

A New Approach to the Preparation of Nanocomposites Based on a Polymer Matrix¹

A. L. Volynskii and N. F. Bakeev

Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia
e-mail: volynskii@mail.ru

Abstract—A new approach to the preparation of nanocomposites is advanced. This approach includes preliminary formation of a nanoporous matrix and subsequent loading of the formed pores by the second component. These advantageous opportunities are provided by one of the most fundamental phenomena of the physical chemistry of polymers: solvent crazing of polymers in the presence of the liquid media. Several examples illustrate that solvent crazing not only provides a universal means of self-induced dispersion of a polymer material into nanoscale aggregates but also offers a universal route for the delivery of diverse low-molecular-mass compounds to the nanoporous structure of the solvent-crazed polymer. The results on the preparation of new types of nanomaterials, such as porous polymeric sorbents, polymeric separation membranes, new types of polymer–polymer nanoblends, fireproof and conducting polymer nanocomposites, and metal-containing polymers, are reviewed. Some aspects of the practical application and technological design of solvent crazing of polymers as a means for the preparation of diverse nanocomposites are discussed.

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INTRODUCTION

In recent years, problems related to the preparation of diverse nanocomposites have been discussed widely [1–3]. The progress in this direction has served as a basis for the development of various industrial sectors.

One of the aspects in this direction is the development of new scientific approaches to the preparation of nanocomposites based on a polymer matrix. The number of scientific publications on this challenging problem has increased in an avalanche-like manner. Note only a few of such publications that summarize earlier studies [4–6].

In the most general case, the problem related to the preparation of a nanocomposite based on a polymer matrix includes introduction of a second component (in some versions, several components) of a different chemical nature into a polymer. The problem of the introduction of modifying additives (thermodynamically compatible and thermodynamically incompatible) into polymers was known long ago and has been solved with varying success by modern chemical technology. Introducing a compatible additive into a polymer is simple. In essence, this compatible additive serves as a solvent for a given polymer. Such additives spontaneously penetrate into the polymer sample and become uniformly distributed throughout its volume, thus forming a true solution. However, compatible

additives introduced into polymers critically decrease such important characteristics as hardness, strength, and mechanical-impact resistance. In other words, although an additive can impart desired functional characteristics (for example, fire retardancy or antibacterial characteristics) to the polymer, the resultant material cannot be processed into any valuable articles (e.g., a film or a fiber) with fair mechanical characteristics.

The introduction of incompatible additives into polymers likewise creates serious problems from the viewpoint of preparing final products with optimum desired characteristics. Such an additive is called an incompatible additive because its penetration into the polymer is prohibited. If an attempt is made to implement compatibilization by force, work against surface forces is performed. For example, the combined grinding of an additive and a polymer in a grinder (an extruder) does not always result in the preparation of a uniform mixture of dispersed components with a high level of mutual dispersion. In this case, an incompatible additive tends to collect into long and randomly distributed inclusions within the volume of the polymer sample. This challenging problem becomes critical for the preparation of so-called “volume-free” articles, such as films or fibers.

In this context, studies focused on solving the above challenges have acquired the utmost importance. This paper presents a brief survey of our studies devoted to the development of basic physicochemical fundamentals of a new universal method for the preparation of nanocomposites based on a polymer matrix.

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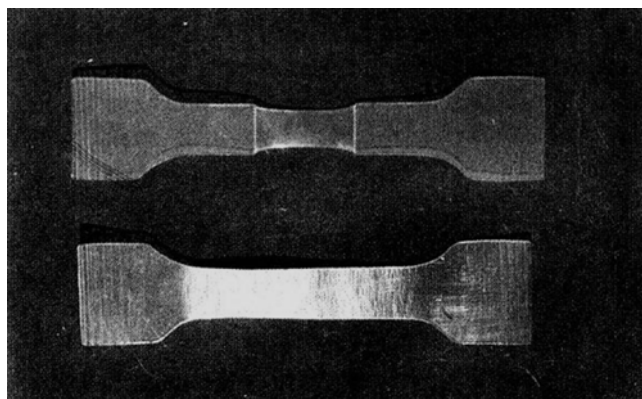


Fig. 1. Visual appearance of the polymer samples (upper image) after stretching in air and (bottom image) in the AALM.

SOLVENT CRAZING AS A BASIS FOR DEVELOPMENT OF A METHOD FOR PREPARATION OF NANOCOMPOSITES BASED ON A POLYMER MATRIX

In the case of nearly incompatible components, the preparation of a nanocomposite includes grinding at least one of the components down to nanoscale dimensions, mixing of the components of the system to form a homogeneous mixture, and stabilization of this mixture to prevent its spontaneous separation into the initial components due to their thermodynamic incompatibility. If all the above-listed procedures are successfully completed, valuable physicochemical characteristics of the matrix polymer can be preserved and the introduced additive can impart the desired functional characteristics (e.g., fire retardancy, antibacterial characteristics, electrical conductivity) to the final product. However, this physicochemical problem is very complicated and its solution requires substantial challenges to be overcome.

This problem can be solved by means of an alternative approach that includes preliminary preparation of a nanoporous polymer matrix and its subsequent or parallel loading with the second component. Long ago, several steps in this direction were made via utilization of one of the most fundamental phenomena of polymer systems: so-called solvent crazing [7–9]. This phenomenon comes into play owing to the tensile drawing of a solid in an adsorptionally active liquid medium (AALM) [10]. In the case of polymers, this deformation is accompanied by unique structural rearrangements, and their use offers evident practical potential.

Figure 1 shows two samples based on the same polymer, but one sample is stretched in air and the other is stretched in the presence of an AALM. Tensile drawing in air (the upper image) leads to a well-pronounced side contraction of the sample, that is, a neck. The mechanism of necking is well known. At the same time, tensile drawing in an AALM (the bottom

image) does not lead to necking, and the stretched polymer sample becomes milky white and opaque. The microscopic studies reveal that the tensile drawing of the polymer sample in an AALM entails the development of a fibrillar–porous structure (Fig. 2). The formed micropores intensely scatter incident light, and the resultant polymer sample becomes milky white. When the polymer sample is stretched in the presence of an AALM, its molecular orientation takes place. However, this orientation is localized not within the monolithic neck but in the well-spaced fine fibrillar aggregates of macromolecules. As was mentioned above, this mode of deformation is the direct consequence of the Reh binder effect [7]. As a result, a solid polymer undergoes self-dispersion into fine nanoscale aggregates of oriented macromolecules (craze fibrils) that are separated by microvoids of nearly the same dimensions.

Let us consider in more detail the mechanism of structural rearrangements that comes into play during tensile drawing of polymers in liquid media. Figure 3 shows a schematic representation of the general pattern of solvent crazing for a polymer film stretched in a liquid medium. Early stages of tensile drawing of the polymer sample involve nucleation of a certain number of crazes that are regions with a unique fibrillar–porous structure.

In the course of subsequent tensile drawing at higher tensile strains, the nucleated crazes grow in the direction perpendicular to the direction of tensile drawing of the polymer sample, but they preserve their almost fixed, small (fractions of a micron) widths (the stage of craze-tip advance). This process proceeds until the growing crazes cross the entire cross section of the sample. Then, the next stage of solvent crazing commences, the stage of craze widening or craze thickening, when the dimensions of the grown crazes increase along the direction of tensile drawing. Evidently, this stage of solvent crazing provides the main transformation of the polymer into the oriented (fibrillar) nanoporous state.

Solvent crazing of polymers in AALMs includes one more stage. Obviously, the stage of craze widening is accompanied by a gradual increase in the overall porosity and in the specific surface of the polymer sample. However, this process cannot last too long and the system finds a way to reduce its excess surface area. When most of the polymer is transformed into the oriented fibrillar state, the formed porous structure collapses [7] (Fig. 4). This stage of the collapse is characterized by a marked decrease in the cross section of the deformed sample, and this side contraction is accompanied by decreases in the porosity, average pore dimensions, and specific surface. In contrast to other stages of solvent crazing, this stage depends on the natural draw ratio of a given polymer, the characteristics of an AALM, and the geometry of the deformed sample. Note that, at the stage of collapse, some liquid entrapped by the polymer sample at the earlier stages

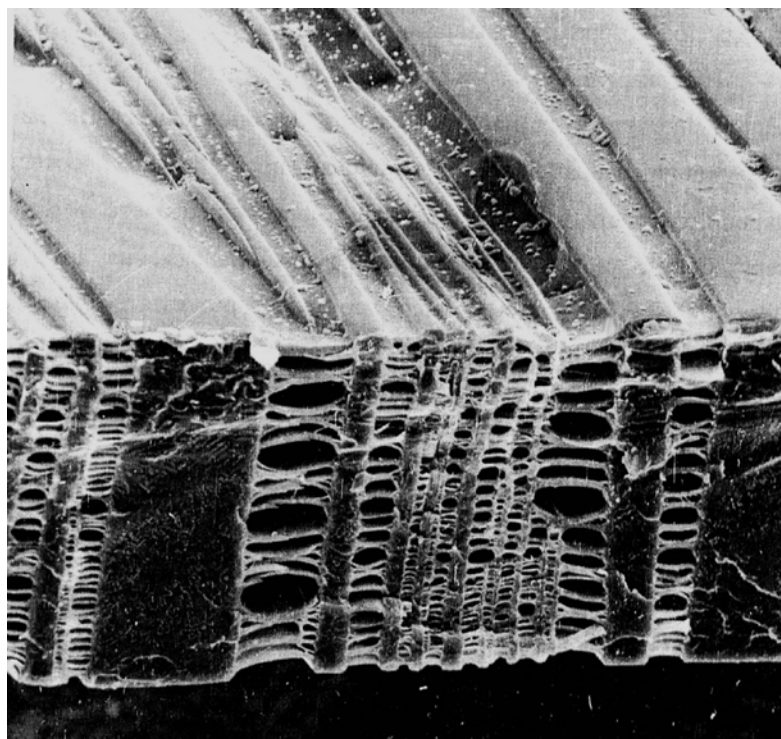


Fig. 2. Electron microscopic image of the solvent-crazed sample. Magnification is $\times 1000$.

of tensile drawing is released into the surrounding medium (the phenomenon of syneresis) [7]. Note that the sizes of craze fibrils and the microvoids between them range from approximately 1 to 10 nm. The development of the unique fibrillar–porous structure due to solvent crazing is allowed only when the formed micropores are continuously filled with incoming surrounding liquid, in which the tensile drawing of the polymer sample occurs.

Hence, the interaction between the deformed polymer and the surrounding AALM can be conditionally divided into two stages. At the first stage of solvent crazing, the dimensions of pores and the amount of liquid entrapped in the nanoporous structure of the solvent-crazed polymer increase. At the second stage, the reverse process occurs: The pores in the polymer structure tend to close, a process that is accompanied by a partial release of the entrapped liquid into the surrounding medium (syneresis). Evidently, the above features of the solvent crazing of polymers in an AALM can be used to develop a new approach to the preparation of diverse nanocomposites based on the polymer matrix.

SOLVENT CRAZING OF POLYMERS IN A LIQUID MEDIUM AS A METHOD FOR DEVELOPMENT OF NANOSCALE POROSITY

Let us consider the first stage in the preparation of a nanocomposite, namely, preparation of a nanoporous

polymer matrix. To this end, we will utilize data on the characteristics of solvent-crazed polymers. The related earlier studies in this direction make it possible, in particular, to gain valuable information on the dimensions of nanopores in the structure of solvent-crazed polymers and to follow their evolution in the course of tensile drawing as tensile strain increases. To solve this problem, a polymer sample should be stretched by a desired tensile strain; then, the stretched sample should be placed in a dye-containing solution and the optical density of the solution should be measured [8]. Figure 5 presents the typical sorption isotherms. The sorption data clearly demonstrate that the solvent-crazed polymer samples possess a highly developed surface. Profiles of the presented sorption isotherms depend on the tensile strain of the solvent-crazed polymer sample. Figure 6 shows the level of adsorption in the interval of equilibrium concentrations corresponding to saturation of the first adsorption layer for the two following sorbates: iodine and the organic dye Rhodamine B. Small iodine molecules (~ 0.5 nm) easily penetrate into the nanoporous structure of the solvent-crazed polymer over the entire interval of tensile strains. At the same time, bigger (1.7 nm) molecules of Rhodamine B can penetrate into the nanoporous structure of the solvent-crazed polymer only in the interval of relatively low tensile strains (below $\sim 200\%$); at higher tensile strains of the solvent-crazed polymer samples, the process of adsorption ceases. This experimental evidence indicates that tensile drawing of the polymer sample in the

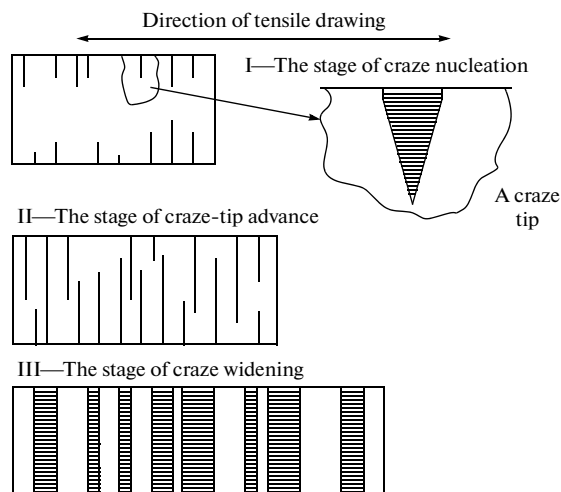
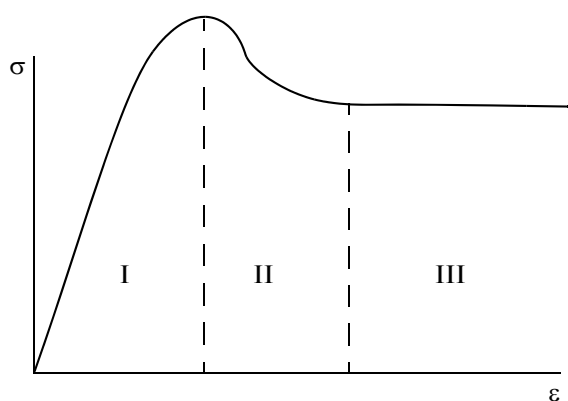


Fig. 3. Stress–strain curve of a glassy polymer in an AALM and the schematic representation of individual stages of solvent crazing in polymers: (I) the region of craze nucleation, (II) the region of craze-tip advance, (III) the region of craze widening.

presence of an AALM is actually accompanied by the spontaneous development of nanoscale porosity. Moreover, in this material, dimensions of the craze pores can be easily controlled through variation of the tensile strain of the solvent-crazed polymer. Table 1 summarizes the data on the dimensions of pores in the solvent-crazed polymers, and this evidence shows that solvent crazing of polymers in an AALM increases the

porosity of the sample, while the dimensions of pores in the crazes remain at the nanoscale level.

SOLVENT CRAZING AS A UNIVERSAL METHOD FOR THE INTRODUCTION OF MODIFYING NANOSCALE ADDITIVES INTO POLYMER FILMS AND FIBERS

As was shown above, the solvent crazing of polymers in an AALM is accompanied by the development of nanoscale porosity; that is, it can be treated as the first stage in the preparation of the nanocomposite. The second stage of this process involves loading of the as-formed nanoporous structure of the solvent-crazed polymer with the target component (or with several components) of a different chemical nature. At the present time, various procedures allowing introduction of such components into polymers have been developed and are being widely used. Let us illustrate this statement for the well-known process of dyeing or coloring textile fibers.

It is known [11] that “dyeing involves a spontaneous transfer of a dye from its solution or dispersion into a fiber until the equilibrium state is attained. The rate of dyeing and the amount of the coloring compound absorbed by the fiber are controlled by the laws of the activated diffusion and sorption.” Dyeing proceeds at a slow rate because this process depends on the spontaneous processes of diffusion of a low-molecular-mass component into the structure of a polymer. To retain the introduced additive within the polymer structure, both components should contain active functional groups that can interact with each other and thus develop sufficiently strong chemical bonds. In the opposite case, the introduced additive can be released from the sample via the same process of diffusion during the appropriate treatment, for example, washing. This obstacle substantially complicates the introduction of modifying additives into hydrophobic polymers that do not contain any active functional groups, such as polyolefins, polyesters, and PVC. To overcome the above difficulties, some additional tricks can be used, for example, for hydrophobic (polyester) fibers: “the yarn is initially soaked with a slightly thickened dispersed suspension of a dye; then, the fibers are dried and heated at 200–210°C (the Thermosol pro-

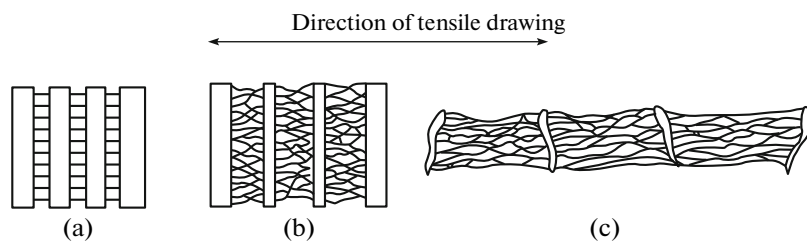


Fig. 4. Scheme of the collapse of polymer structure at high tensile strains of solvent crazing: (a)–(c) consecutive stage of tensile drawing.

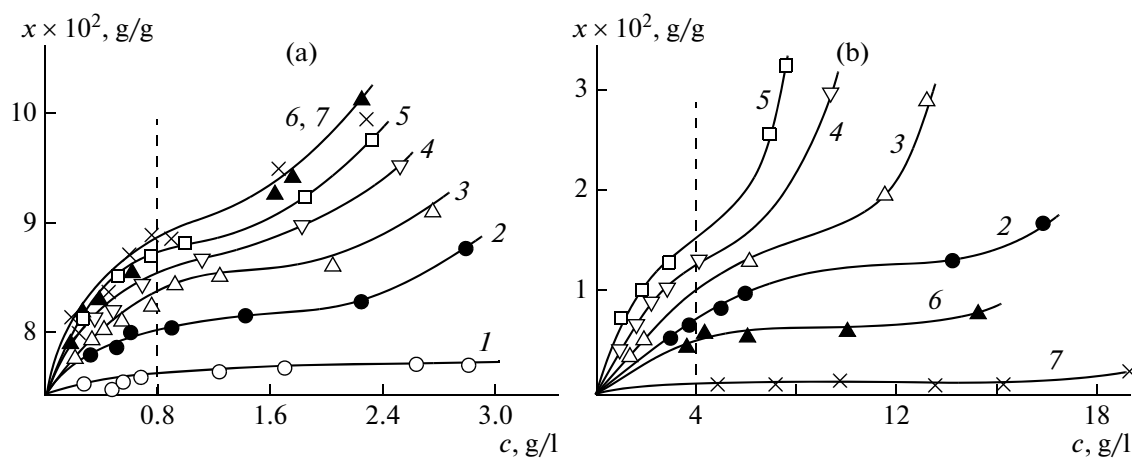


Fig. 5. Sorption isotherms for (a) iodine and (b) Rhodamine B illustrating sorption from their aqueous solutions by the solvent-crazed PET samples. The values of the tensile strain are (1) 20, (2) 50, (3) 100, (4) 150, (5) 200, (6) 300, and (7) 400%.

cess) or are subjected to the action of trichloroethylene vapors (the Vapokol process)” [11]. The above processes proceed in the batch mode and require significant energy consumption and time. Furthermore, all these processes encounter problems related to the homogeneous distribution of the dye over the entire cross section of a fiber. In this context, let us consider some specific features of the solvent crazing of polymers in bicomponent liquid media.

The use of solvent crazing for the introduction of modifying additives to polymers makes it possible to overcome the above difficulties. Structural rearrangements depicted in Fig. 4 offer the simplest scenario for loading the forming porous structure of a solvent-crazed polymer with the required low-molecular-mass additive. The only limiting condition is the fact the

additive should be soluble in the selected AALM. Once the porous structure of the solvent-crazed polymer is filled with the solution of the additive in the AALM, the liquid can be removed, for example, via annealing (thermal fixation) of the solvent-crazed fiber or film. When the AALM is removed from the porous structure of the solvent-crazed polymer, the dissolved modifying additive crystallizes within the nanopores and forms a nanocomposite. As a result, diverse materials with a uniform distribution of almost any low-molecular-mass component can be prepared.

Let us consider in more detail the mechanism of interaction between an active liquid and a stretched polymer when the active liquid contains a dissolved modifying additive. In [12, 13], various organic dyes were used as additives. Figure 7 shows the scheme of

Table 1. Parameters of the porous structure of several solvent-crazed polymers after tensile drawing in adsorptionally active liquid media

Polymer	Tensile strain, %	Porosity, vol %	Pore size, nm
PET	50–250	35–45	2–5
HDPE	100–350	30–55	5–10
Ultra-high-molecular-mass PE	100–250	20–30	2–3
PP	50–250	30–45	3–6
PA-6	50–200	30–40	2–3
PA-4,6	50–150	30–40	3–5
PVA	50	20	6
PVA–PolyVAc copolymer	50	30	6
PVC	10–50	8–25	6
PVC + MBS*	25–150	10–35	4–5
PVC + DOP**	25	15–45	4–6

* Latex of the methacrylate–butadiene–styrene copolymer.

** Dioctyl phthalate.

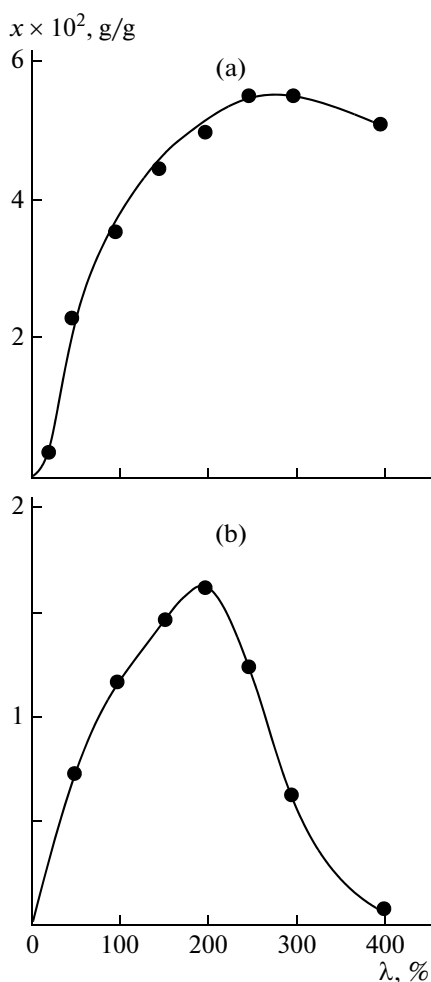


Fig. 6. Adsorption plotted against tensile strain of the solvent-crazed PET samples: (a) aqueous iodine solutions at an equilibrium concentration of 0.8 g/l and (b) Rhodamine B at an equilibrium concentration of 0.04 g/l.

interaction of a deformed polymer with a solution of a modifying additive in an AALM.

The early stages of tensile drawing are accompanied by the growth of crazes; as a result, the overall volume of microvoids filled with the dye-containing solution of AALM increases (Fig. 7a). In this case, the overall amount of dye entrapped by the pores increases as the tensile strain of the solvent-crazed polymer increases. For each particular polymer, tensile drawing by a certain tensile strain approaches the stage of collapse of the fibrillated material of crazes and the loosened structure is transformed into a compact structure. As was mentioned above, this transformation is accompanied by syneresis and by the release of a certain amount of the solvent from the volume of the crazes. However, this release of the solvent into the surrounding space proceeds via flow through the nanoporous fibrillar structure of the solvent-crazed polymer. The distance between the craze fibrils in this structure due to their coagulation during tensile draw-

ing decreases and is comparable to the dimensions of bulky dye molecules. As a result, a specific ultrafiltration of the dye-containing solution occurs when the dye molecules are entrapped within the polymer structure owing to purely geometric (steric) causes, and a pure solvent is filtered out into the surrounding medium. Therefore, the amount of dye entrapped by the solvent-crazed polymer increases with an increase in tensile strain but remains unchanged at later stages because, once the loosened structure of the solvent-crazed polymer is transformed into the compact structure, no fresh portions of solution are delivered to the polymer (Fig. 7b). These structural rearrangements highlight the potential of introducing diverse modifying additives into polymers, their homogeneous distribution in the volume, and the immobilization within the structure of fibers.

The key difference between the proposed method of introduction of additives into polymers and the traditional approach [11] can be formulated as follows. The traditional approach includes the spontaneous penetration of the molecules of the modifying additive into the polymer structure via diffusion. According to the definition advanced by Rusanov, solvent crazing involves a "forced" delivery [14] of the solution containing the modifying additive into a gradually evolving nanoporous structure of a polymer sample. Hence, it is not surprising that the amount of the thus delivered additive can markedly exceed the concentration of the same additive in the sample achieved via equilibrium sorption from the same solvent [8].

SOME CHARACTERISTICS OF NANOCOMPOSITES BASED ON THE POLYMER MATRIX PREPARED VIA SOLVENT CRAZING

In the case of solvent crazing, the second component is delivered into the solvent-crazed polymer as nanoscale aggregates; hence, this factor controls the resultant structure and thermophysical characteristics [8]. Moreover, when the added component is capable of crystallization in the nanoscale pores, well-pronounced orientational effects are observed. Of special importance is the almost parallel alignment of the craze fibrils composed of mutually oriented macromolecules in the structure of the craze (Figs. 2, 3). This phenomenon implies that the narrow nanoscale asymmetric pores separating the individual craze fibrils likewise are mutually oriented along the direction of tensile drawing of the polymer sample. A well-pronounced asymmetry of the structure of the craze should control crystallization of a low-molecular-mass component in the crazed volume.

This effect was revealed by the X-ray structural study of many systems based on a solvent-crazed polymer and a low-molecular-mass filler [15–17]. Independently of the polymer and the nature of the added crystallizable component, the crystallization of this

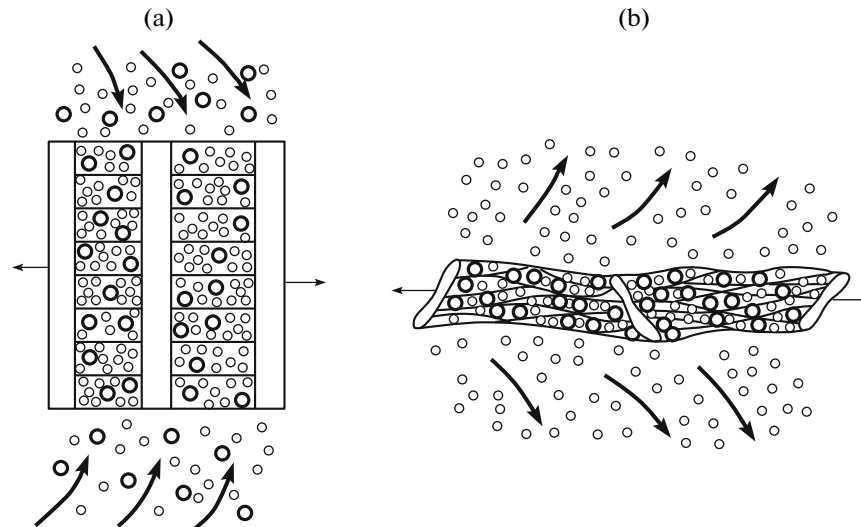


Fig. 7. Scheme of structural rearrangements during solvent crazing of a glassy polymer in a bicomponent AALM. The arrows show the direction of mass transfer at different stages of solvent crazing.

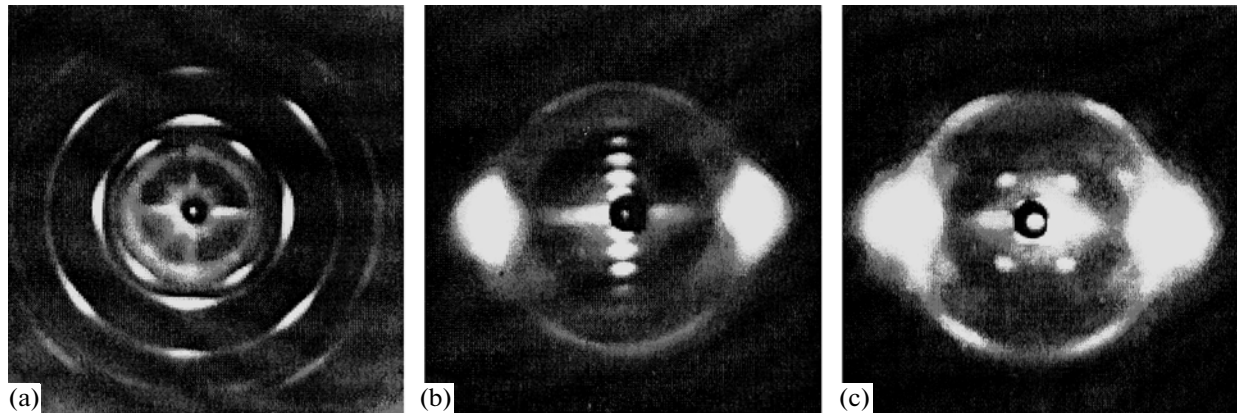


Fig. 8. X-Ray patterns of (a, b) the solvent-crazed PET samples containing (a) KJ and (b) *n*-octadecane and (c) the solvent-crazed PC sample containing TDA.

component proceeds to form highly ordered textures. Figure 8 illustrates this scenario for the solvent-crazed PET sample containing various low-molecular-mass components and for the PC sample containing tridecanoic acid (TDA). In all cases, crystallization of the low-molecular-mass compounds leads to formation of highly ordered textures, and the corresponding X-ray patterns are similar to the X-ray patterns of single crystals.

The above phenomenon shows a universal character and can be observed for various solvent-crazed polymer matrices based on crystallizable polymers (PET, PC) and amorphous polymers (atactic PMMA) [16, 17]. The above features remain the same for the introduction of ionic and molecular crystals into the solvent-crazed polymer matrices.

Although the orientation of low-molecular-mass compounds in the crazed structure is universal for all

cases, the mode of orientation depends on the nature of a polymer and an additive. In [15, 18–24], various nanocomposites based on solvent-crazed polymers and incorporated long-chain fatty alcohols, hydrocarbons, and acids were studied. Crystallization of the above-listed compounds leads to the formation of ordered layers, a circumstance that simplifies interpretation of the corresponding X-ray patterns. Analysis of the X-ray patterns shows that a set of pointlike X-ray reflections located at the meridian, equator, or diagonal can be attributed to X-ray scattering from the oriented layered planes [24]. Figure 9 shows the schematic representation of the packing of asymmetric molecules in the oriented pores of crazes and the corresponding X-ray reflections.

The orientation and concomitant crystallization of low-molecular-mass compounds in narrow (~10 nm) asymmetric pores of solvent-crazed polymer matrices

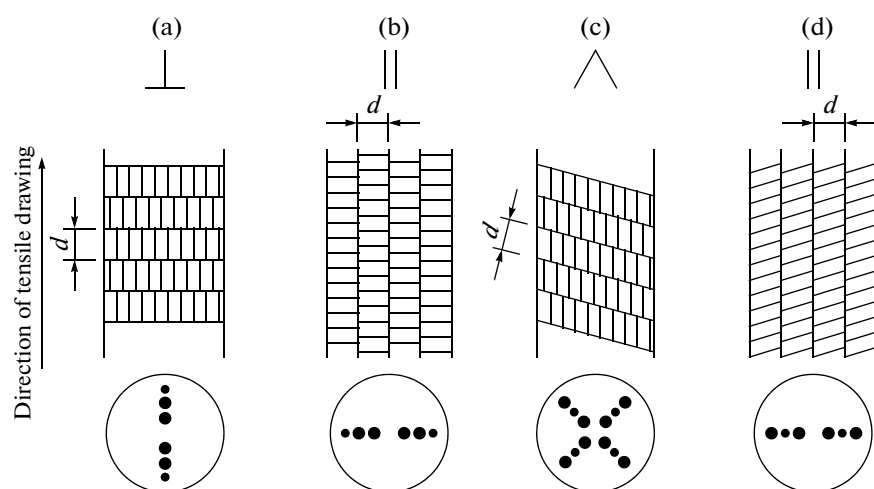


Fig. 9. The layered orientation of (a) the linear hydrocarbon heneicosane, (b) cetyl alcohol, and (c, d) carboxylic acid within the pores of the solvent-crazed polymer matrices and arrangement of the corresponding X-ray reflections on the X-ray patterns.

are primarily controlled by the thermodynamic stability of the ordered state relative to their random arrangement. When crystallites of the low-molecular-mass compound in the crazes are ordered, the inter-crystallite surface energy is minimum. The character of orientation of low-molecular-mass compounds in polymer matrices is controlled by the minimum of the surface component of the free energy at the polymer/low-molecular-mass compound interface. Therefore, each orientation-dependent type of interaction between crystalline planes has its own value of surface energy.

It was shown in [15, 25] that there is a certain factor that controls the parameters of the crystalline lattice of a low-molecular-mass compound that is dispersed down to the nanoscale inclusions in the polymer matrix. This factor is related to the existence of internal stresses in the solvent-crazed polymer. Note that the intensity and orientation of the above stresses control changes in the deformation of the crystalline lattice of the low-molecular-mass compound in the volume of the crazes.

In the conclusion of this section, it is necessary to advance certain assumptions about the nature of the orientation of low-molecular-mass compounds in the nanoporous structure of crazes that was first described in [15–17]. The orienting effect of the solvent-crazed polymer matrix on the crystallization of the incorporated low-molecular-mass compounds cannot be referred to as epitaxy. Epitaxy is the formation of uniformly (with respect to each other) oriented crystals of one compound at the face of the crystal of another compound [26]. As was shown above, crystallization of the low-molecular-mass component leads to the formation of highly ordered textures, independently of whether the solvent-crazed polymer matrix is crystalline or fully amorphous. In the case under consideration, the key orienting factor is apparently related to

a strictly ordered arrangement of asymmetric nanopores in the craze structure.

However, nanoscale aggregates, rather than individual molecules of the low-molecular-mass component, are oriented in the craze structure. Figure 10 presents the IR dichroism (the band at 2925 cm^{-1}) and heat of fusion of TDA in a PTFE-based solvent-crazed matrix plotted against the content of the low-molecular-mass component. The content of TDA in the polymer matrix can be controlled by performing solvent crazing in TDA solutions of different concentrations. As follows from Fig. 10 (curve 1), the heat of fusion of TDA decreases with a decrease in the feed-solution concentration. This behavior can be explained as follows: As the content of TDA in the solvent-crazed polymer matrix decreases, the dimensions of the formed crystallites are expected to decrease. This decrease is probably accompanied by an increase in the specific surface of the compound. In turn, this increase in the specific surface decreases the heat of fusion because the surface layer of the crystallite does not make any energy contribution to the melting process and does not produce any three-dimensional crystalline lattice.

At the same time, the degree of orientation of a low-molecular-mass compound in the polymer matrix, a parameter that is characterized by the IR dichroism, changes somewhat differently (Fig. 10, curve 2). The orientation of TDA remains unchanged as its concentration in the feed solution; only once the concentration reaches 3% does the IR dichroism dramatically decrease. This result is likely due the fact that, at high concentrations (above 3%), TDA exists in the polymer matrix primarily in the crystalline state (as nanocrystallites). When the concentration of TDA decreases, this component is molecularly dispersed in the crazed structure. In this concentration interval, the overall content of the crystalline phase dramati-

cally decreases; dichroism critically drops; and, hence, the orientation of TDA decreases. This evidence indicates that, in the volume of crazes, the orientation of crystallites, rather than individual molecules, occurs.

Therefore, crystalline and LC compounds [27] incorporated into the nanoporous structure of the solvent-crazed polymer matrices are oriented with a high degree of ordering that can be reversibly changed during phase transitions. Also, note that the high level of self-organization of the solvent-crazed polymer controls the high level of ordering of nanoscale low-molecular-mass components incorporated into the structure of crazes.

APPLIED ASPECTS OF INTRODUCTION OF NANOSIZED ADDITIVES INTO POLYMERS VIA SOLVENT CRAZING

In the general case, the introduction of a nanoscale additive into a polymer (preparation of a nanocomposite) can be directed to solve at least two applied problems. First, the introduced additive can change and modify characteristics of the initial polymer, for example, it can impart fire-retardant or conducting characteristics to the polymer. In this case, the additive should be tightly immobilized within the polymer matrix and should be unable to migrate from it during different modes of external treatment, such as washing and/or treatment with solvents. Second, the final product (the nanocomposite) should affect the surrounding medium. (E.g., it should suppress the growth of microorganisms or be capable of prolonged drug release.) Hence, the incorporated additive should be released from the polymer into the surrounding medium over long periods. Solvent crazing makes it possible to solve both problems. The corresponding examples will be considered below.

Preparation of flame-retardant polyester fibers.

To impart fire retardancy to polyester fibers, the fibers were stretched in a solution containing a fire-retardant agent (phosphonic acid amide) on a lab-scale stretching unit under the continuous regime; then, the stretched fibers were thermally fixed by annealing at 120°C. The as-prepared fibers were tested in limiting-oxygen-index and tensile tests (strength characteristics), and the effect of standard treatments (washing, maceration, extraction, etc.) on the above parameters was studied. All data are summarized in Table 2. Regular stretching of PET fibers in the solution of the fire-retardant agent makes it possible to increase PET's limiting oxygen index above 40. (The limiting oxygen index of the initial sample is 19.) This evidence implies that this material is resistant to ignition and cannot support flame spreading in air. At the same time, the modified fire-resistant fibers retain fair strength characteristics, which decrease by no more than 25%. This effect is primarily related to the fact that, in these experiments, strength was estimated through division

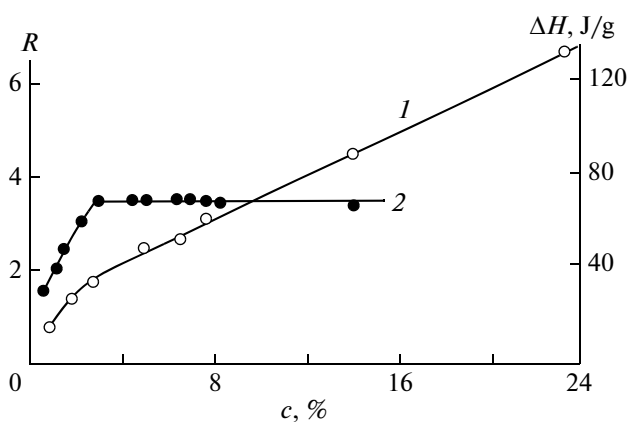


Fig. 10. (1) Heat of fusion and (2) IR dichroism of the absorption band at 2925 cm^{-1} of TDA incorporated into the solvent-crazed PTFE matrix plotted against the TDA content in the polymer.

of the breaking force by the initial cross-sectional area of the yarn. However, owing to the above treatment, the polymer gains up to 15% of the fire-retardant agent and its cross section slightly increases, thereby changing the estimated strength. Note that the attained parameters are practically independent of the mode of treatment of the material, including repeated washing with detergents (up to 50 washing cycles).

Preparation of electrically conductive polymer-polymer nanocomposites. Several attempts have been made to prepare polymer-polymer nanocomposites in which one of the components shows conducting characteristics. Despite the evident progress achieved in recent years in this particular area, the use of conducting polymers is limited because, as a rule, they are infusible and insoluble powders that cannot be subjected to any processing [28].

The current study has been focused on the development of new approaches to the preparation of nano-

Table 2. Effect of the type of subsequent treatment of the solvent-crazed polyester fibers containing a fire-retardant additive on strength and limiting oxygen index

Type of treatment	Strength, g/tex	Limiting oxygen index
Without treatment	32	43
Washing	30	37
Boiling in a solution of Na_2CO_3	31	37
Maceration in detergents	30	31
Extraction with solvent (dichloroethane)	28	41

Note: The strength of the flame-retardant-free sample is 40 g/tex; the limiting oxygen index is 19; and for the fiber after solvent extraction, the corresponding parameters are 38 g/tex and 19, respectively.

Table 3. Mechanical characteristics of the nanoporous matrices based PET and PE and of the related polymer–polymer nanocomposites containing polyaniline

Matrix or nanocomposite	c, %	λ , %	E, MPa	σ_p , MPa	ε_p , %	E, MPa	σ_p , MPa	ε_p , %
			along the direction of tensile drawing			perpendicular to the direction of tensile drawing		
PET	—	100	690	48	190	660	34	380
PET–Polyaniline	40.8	100	1210	51	7	1000	17	4
PE	—	100	310	64	150	360	29	550
PE–Polyaniline	26.6	100	730	64	180	650	31	550
PE	—	200	320	88	80	280	28	680
PE–Polyaniline	42.2	200	930	86	90	870	30	5

composites in which the second polymer component incorporated into the solvent-crazed polymer matrix is characterized by high electrical conductivity [29–31]. Initial polymer films (HDPE and PET) were subjected to solvent crazing, and the formed nanoporous structure was filled with the corresponding monomers (acetylene and aniline). The subsequent in situ polymerization of the incorporated monomers and the doping of the prepared samples allowed preparation of various nanocomposites that advantageously combine excellent electrical conductivity typical of polyacetylene and polyaniline with high mechanical characteristics of HDPE and PET (Table 3).

The introduction of comparatively small amounts of polyacetylene (8%) into HDPE and the subsequent doping of the polymer blend with iodine increase electrical conductivity by 14–16 orders of magnitude, i.e., to $(0.2\text{--}1.4) \times 10^2 \Omega^{-1} \text{cm}^{-1}$ [28]. With allowance for the fact that the specific volume conductivity of pure polyacetylene is $\sim 1 \times 10^2 \Omega^{-1} \text{cm}^{-1}$, the above evidence indicates that the structure of the prepared polymer blends provides a low percolation threshold of electrical conductivity. Note that the electrically conductive polymer incorporated into the solvent-crazed polymer matrix acquires a distinctive molecular orientation that noticeably increases its electrical conductivity.

The attempts to incorporate another conducting polymer, polyaniline, into the solvent-crazed polymer matrices based on PE and PET likewise were successful [30, 31]. The main results of this study are listed in Tables 3 and 4. The mechanical characteristics of pure solvent-crazed polymer matrices stretched by a tensile strain of 100 or 200% are compared to the corresponding characteristics of the related nanocomposites in Table 3. Such important mechanical parameters as the elastic modulus and strength of the nanocomposites lie within the same interval as the values typical for pure solvent-crazed polymer matrices and, in some cases, even exceed them. At the same time, the prepared nanocomposites show excellent electrical conductivity that is nearly the same as the electrical conductivity of pure polyaniline (Table 4). Volume electrical conductivity σ_v of both nanocomposites is high,

regardless of the type of the polymer matrix. At the same time, as follows from the data shown in Table 4, surface electrical conductivity along the direction of tensile drawing, σ_s^{\parallel} is appreciably different from that in the normal direction, σ_s^{\perp} . This result makes it possible to control the conducting characteristics of the nanocomposites. This evidence confirms that the development of new types of electrically conductive polymer–polymer nanocomposites based on solvent-crazed polymer matrices offers marked advantages for diverse practical applications.

Preparation of polymer films and fibers with a controlled effect on the surrounding medium. Solvent crazing can be used also for the preparation of new types of polymer nanocomposites that can have an effect on the surrounding medium. Such nanocomposites can be prepared through the introduction of a heavy, low-volatility liquid. As follows from Fig. 11, the migration of this liquid from the nanoporous structure can last for many months or even years. This phenomenon can find practical application when the long-lasting effect of some target additives is required (e.g., the prolonged release of repellents, bactericidal components, or odors). Note that such materials can be easily processed as fibers, films, or textiles, a circumstance that makes them attractive for applied use in different practical areas, including medicine, perfumery, and the textile industry.

Let us consider the example of the results of the study described in [32]. Solvent crazing was used to load PET fibers with Katomin and Altozan, in which alkyl dimethylbenzylammonium chloride served as the active bactericidal component. The biocidal action of the as-prepared fibers was assessed in microbiological tests. For this purpose, the samples were placed into Petri dishes containing the agar-cultivated bacterial strains *Staphylococcus aureus* and *Pseudomonas aeruginosa*. The size of the region of persistent suppression of bacterial growth was measured according to the requirements of GOST (Russian State Standard) 9.802-84. Typical results shown in Fig. 12 demonstrate the high bactericidal activity of the prepared materials.

Table 4. Specific electrical conductivity of the polymer–polymer nanocomposites based on polyaniline and solvent-crazed PET and PE matrices

Nanocomposite	Dopant	$c, \%$	$\lambda, \%$	$\sigma_v, \Omega^{-1} \text{ cm}^{-1}$	$\sigma_s^\perp, \Omega^{-1} \text{ cm}^{-1}$	$\sigma_s^\parallel, \Omega^{-1} \text{ cm}^{-1}$
PET–polyaniline	HBF ₄	29.2	50	1.6×10^{-3}	3.7×10^{-2}	5.4×10^{-3}
		40.8	100	2.2×10^{-2}	3.7×10^{-1}	2.7×10^{-2}
		39.4	200	7.2×10^{-5}	1.0×10^{-1}	4.7×10^{-2}
		12.8	300	–	7.5×10^{-4}	3.7×10^{-3}
PE–polyaniline	HCl	45.8	100	4.8×10^{-3}	2.9×10^{-2}	3.6×10^{-3}
		42.2	200	5.4×10^{-2}	8.8×10^{-1}	7.8×10^{-1}
	HCl	26.6	100	2.9×10^{-2}	5.4×10^{-2}	3.0×10^{-2}
		42.2	200	2.3×10^{-2}	2.4×10^{-1}	1.6×10^{-1}

Note that the bactericidal activity is preserved at the initial level, even after ten washing cycles in detergent solutions at 40–45°C.

THE PRACTICAL ASPECT OF PREPARING NANOCOMPOSITES BASED ON POLYMER MATRICES VIA SOLVENT CRAZING OF POLYMERS IN LIQUID MEDIA

Solvent crazing of polymers is one of the main types of inelastic plastic deformation of polymers. This deformation is involved in the conventional processing of polymer fibers and films, which is called orientational drawing of polymers. At present, the existing production equipment includes many modern high-speed machines that allow orientational drawing of polymer films and fibers in a continuous mode. Modification of polymers via solvent crazing, in essence,

implies combination of the stage of orientational drawing of polymer films and fibers and introduction of a modifying additive. This process includes orientational drawing of the polymer in a solution of the modifying additive in an AALM, but the traditional approach is supplemented by a simple unit that is schematically shown in Fig. 13. The described method has triggered several successful attempts [33, 34] to perform solvent crazing in a continuous mode. In other words, there it is generally possible to prepare nanocomposites in the form of polymer films and fibers with good mechanical characteristics, on the one hand, and with diverse valuable properties (electrical conductivity, fire retardancy, electrostatic char-

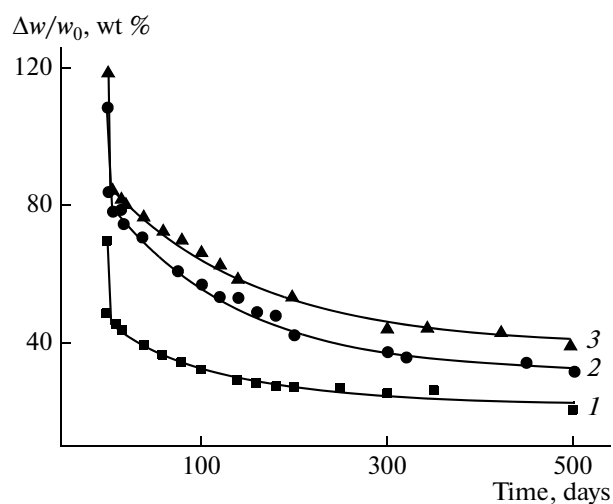


Fig. 11. Relative weight loss of the glycerol-containing solvent-crazed PET samples plotted against time. Samples were stretched in the liquid medium by (1) 100, (2) 200, and (3) 300%.

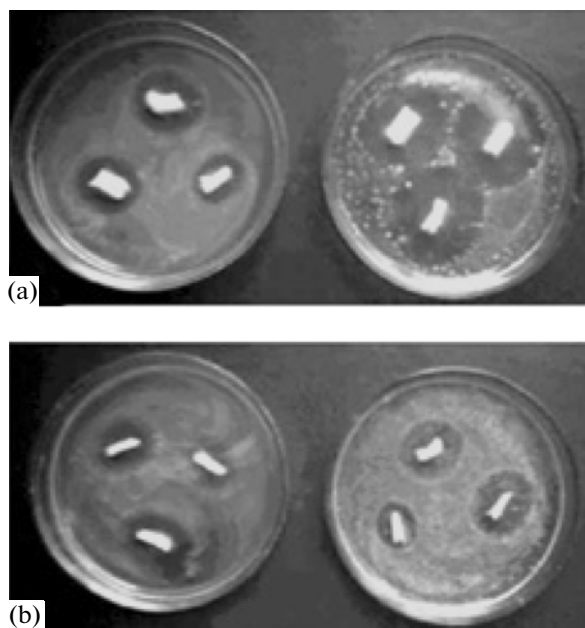


Fig. 12. Petri dishes with 15-day bacterial strains (a) *S. aureus* and (b) *P. aeruginosa* in the presence of the solvent-crazed PET fibers containing (left image) Altozan and (right image) Katomin [32].

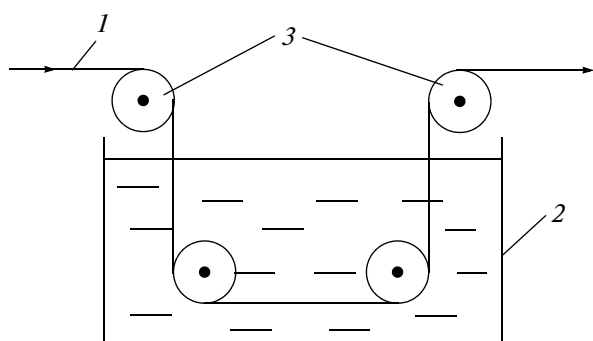


Fig. 13. Schematic representation of a unit for the modification of polymer fibers via the mechanism of solvent crazing: (1) a polymer film or a polymer fiber, (2) a bath filled with an active liquid medium containing a dissolved additive, and (3) feed and take-off rolls.

acteristics, etc.) of the target additives, on the other hand. Note that these nanocomposites can be processed on existing equipment in a continuous regime and at high speeds typical of the modern production of polymer films and fibers.

It is especially important that solvent crazing allows preparation of nanocomposites when the stage of direct introduction of modifying additives during tensile drawing is missing. There is a method of indirect introduction of additives, which includes the use of precursors and their subsequent in situ reactions directly in the volume of the polymer. This approach has allowed preparation of highly dispersed blends of polymers with inorganic salts [35] and metals [36] as well as some new types of polymer–polymer blends [37].

In conclusion, let us briefly outline the principles for the preparation of new types of nanocomposites based on a polymer matrix via solvent crazing in liquid media.

(i) A broad range of diverse large-scale commercial polymers can be used as starting materials for the preparation of new types of nanocomposites based on a polymer matrix via solvent crazing.

(ii) Solvent crazing can be accomplished as a high-speed process, in which the conventional stage of orientational drawing of polymer films and fibers is coupled with the introduction of modifying additives in the nanosize state. It is of key importance that this process can be performed on existing industrial equipment for the orientational drawing of polymer films and fibers after minor modifications.

(iii) This approach involves principally new mechanisms of delivery and immobilization of the nanoadditive within the structure of the polymer. A modifying additive is introduced into the volume of the polymer not by diffusion but by the flow of the solution through a system of micropores typical of the craze structure. In this case, immobilization of the additive within the structure of the fibers does not require a strong inter-

molecular interaction between the polymer and the incorporated additive; therefore, the scope of the additives can be unlimitedly broadened. In particular, this process proceeds at room temperature; hence, there are no limitations to the introduction of thermally unstable additives, another circumstance that broadens the scope of the allowed additives.

(iv) Another key benefit of this approach is the possible introduction of any combination of modifying additives (for example, a flame retardant and a dye) into the polymer fibers in one production run.

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