the stretching device. As a result of this procedure, octadecane, being an effective adsorption-active medium, fills the porous craze structure and then crystallizes in the polymeric matrix. In this way, nanocomposites with 50 wt % and more contents of the low-molecular component are available. The amount of incorporated low-molecular component depends on the evolution of the porous structure of the polymer in the course of its stretching in the adsorption-active medium (Figs. 2 and 3). Irrespective of the degree of stretching, the low-molecular component turns to be dispersed in the smallest aggregates not exceeding, evidently, the pore size in the crazed structure (ten–hundred angstroms). The preparation of the above nanocomposites not only opens the prospects of creating a new class of promising materials, but also makes possible investigations into the properties of matter in a highly dispersed, colloidal state. We now consider some results of such investigations.

2.1.1. Characteristics of phase transitions in low-molecular substances incorporated into the craze volume. Figure 4 show typical calorimetric curves for crystallization of octadecane in the free state and incorporated in the porous structure of polyethylene terephthalate. It is readily seen that the free hydro carbon crystallizes at 24°C, which gives rise to an asymmetrical exothermic peak. The latter circumstance is probably caused by the known, for saturated hydrocarbons, transition from the orthorhombic to hexagonal packing in the melting region [23]. At the same time, octadecane incorporated in the polymeric matrix exhibits earlier unknown peculiarities in thermophysical properties. As seen from Fig. 4 (curve *2*), crystallization proceeds as if in two stages. The
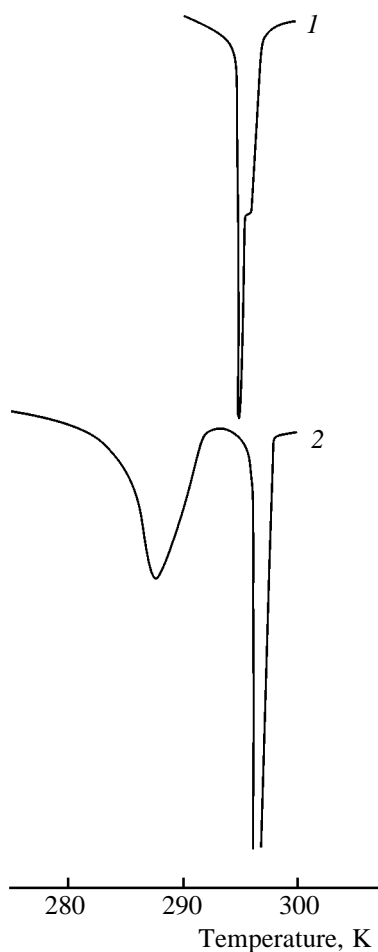
Fig. 4. DSC curves for crystallization of (*1*) free octadecane and (*2*) octadecane incorporated into polyethylene terephthalate crazes. The degree of stretching of polyethylene terephthalate in octadecane is 50%.

Fig. 5. Dependence of the weigh loss of a sample of polyethylene terephthalate containing octadecane incorporated by crazing in the course of sample washing with heptane.

transition coinciding in temperature with the corresponding transition in the free octadecane is observed first. Then an exothermic peak is observed at a temperature by 6–8°C lower than the melting point of the free octadecane. It is readily seen that the main contribution (~80%) to the crystallization heat originates from the broad low-temperature peak.

The reasons for the above difference can be revealed by studying the process of elution of octadecane from the porous structure of polyethylene terephthalate. Figure 5 represents the dependence of the relative weight loss a polyethylene terephthalate sample containing octadecane on the time of washing the sample with hexane. It is readily seen that a considerable part of the incorporated octadecane is actually washed out, but its large amount still remains inside the polymer. Fig. 6 shows the calorimetric
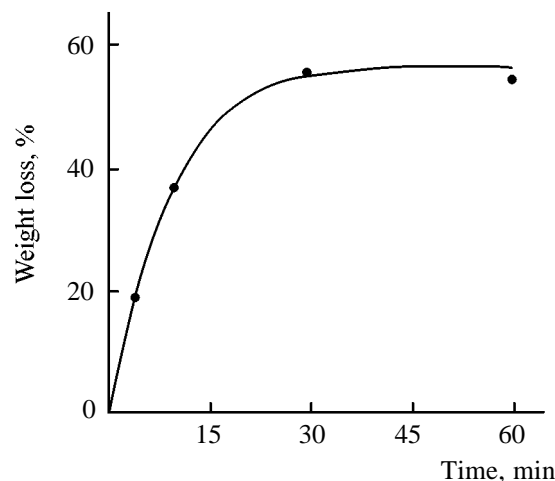
crystallization curves for polyethylene terephthalate samples subjected to washing with hexane for various time. As seen, that part of the incorporated octadecane is washed out, whose crystallization point coincides with the crystallization point of the free octadecane (Fig. 6, curves *1* and *2*). Further washing gradually leads to extraction from the polymer of the part of octadecane, responsible for the broad low-temperature crystallization peak (Fig. 6, curves *2–7*). Although long washing leads to complete disappearance of temperature transitions in the system polyethylene terephthalate–octadecane and also to disappearance of the corresponding X-ray reflexes, a significant fraction of the hydrocarbon remains in the polymer (Fig. 5).

Evidently, the high-temperature crystallization peak is related to a small amount of octadecane residing in microscopic hollows or big pores of the sample surface. Naturally, this part of octadecane does not differ noticeably in thermophysical properties from the free octaecane (cf. Fig. 4a and Fig. 6). The broad high-temperature crystallization peak is evidently related to the part of octadecane residing directly in the porous structure of polymer crazes. The lowering of the crystallization temperature is caused by the fact that the transition temperature depends on the size of the nucleus. According to the formal theory of nucleation, the smaller the nucleus size or the new phase area, the lower is the crystallization temperature. The lowering of the crystallization temperature can be used to estimate the size of the characteristic nucleus of the free octadecane. From DSC data, this value was estimated at 165 Å. The nucleus size turned to be

appreciably larger than the size of the most part of pores in the structure of polyethyleneterephthalate strained in an adsorption-active medium. The dimensions of the crystallizing phase are confined by pore walls and are smaller than the nucleus of the free octadecane. As a result, the crystallization temperature of the substance dispersed to such small aggregates noticeably decreases. The pore sizes in the polymer varies over a wide range, as judjed from the fact that the low-temperature crystallization peak is extended along the temperature scale. This circumstance allows the discovered phenomenon to be used for estimating pore size distribution for a polymer strained in a given adsorption-active medium. The algorithm of such calculations is given in [22]. The results of these calculations are represented in Fig. 7 as the pore size distributions for polyethylene terephthalate samples stretched in octadecane by 50 and 400%. It is readily seen that increase in the polymer stretching degree results in an appreciable decrease in the effective pore radius as determined from the lowering of the crystallization temperature. This result corresponds to the notion of the evolution of the porous structure of a polymer in the process of its strain in an adsorption-active medium, deduced above from other experimental evidence (Figs. 2 and 3).

However, the distribution curves obtained are evidently unable to describe the polymer porous structure exhaustively. As follows from Figs. 5 and 6, a considerable amount of octadecane remains in the samples after washing, when thermophysical transitions and X-ray reflexes are no longer observed. The fraction of unextractable octadecane increases with stretching degree and attains a significant value (~25%) [22]. This finding show that a polymer stretched in an adsorption-active medum to high degrees still contains much internal microcavities inaccessible for the solvent. As a result, the incorporated low-molecular substance cannot be extracted from the polymer. Such a structure is formed by craze collapse (Fig. 2.) At the same time, the microcavities are so small that octadecane resing in them cannot form an extended crystalline phase, and, therefore, its phase transitions are not registered in thermograms. The corresponding X-ray patterns lack X-ray reflexes characteristic of the crystal structure of octadecane. In other words, a part of the low-molecular component resides in so small pores that it cannot form an extended crystalline phase. An interesting possibility appears to determine the size of a molecular aggregate below which the thermodynamic notion of phase does not apply. As follows from Fig. 7, that size is about 25 Å in the case of octadecane.
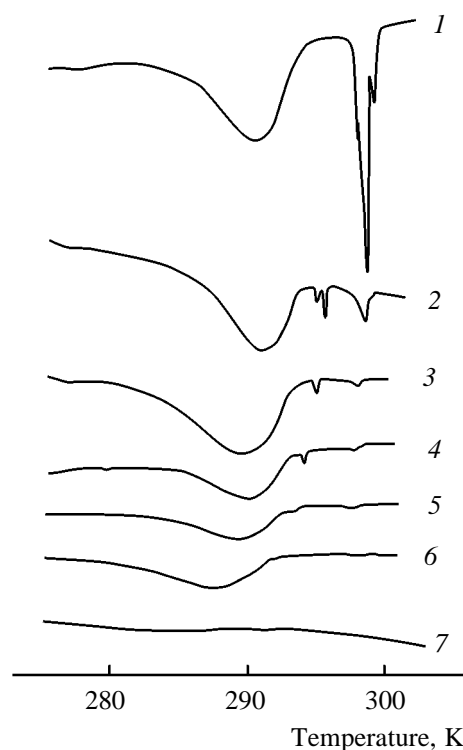

Fig. 6. Thermograms of polyethylene terephthalate samples containing octadecane after washing with heptane for (*1*) 0, (*2*) 5, (*3*) 10, (*4*) 15, (*5*) 20, (*6*) 30, and (*7*) 60 min.
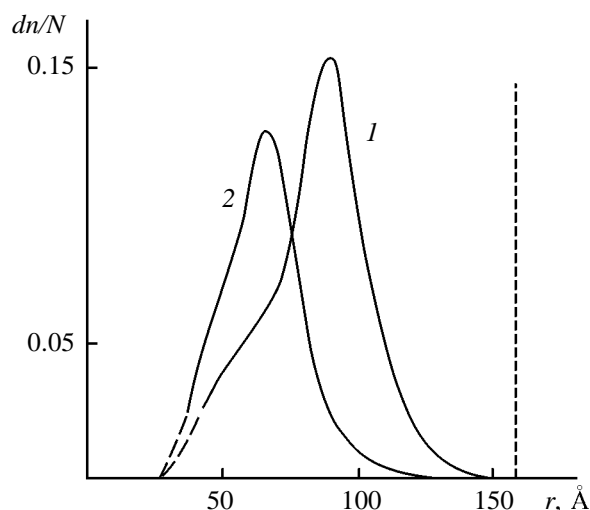

Fig. 7. Pore size distribution in polyethylene terephthalate samples strained in octadecane by (*1*) 50 and (*2*) 400%. The dashed line shows the size of the critical nucleus of octadecane in the free state.
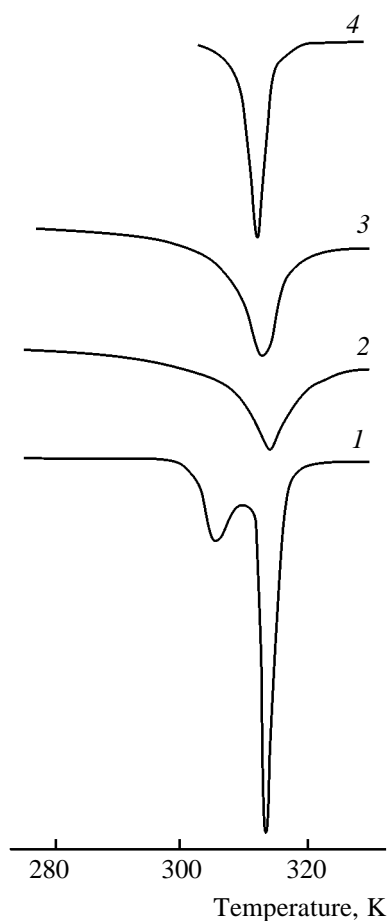
Fig. 8. DCS curves for melting of geneicosane in (*1*) the free state and in crazed samples of (*2*) high-density polyethylene, (*3*) Polyamide-6, and (*4*) polyethylene terephthalate.

Further investigations showed a general character of the above peculiarities of phase transitions of low-molecular substances in crazed polymeric matrices. Such peculiarities (broadened phase transitions and their shift to the low-temperature region) are observed for various low-molecular substances (hydrocarbons and fatty acids and alcohols) and various crazed polymers (polyethylene terephthalate, high-density polyethylene, polypropylene, Polyamide-6, polytetra-fluoroethylene, polymethyl methacrylate, and poly-vinyl chloride) [24–30]. Evidently, such a generality of the above phenomena is caused by structural peculiarities of the fibrillar-porous structure of crazes. It is of note that these peculiarities are observed for polymers subjected both to classical and delocalized crazing. The matter is that, in this case, not the morphological peculiarities of the polymer porous structure, but the absolute size of pores is of decisive significance. For both the kinds of crazing, the pore

size lies within 10–500 Å, i.e. in the range of typical colloidal dimensions. This just determines the main specific features of phase transitions of low-molecular substances in such systems.

The above characteristics of the thermophysical behavior of low-molecular substances in the structure of crazes are not unique. Crystallization in narrow pores has its own peculiarities for substances able to polymorphous transitions. The phase composition of low-molecular compounds incorporated into porous polymeric matrices was investigated by differential scanning calorimetry [27, 29]. Figure 8 displays the DSC curves for the normal hydrocarbon geneicosane in the free state and incorporated in crazes of a number of polymeric matrices. The two peaks in the DSC curve (curve *1*) relate to the polymorphous transition of geneicosane from the R to A modification. Curves *2–4* show a single broad high-temperature peak associated with melting geneicosane in a polymer. Therefore, one can conclude that geneicosane in various polymeric matrices in present exclusively in the high-temperature R modification. Similar results, confirming the existence of a high-temperature modification of a low-molecular compound in crazes, were also obtained for tridecanoic acid and cetyl alcohol [27, 29]. In all the cases, the substance, incorporated in the polymer porous structure, is in a high-temperature modification that is unstable for the same substance in the free state.

The high stability of the modifications of low-molecular compounds, unstable in the free state, can be explained by the high dispersity of microporous structures. In micropores, polymorphous transformations can proceed only within the temperature range where the radius of the critical nucleus of the low-temperature phase is smaller or equal to the pore radius. If the temperature satisfying this condition do not fit the temperature range where the rate of formation of a new phase is high enough, no polymorphous transitions occur, and the only product is a high-temperature modification of the low-molecular compound.

Low-molecular compounds crystallized in the micropores of crazed oriented polymeric matrices are in a highly dispersed state. Therefore, phase transitions in such systems should be analyzed in terms of surface components of thermodynamic functions (free energy, enthalpy, and entropy). We represent the thermodynamic functions of a low-molecular compound as a sum of bulk and surface components and take into account that the specific surface area of a system does not change on polymorphous transforma-

tion of the low-molecular compound in polymeric micropores. Then it is easy to obtain equations describing the variation of specific surface components of thermodynamic potentials at the polymer–low-molecular substance interface, as well as the dependence of thermodynamic parameters of melting of the low-molecular compound on nucleus size (size of confining pores).

It is of note that not only the process of melting of a low-molecular substance, but also its crystallization in the porous polymeric structure depend on the pore size of the polymeric matrix. This fact was convincingly proved by the results of a DSC study of melting and crystallization of tridecanoic acid in polytetrafluoroethylene crazes (Fig. 9). Crystallization of the low-molecular substance in polymeric pores proceeds at temperatures when the critical nucleus becomes equal to the pore radius. In this case, the critical nucleus size can also be estimated from experimentally determined thermodynamic parameters of phase transitions of a low-molecular substance in polymeric matrices and in the free state.

To check the applicability of the above thermodynamic approach for description of phase transitions of a low-molecular substance in the porous structure of polymeric matrices, we determined parameters of crazed structure (pore and fibril size) by small-angle X-ray scattering. Table 1 compares these results with DSC data [30, 31]. As seen, there is a good correlation between values obtained by the two methods. This is convincing evidence for the applicability of the thermodynamic description of phase transitions of low-molecular substances in polymeric crazes.

2.1.2. Orientation effects on crystallization of low-molecular substances in the craze volume. The above peculiarities of thermophysical properties of low-molecular compounds incorporated into the structure of crazes are caused by the specificity of crystallization of low-molecular substances in narrow (1–30 nm) pores. Such a small pore size is not the only peculiarity of the craze structure. It is very important that there an almost parallel arrangement of fibrils in the craze structure (Fig. 1). This means that narrow asymmetric pores that separate fibrils, too, turn mutually are oriented with respect to the polymer stretching axis. The pronounced asymmetry of the craze structure should also influence the process of crystallization of a low-molecular substance in the craze volume.

This influence was discovered by an X-ray diffraction study of numerous crazed polymer–low-mole-
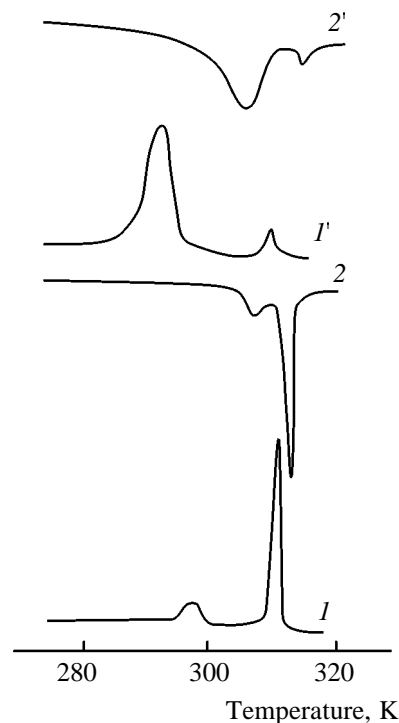
Fig. 9. DSC curves for (*1, 1'*) crystallization and (*2, 2'*) melting of tridecanoic acid in (*1, 2*) the free state and (*1', 2'*) in polyethylene terephthalate crazes.

cular filler systems [20, 21, 31]. It was found that, irrespective of the polymer and the substance to be incorporated and crystallized, the low-molecular substance always crystallizes to form highly ordered textures. The X-ray patterns of such substances resemble those usually obtained for single crystals. This phenomenon is of a general character and is observed with crystallizable (polyethylene terephthalate, polycarbonate) and amorphous (atactic polymethyl methacrylate) crazed polymeric matrices [20, 21]. All the above characteristics are preserved when crazed polymeric matrices incorporate both ionic and molecular crystals.

Although the orientation of low-molecular substances in the craze structure is observed in all cases, the type of orientation depends on the nature of the polymer–low-molecular substance pair. A great number of nanocomposites was investigated [24–31], on the example of a number of crazed polymers, on the one hand, and dispersed long-chain fatty alcohols, hydrocarbons, and acids, on the other. Such compounds crystallize with formation of ordered layers, which makes their X-ray patterns easier to interpret.

Analysis of the X-ray patterns showed that the set

Table 1. Parameters of the porous structure of crazed polymers

System	Diameter of fibrils, nm	Diameter of pores, nm	
		small-angle X-ray scattering	differential scanning calorimetry
Polyethylene terephthalate/geneicosane	8.0	6.0	6.5
Polyethylene terephthalate/tridecanoic acid	10.5	7.0	5.0
Polycarbonate/tridecanoic acid	29.0	7.0	5.0
Nylon-6/acetyl alcohol	8.3	4.6	7.0

ofpoint reflexes located at the meridian, equator, or diagonal can be assigned to X-ray scattering from oriented layer planes [29]. The character of packing of asymmetric molecules in oriented craze pores and the corresponding X-ray reflexes are represented in Fig. 10. The normal and parallel orientation of layer planes of low-molecular substances with respect to the polymer stretching axis are designated as ⊥ and ||, respectively. The oblique order of layer planes of *n*-carboxylic acids is designated as ∧. Table 2 represents the layer spacing and the character of orientation of low-molecular substances in pores of various polymers. The corresponding data for the same substances in the free state are also given for comparison.

It follows from Table 2 that all the low-molecular substances studied are oriented when crystallized in polymeric matrices. The layer orientation in the linear hydrocarbon geneicosane and in cetyl alcohol is perpendicular or parallel to the polymer stretching axis (and to the pore direction, Figs. 10a, 10b, and 10d). Long-chain acids exhibit both parallel and oblique orientations of crystalline layers (Fig. 10c).

Orientation of low-molecular substances on their crystallization in low-molecular substances in the narrow (~10 nm) asymmetric pores of crazed polymeric matrices is mainly determined by the thermodynamic stability of the ordered state as compared with chaotic. The intercrystallite surface energy is a minimum on ordering of crystallites of a low-molecular substance in crazes. The character of orientation of low-molecular substances in polymeric matrices is determined by the minimum surface free energy at the polymer–low-molecular substance interface.

As shown in [31, 32], there is a certain factor that determines parameters of the crystal lattice of a low-molecular substance in a polymeric matrix. This factor is related to the existence of internal stresses in crazed polymers. Importantly, the magnitude and direction
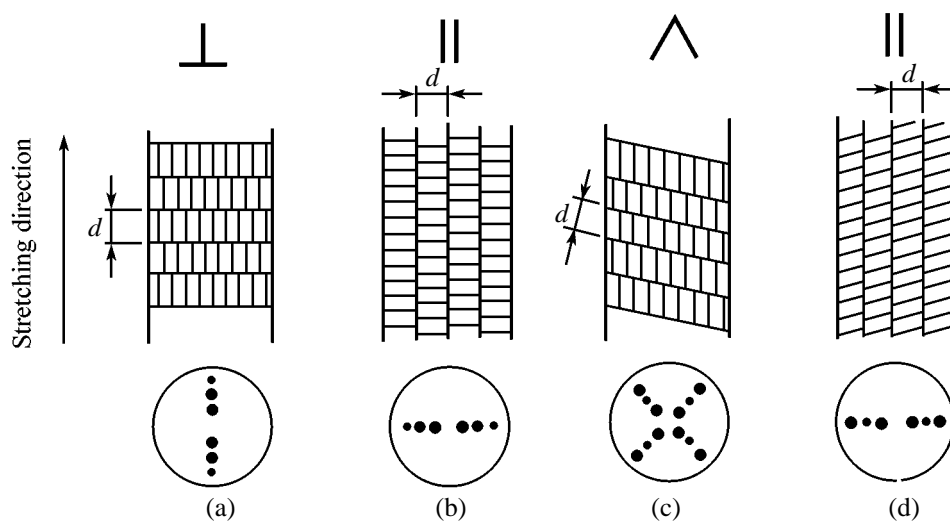

Fig. 10. Layer orientation in (a, b) geneicosane and cetyl alcohol and (c, d) carboxylic acids in pores of polymeric matrices and arrangement of the corresponding reflexes in X-ray patterns.

Table 2. Orientation and phase composition of low-molecular substances in crazed polymeric matrices

Low-molecular substance	Polymeric matrix	Orientation	Layer spacing, $d \times 10$ nm	
			in polymer	in free state
Geneicosane	High-density polyethylene	⊥	28.8	
	Polytetrafluoroethylene	⊥	28.6	
	Polypropylene	⊥	28.7	
	Polyethylene terephthalate	⊥	28.8	28.65 (A)
	Nylon-6	⊥	28.8	28.92 (R)
	Polycarbonate	∥	28.5	
	Polyvinyl chloride	∥	28.6	
Cetyl alcohol	High-density polyethylene	⊥	45.5	
	Polytetrafluoroethylene	⊥	45.4	37.37 (γ)
	Polyethylene terephthalate	⊥	45.4	43.83 (α)
	Nylon-6	⊥	4.54	44.9 (β)
	Polycarbonate	∥	4.54	
Undecanoic acid	High-density polyethylene	∧	26.1	25.68 (C')
	Polytetrafluoroethylene	∥	25.9	30.16 (A')
	Polycarbonate	∥	26.1	
Dodecanoic acid	High-density polyethylene	∧	27.7	
	Polypropylene	∧, ∥	27.7	31.2 (A)
	Polyethylene terephthalate	∧, ∥	27.7	27.42 (C)
	Polycarbonate	∥	27.7	
Tridecanoic acid	High-density polyethylene	∧	30.1	
	Polytetrafluoroethylene	∧	29.8	
	Polypropylene	∧, ∥	30.0	
	Polyethylene terephthalate	∧, ∥	30.1	35.35 (A')
	Nylon-6	∧	29.7	30.0 (C')
	Polycarbonate	∥	29.7	
	Polyvinyl chloride	∥	29.8	
	Polymethyl metacrylate	∥	29.8	
Pentadecanoic acid	High-density polyethylene	∧	35.5	40.2 (A')
	Polypropylene	∧, ∥	35.7	35.8 (B')
	Polyethylene terephthalate	∧, ∥	35.6	34.4 (C')
	Polycarbonate	∥	35.8	

of stresses determine strains of the crystal lattice of the low-molecular substance inside the craze volume.

The orienting effect of the highly developed craze structure shows up not only in the process of crystallization of ordinary low-molecular substances. This effect is also observed in phase transitions in liquid-crystalline compounds. As shown in [33], n-butoxybenzylideneaminobenzonitrile is also orinted in the narrow pores of polymeric crazes. This orientation is clearly detected by infrared dichroism.

Thus, crystalline and liquid-crystalline substances, incorporated into the porous structure of crazed polymeric matrices, are oriented with a high degree of ordering changing reversibly on phase transitions.

2.2. Indirect Method of Incorporating Low-Molecular Substances in Craze Structure

Thus, we have considered some characteristics of crystallization of low-molecular substances in the nanoporous craze structure. As was noted above and for the above reasoning, only a restricted number of low-molecular substances can be incorporated into the craze volume by the direct method. Evidently, substances insoluble in an adsorption-active medium and not melting below the vitrification (melting) point of the polymer under strain, cannot be incorporated into the craze volume by the direct method. Nevertheless, it is nanocomposites based on polymers containing metals, semiconductors, ferroelectrics, and other target additives wich are of undoubted practical interest. In

this connection, methods for preparing nanocomposites via chemical reaction of corresponding precursors directly in a polymeric matrix (*in situ*). In fact, micropores in the craze structure can be used in this case as microreactors for synthesis and stabilization of nanophases of a necessary level of dispersity and morphology. The formation of nanosized cavities makes possible their utilization as microreactors for performing chemical reactions (reduction, exchange, etc.) This approach solves such fundamental problems of nanocomposite synthesis as stabilization of nanophases due to the confining factor of walls and mixing of thermodynamically incompatible components on the nanometric scale.

The first attempt of realizing an *in situ* chemical reaction in the structure of a crazed polymer was undertaken in [21]. In that work, a classical photographic process was effected in crazed polyethylene terephthalate [21]. For this purpose, a polyethylene terephthalate film was stretched in an aqueous-alcoholic solution of potassium iodide. As a result, 25 wt% of potassium iodide was incorporated into the film. Then the film was placed in an aqueous-alcoholic solution of silver nitrate. This resulted in the formation of silver chloride crystals in the polymer structure. Finally, the sample was exposed in a standard developing solution. This treatment led to the decomposition of silver chloride to metallic silver. All the stages of the process were controlled by X-ray diffraction. A specific feature of this process is that the low-molecular is gradually completely disorientated in reactions in situ. For example, if, on the first stage, potassium iodide crystallizes to form a good texture, silver chloride is only slightly oriented on the second stage of the process, and the silver formed on the last stage is absolutely isotropic.

The above method of incorporating metal into the craze structure is restricted with respect to filling the craze volume with the low-molecular component. Indeed, as the concentration of the solution of an inorganic substance, filling the porous structure of a polymer increases, the content of the low-molecular component after removal of the solvent increases [34]. Evidently, the polymer porous structure is impossible to fill completely in this way, as it happens when a polymer is stretched in the melt of a low-molecular substance. The amount of the inorganic component does not exceed 30–50 wt% even with very readily soluble substances, for example, with potassium iodide in aqueous alcohol [34]. According to electron microscopy data, even the case of a saturated solution of potassium iodide, the larger part of the craze structure turns to be not occupied with the low-molecular component.

At the same time, it is well known that the porosity developing in the process of polymer stretching in an adsorption-active medium can be very high. Glassy polymers in liquid media are often uniaxially strained so that changes in the geometrical dimensions of the sample are associated almost exclusively with development of porosity, whereas the contribution of other kinds of deformation is negligible. Simple estimates show complete pore filling in a sample stretched in this way by 100%, with a low-molecular substance with a specific weight of 3 g/cm^3 should yield a weight gain of 300% with respect to the initial weight of the polymeric matrix.

To overcome the above contradiction and attain high degrees of filling the polymer porous structure with an inorganic substance, one may invoke the mutual diffusion method described in detail in [35]. This way of incorporating a low-molecular substance is principally different from the above one. A crazed polymeric film, i.e. a film with a permeable porous structure, is placed as a membrane in a dialysis cell. The compartments on both sides of the membrane are filled with solutions of components able to interact with each other. In this case, low-molecular substances will diffuse to each other and meet just in the membrane pore volume. Therefore, the chemical reaction will occur in pores, which makes possible to fill them more effectively than in could be done in [20, 34].

This method was again illustrated with a classical photographic process in [20]. Crazed polyethylene terephthalate was placed in a dialytic cell filled with an aqueous-alcoholic solution of silver nitrate, on the one hand, and with a sodium chloride solution, on the other. The film was taken off after 24 h, washed with water, dried, and examined by means of scanning electron microscopy.

It was found that the process of segregation of the low-molecular component in this case is quite different from those considered above. Electron microscopy showed that close to the middle of each craze there is a single crystal of silver chloride 15 μm in height and equal in width the distance between walls of a craze. Thus, one can indeed manage to sufficiently effectively fill the craze volume with a low-molecular inorganic substance.

In the same work, the photographic process in a polymeric matrix could be accomplished, i.e. silver chloride was decomposed completely to metallic silver. For this purpose, a sample of polyethyleneterephthalate was transferred to a standard developer and kept for two days. Then the sample was dried and studied by electron microscopy.

Treatment of silver chloride with the developer actually leads to segregation of fine crystals of metallic silver in the craze volume. Such crystals possess a looser structure as compared with the silver chloride crystals from which they are formed. At the same time, the decomposition of silver chloride gives insight into the problem of interaction of the growing crystal with the fibrillar craze structure. According to electron microscopy data, silver crystallites are deposited on individual craze fibrils to form, in some cases, a bed-like structure.

Subsequently, the mutual diffusion method was repeatedly used for creating various nanocomposites on the basis of a number of polymers (polypropylene, high-density polyethylene, Polyamide-6, etc.), on the one hand, and metals and oxides, on the other [36–43]. In particular, metal polymers were obtained by mutual diffusion of salts of corresponding metals and of a reducing agent, for example, a solution of sodium borohydride. It was shown that the elaborated method is universal and allows preparation of various nanocomposites. Such nanocomposites can be conductors and semiconductors produced in the form of films with excellent mechanical properties characteristic of initial polymeric matrices. The resulting composites exhibit a great variety of morphological forms. In particular, metallic nickel forms spherical crystallites 0.2–0.3 μm in size in a polypropylene matrix. One can easily regulate not only the total content, compactness, and dispersity of the low-molecular dispersed phase, but also location inside the polymeric phase. Some possible variants of location of a low-molecular phase inside a polymeric film are schematically represented in Fig. 12.

In addition to the considered above, there is one more universal method of segregation of metals from their compounds: electrolysis. This method was applied to preparing mixtures of polymers and metals
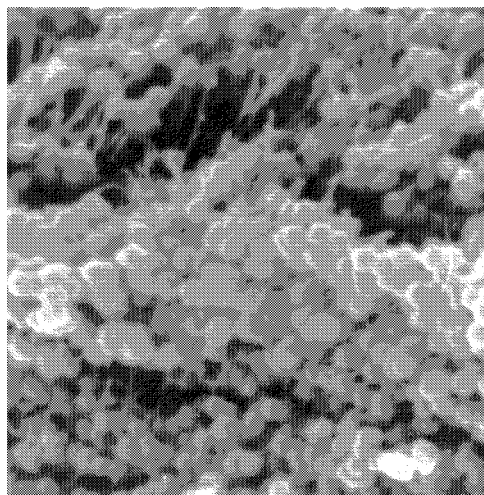

Fig. 11. SEM image of crazed polypropylene containing 85% of nickel introduced by the mutual diffusion method.

with using crazed polymeric matrices [44]. The procedure of electrolytic preparation of metal polymers is as follows. A crazed polymeric film is placed on a graphite cathode of a special electrochemical cell filled with a solution of a metal salt. Controlled voltage is generated with the aid of one more electrode placed in the same solution. Since the cathode is covered with a thin porous polymeric film, the metal is deposited in the pore volume of the polymeric matrix. In this way, crazed polymeric matrices (polyvinyl chloride, polyethylene terephthalate, high-density polyethylene, polypropylene, etc.) filled with various metals (copper, nickel, iron, cobalt, silver, etc.) were prepared. The amount of the metal deposited can be controlled by changing the duration of electrochemical reduction or by changing the porosity of the initial polymeric matrix. Depending on the crazing type [16–19], metal particles can be located in separate narrow regions, crazes, or can form a highly
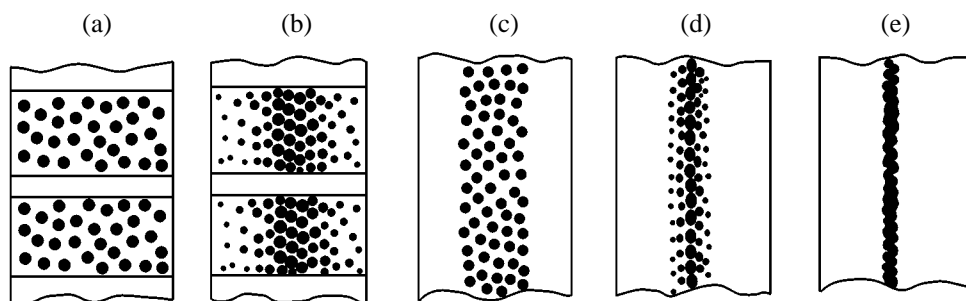

(a) (b) (c) (d) (e)

Fig. 12. Possible distributions of a low-molecular component in crazed polymeric matrices obtained by (a, b) classical and (c, d, e) delocalized crazing by the mutual diffusion metod at various experimental conditions (reagent concentrations, temperature, viscosity of the medium).
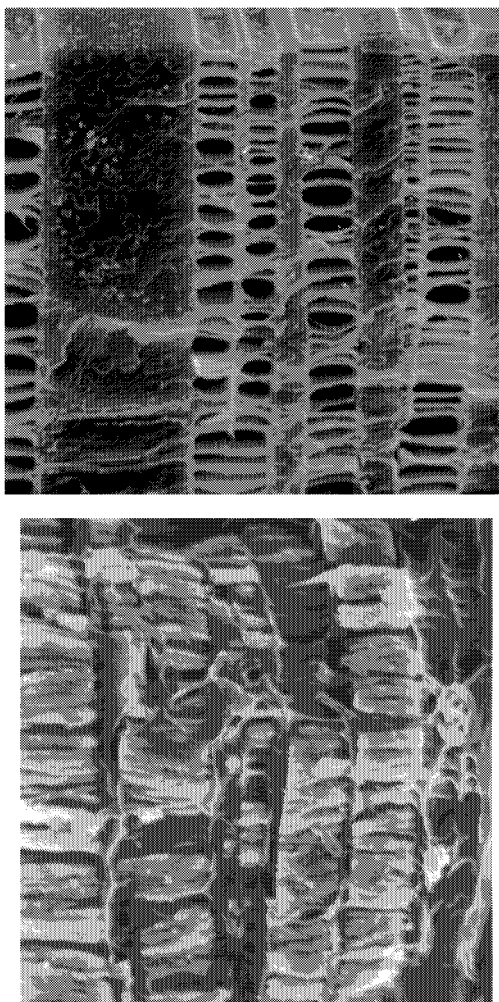
Fig. 13. SEM image of (a) a sample of crazed polyethylene terephthalate and (b) the same sample with metallic copper incorporated by the electrochemical deposition method.

dispersed continuous phase inside the polymeric matrix. Figure 13 exemplifies the electronic micro-photophotographs crazed samples of polyethylene terephthalate (a) before and (b) after treatment in an electrochemical cell. It is readily seen that in this way one can fill the porous structure of the crazed polymer from one film surface to the other. As in the mutual diffusion metod, the metal in the craze volume is not monolithic but is dispersed in the polymeric matrix. As was noted above, the pore size determining the size of the metallic phase is ten to hundred angstroms.

Thus, as follows from the data presented, there is a principal possibility of filling a crazed porous polymeric matrix with any target additives in a highly dispersed state. The amount of incorporated matter can be more than 300 wt % with respect to a relatively unfilled polymeric matrix. The preparation of such composites opens the way to creating new kinds of combined materials on the polymeric basis.

In conclusion, we note one more important circumstance emphasizing the prospects of creating nanocomposites with use of polymer crazing in liquid media. The matter is that crazing is actually one of the kinds of inelastic plastic deformation. Such deformation forms the basis of a technological operation widely used in production of polymeric fibers and films, orientational polymer stretching. Because of the importance of this process, orientational polymer stretching is realized on a high-quality technological equipment. At the present time, there are numerous highly efficient apparatus in industry for orientational stretching of films and filaments, operating in a continuous mode. In this connection, there have been repeated and successful attempts [45, 46] to effect continuous polymer crazing. In other words, there is a principal possibility of obtaining nanocomposites in the form of polymeric films and filaments having, on the one hand, good mechanical characteristics and, on the other, various valuable properties (conductance, incombustibility, electrostatic properties, etc.) imparted by target additives. Importantly, such nanocomposites can be made on the existing technological equipment, in a continuous mode, and with high speeds characteristic of the production of polymeric films and filaments.

CONCLUSION

The presented experimental evidence shows that crazing is not only some kind of spontaneous disperga-tion of polymers under joint action of a mechanical stress and of an active liquid medium. Crazing also is the method of colloidal dispersion of low-molecular substances. In the process of crazing, the active liquid fills in the porous structure of crazes and transports various low-molecular substances into the polymer volume. As a result of colloidal dispergation, low-molecular substances acquire specific properties. The temperature and extention of phase transitions, as well as the temperature ranges of stability of one or another polymorphous modification change in such substances. Of especial interest is the ability of low-molecular substances incorporated into the craze volume to orientation with respect to the polymer stretching axis. Such orientation is universal and is determined by the character and intensity of interaction of the low-molecular substance with the polymeric matrix. Crazing opens new possibilities for preparing highly dispersed nanocomposites on the basis of a wide range

of polymers with various low-molecular substances, such as metals, oxides, and salts, as well as with other polymers. The work on production of nanocomposites on the basis of crazed polymers is at the beginning of intensive development. However, one can already predict promising prospects.

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