

MODERN MODELS OF FORMATION OF WELDED JOINTS OF POLYMER MATERIALS (REVIEW)

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ABSTRACT

The process of welding plastics is determined as a gradual disappearance of the interface between parts to be joined and the formation of a transition layer between them, whose structure is significantly different from the structure of the base polymeric material. The models of formation of welded joints of polymers existing today are based on different physical phenomena: mutual adhesion of substrates, diffusion of macromolecules and melt rheology. The most common is the diffusion model of macromolecules reptation in the welding zone, which many researchers refer to in order to explain experimental data. Without denying the possibility of progressive diffusion of elements of the molecular chain through the fusion surface, the postulate that this diffusion provides the main mass transfer during the formation of welded joints of polymers is considered to be controversial. The theory of the formation of welded joints of polymers due to conformational transformations of macromolecule fragments, being developed by the Scientific School of the PWI, is more realistic. In the development of this conformational theory, the model of homogenization of the transition layer on the interface during welding of polymers is proposed based on a vacancy-conformational principle.

KEYWORDS: polymer materials, welding, diffusion of macromolecules, conformational transformations

INTRODUCTION

Understanding of the mechanism of polymer welded joint formation is required for adequate selection of welding technology and mode parameters, as well as methods of welded joint quality evaluation. However, there is still no common point of view and there exist several hypotheses for this mechanism. Since the 80s, the PWI Scientific School has introduced and has been developing the theory of formation of polymer welded joints due to conformational transformations of macromolecule fragments. The objective of this work is to review the currently available explanations of the mechanism of producing a welded joint of polymer materials, and to give additional arguments in favour of the conformational theory.

The physicochemical properties of metals and plastics differ cardinaly. However, the processes of welding these material types have a lot in common, as both are solids from the physical point of view. The scientific definition of the welding process is as follows: producing a permanent joint of solids, the monolithic nature of which is achieved by ensuring the physicochemical, and atomic-molecular bonds between elementary particles of the bodies being joined [1]. Or the so-called thermodynamic definition of welding: welding is a process of producing a monolithic joint of materials due to supply and thermodynamically irreversible transformation of energy and substance in the joining point.

A common property of solids, in particular, plastics, is preservation of an interface between the contact surfaces of individual bodies. That is why the following

definition of welding of plastics was formulated: it is a technological process of producing a permanent joint of structural elements by diffusion-rheological or chemical interaction of polymer macromolecules, resulting in disappearance of the interface and formation of a structural transition from one polymer element to another one [2]. Another variant of such a definition is as follows: polymer material welding is a technological process of producing a permanent joint of parts and elements of a structure, resulting in disappearance of the primary interface between the parts from polymer materials, transforming into a transition layer with a homogeneous or heterogeneous chemical structure [3].

The ISO International Standard gives a rather simple definition: “welding of plastics is a process of joining the softened surfaces of materials, as a rule, through application of heat” [4].

Thus, blurring and disappearance of the interface between the parts is regarded as the essence of the welded joint, unlike an adhesion joint, where the interface always remains and is clearly visible. With the start of application of the first methods of plastics welding, scientists began putting forward hypotheses of the mechanisms of formation of polymer material welded joints.

MAIN BODY OF THE ARTICLE

In work [5], the researchers when studying the features of thermal welding of polymethyl methacrylate (PMMA) suggested that the welded joint forms by the diffusion mechanism of autohesion (bonding of surfaces of one and the same polymer material brought into contact). Furtheron, the theory of diffusion autohesion was developed, mutual movement of macromolecular

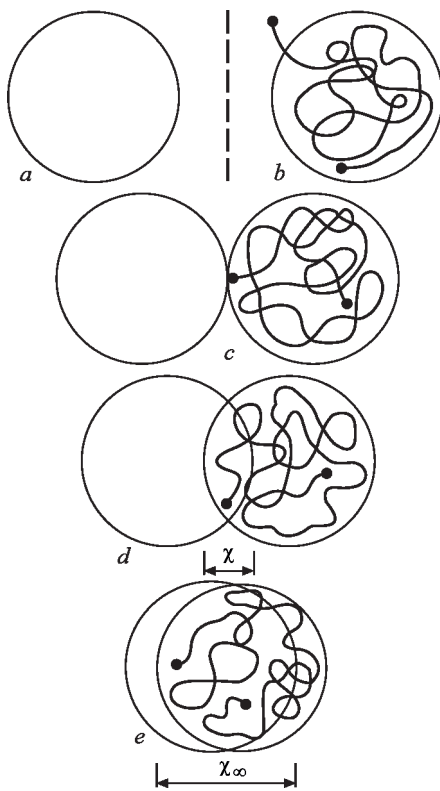


Figure 1. Block-diagram of stages of welded joint formation by R. Wool

fragments through the contact surface in welding was explained by thermal Brownian motion of molecular segments and their relative sliding in high-elastic (for amorphous polymers) and plastic states [6, 7].

Later on, US researcher R. Wool proposed the diffusion hypothesis of “crack healing in polymers”, which consists of five stages, schematically shown in Figure 1 [8]. A dashed line marks the conditional dividing line of the joint, and inside the circle is the so-called random tangle of the macromolecular chain (shown only from one side for the sake of clarity). The first two stages are surface restructuring (usually melting under the impact of heat) and drawing of the surfaces together up to their contact (*a*, *b*). The third stage is mutual wetting of the surfaces (*c*), the fourth

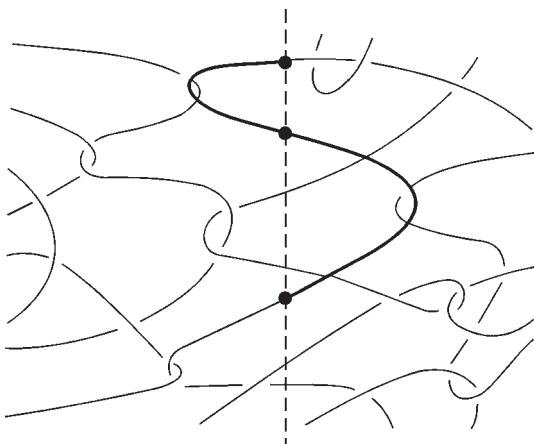


Figure 2. Illustration of a model of polymer welded joint formation due to macromolecule engagement in work [11]

one is the start of diffusion to a certain distance (*d*) χ and the last fifth stage (*e*) is mutual diffusion to distance χ_∞ and blurring of the interface line.

The structure of amorphous polymers is schematically represented as a network structure of random bonds between the macromolecular chains. There exist alternative hypotheses of formation of such bonds: due to folded cluster structures [9, 10] and through the direct engagement of one molecular chain at least one with another — the theory of bridge bonds in a polymer massive [11]. In keeping with this theory, at formation of a welded joint, bridge bonds — engagements should also form between the macromolecules along the fusion line, which are schematically shown in Figure 2. A thick line shows a minimal structure of the molecular bridge through the interface line, which is required to form the weld. This model is used for explaining the mechanism of formation of structures of different strength along the fusion line, depending on thermo-physical condition of the welding process [12].

In Western publications the “healing” term is used within the diffusion hypothesis for description of the process of formation of polymer welded joints, which is illustrated in Figure 3 [13]. After formation of contact between the partially melted surfaces of polymer elements being joined, the process of molecular chain diffusion through the butt surface and their entangling begins. It is shown that a rather long time of the polymer staying in the molten state, when the processes of macromolecule displacement are active, should be regarded as the main condition for “healing”. However, the question of the very diffusion mechanism of “healing” (blurring, disappearance) of the fusion boundary in the welded joint is still debatable.

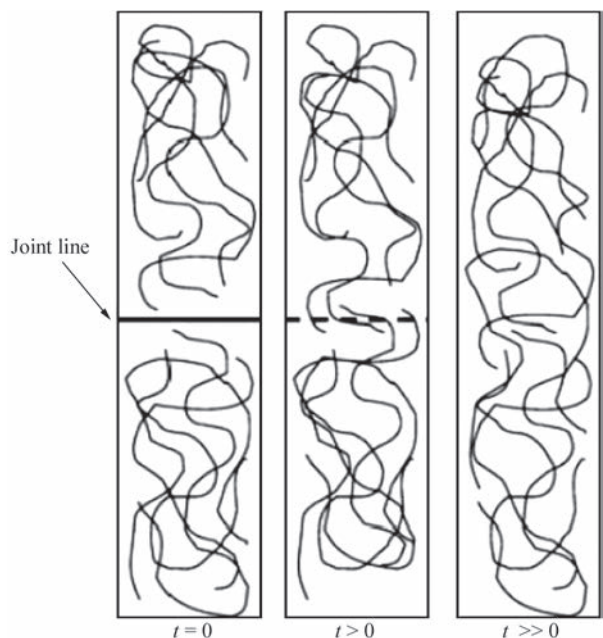


Figure 3. Illustration of the diffusion model of polymer welded joint formation in work [13]

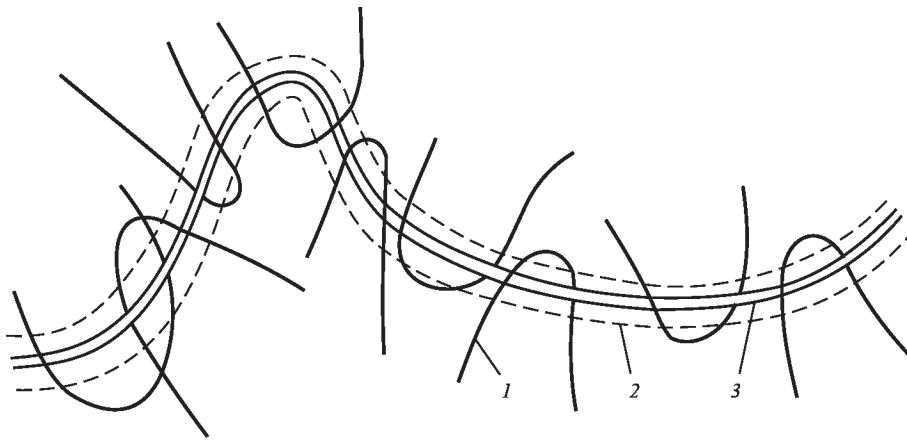


Figure 4. Schematic of formation of a “tube” from molecular chains by reptation theory: 1 — surrounding molecules; 2 — conditional boundaries of the tube; 3 — chain, capable of reptation

To clarify the mechanism of possible self-diffusion of the polymer chain, French physicist Pierre de Gennes with colleagues developed the reptation theory. It is believed that the macromolecule is surrounded by other chains on all sides, and it cannot move to the side, but can move in the longitudinally through such a medium as though through a kind of tube or tunnel (Figure 4). Such a movement of the macromolecule was called reptation, and it was conditionally compared with that of a snake crawling through a bunch of branches [14]. As under the melt conditions, all the molecules are in thermal Brownian motion, the chains forming the tube walls are constantly renewed.

It is believed that the main factor influencing the reptation tube parameters, is density of fluctuation network of engagements of macromolecules, present in the polymer melt. For flexible polymer chains, the distance between individual engagements is estimated to be in the range from 50 to 500 statistical molecular segments. It corresponds to rather long segments of the chain of length within 10^4 – 10^5 . Therefore, it was assumed that such long segments add up to form a sequence of sub-molecular tangles, which is located inside the reptation tube (Figure 5). The characteristic size of the tangle (1) is what determines the average tube diameter d .

It should be noted that within the reptation theory the macromolecule mobility essentially depends on its length, i.e. molecular mass. It is believed that the

time of molecule movement during reptation grows in proportion to the cube of its molecular mass. Therefore, such movements are most likely to be observed for short molecular chains. However, also considered is the possibility of reptation movement of fragments of molecular chains of a complex structure, namely branched, starlike and cyclic ones. So, a branched polymer chain can draw a side branch into the reptation tube during movement with its subsequent new random conformation outside. Cyclic polymer chains can fold into a linear conformation and can perform reptation movements in such a form. Owing to a high complexity of movement mechanisms of chains of a non-linear shape in the melt, the reptation displacement of macromolecules of complex shapes can proceed very slowly.

Let us consider the possible alternative mechanisms of formation of polymer welded joints. The processes of welding polymer materials and metals are similar in many cases. In flash-butt welding of metal parts, a structure forms which is similar to polymer material welds made by hot plate butt welding. Figure 6 shows the microstructure of a flash-butt welded joint of hot-rolled layered ferritic-pearlitic steel. In welding without flashing (a) the horizontal layered steel structure changes its orientation, deviating in the vertical direction along the joint line. In welding with flashing (b) a continuous layer of molten material forms on the end faces as a mixture of the melts of both parts, the

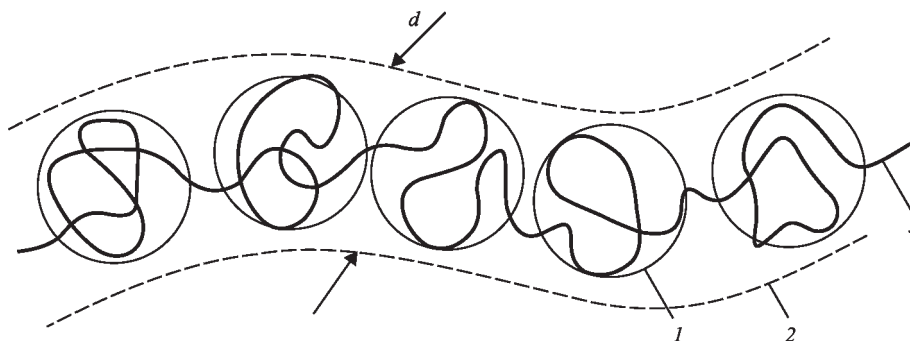


Figure 5. Molecule, consisting of a sequence of small tangles (submolecules) inside a “tube”: 1 — molecular tangle; 2 — conditional boundary of the tube; 3 — polymer chain

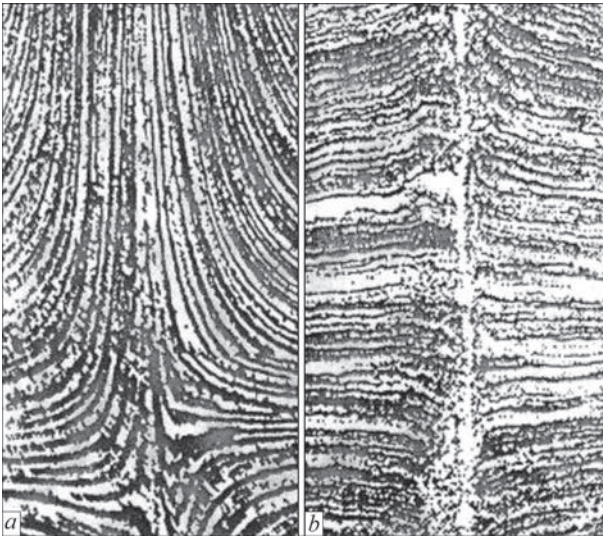


Figure 6. Macrostructure of flash-butt welded joints of pipe steel: *a* — welding without flashing; *b* — welding with flashing [15]

greater part of which is pressed out into flash by upset force. At cooling, the metal solidifies to form a welded joint. It is believed that the first butt joints form in the solid phase and the second ones — in a combined manner in the solid-liquid phase of the heated material [15]. In the latter case, the welded joint forms due to solidification of a thin layer of molten metal on the interface. A “rheological concept” of formation of welded joints of thermoplastic polymers was proposed by analogy with this mechanism. It was believed that the determinant role in the joint formation is played by “rheology”: polymer melt flow at part upsetting under the impact of working pressure. Here, all the ingredients, hindering the intermolecular drawing together, namely gases, oxidized and contaminated areas, are driven out of the contact zone. As the shear rate of individual melt layers differs because of a nonuniform distribution of temperature and pressure, it causes the melt mixing, particularly on the fusion surface. Diffusion of macromolecule segments which occurs at the joint cooling, has little influence on the butt joint formation and is of a secondary nature [16].

A photo of the cross-section of a butt joint of layered polymer material cooled at the initial upsetting stage, is given to confirm mixing of melt microvolumes (Figure 7, *a*). Indeed, one can see from the photo that the polymer material layers are strongly deformed, but nothing points to their significant mixing. Similar work on hot plate butt welding of coloured layered samples of thermoplastics was conducted at PWI. In the cross-section of the layered welded joint (Figure 7, *b, c*) one can see that all the base material layers of the samples completely preserve their sequence, even in outer flash, changing just their thickness [2]. Thus, we cannot talk about any significant mixing of the melt during melting and deposition.

Yu.S. Lipatov with colleagues studied the specifics of interphase phenomena in heterogeneous systems of polymer-filler and polymer-polymer [17]. It was noted that different types of polymers are thermodynamically incompatible and they cannot form common crystalline shapes. However, different polymers are compatible morphologically, and at contact in the molten state they form common supermolecular structures as a transition layer. This layer is formed both by interdiffusion of the components through the interface, and due to one component adsorption on the surface of the other.

A polymer is a mixture of molecular chains of different size. Thermal fluctuations on the fusion surface lead to molecule differentiation by size and enrichment of the transition zone by molecules of smaller mass. Local diffusion through the surface of interfacial contact usually goes to a small depth and forms a transition layer of the thickness of several nanometers. On the other hand, different studies report the presence of the transition zones in polymer-polymer joints of 0.1–1.0 μm thickness. It is probable that alongside regular diffusion, transfer of rather significant volumes of one polymer into the interstructural regions of the adjacent polymer takes place in polymer melts at higher temperatures due to segmental mobility of macromolecules.

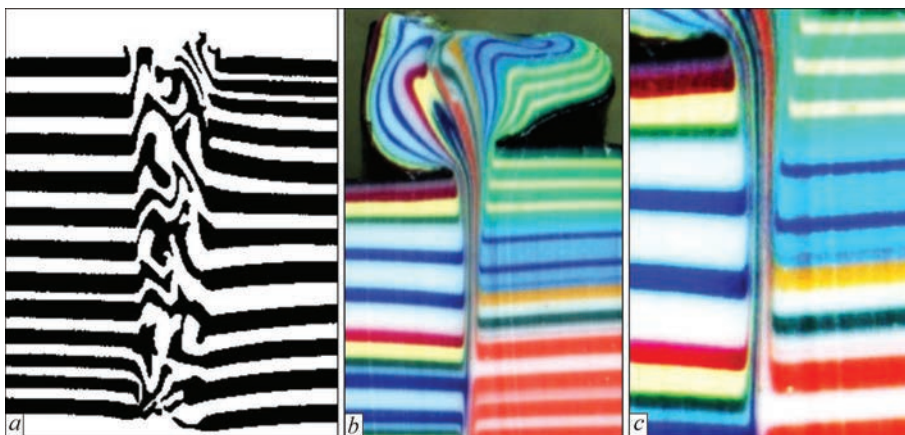


Figure 7. Results of studying the rheological processes in hot plate butt welding of layered thermoplastics: *a* — in work [16]; *b, c* — by PWI data [2]

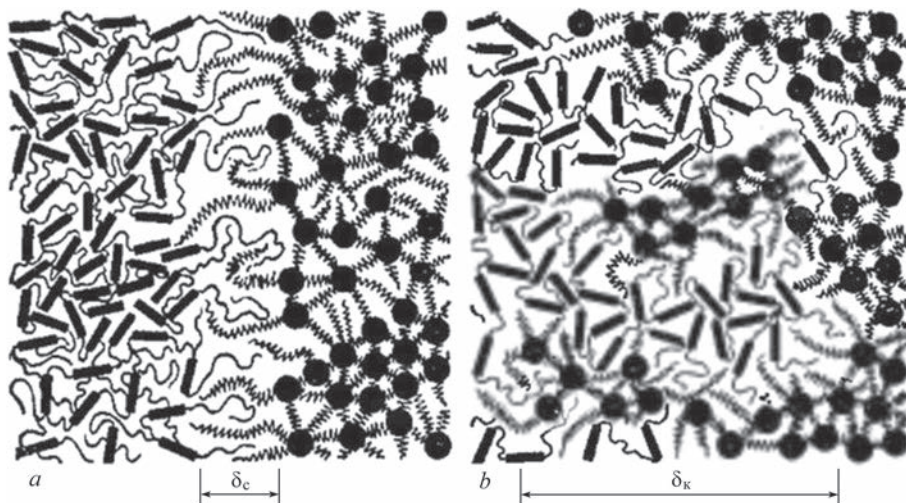


Figure 8. Model of the transition layer on the interface of different objects: *a* — allowing for only segmental diffusion; *b* — at displacement of structural elements [17]

Based on experimental data analysis, Yu.S. Lipatov developed a model of stage-by-stage formation of a transition zone on the contact boundary of the two polymers (Figure 8). At the initial stage, a thin transition layer forms at contact of molten surfaces due to conformational turns of macromolecule segments. If the temperature in the contact zone remains high enough for a certain time, the second stage comes, where not only segments, but whole macromolecules move through the fusion surface in the form of small supermolecular objects, under the impact of thermal motion. As a result, a much wider layer forms instead of a primary thin transition layer, where microvolumes of one polymer are immersed into the structure of the other one.

Similar processes, apparently, can take place also at formation of the welded joint between the contacting surfaces of the same polymers. While at joining different types of polymers, even with formation of a wide transition layer, a pronounced interface always remains, in polymers of one type this boundary disappears and is blurred during autohesion and diffusion. The welded joint strength is mainly influenced exactly by the properties of this transition structure in the fusion zone.

The general theory of diffusion in any environments, in particular, in polymers, treats this process as a totality of elementary acts of molecular particle movement. It is understandable that movement of any molecules or its fragment requires free space, into which it will be displaced. Therefore, the vacancy (hole) mechanism is believed to be the base of the diffusion process [18]. The elementary act of diffusion consists in formation of a microvoid (hole) near the molecule as a result of thermal motion, and their subsequent exchange of places. In high-molecular polymers the microvoids usually form owing to conformational turns of individual chain segments — so-called kinetic segments. Accordingly, assumptions are made that formation of a transition structure between

the polymer parts in welding takes place mainly due to segmental interpenetration of macromolecules through the joint surface [19]. Here, the determinant role of temperature in the welding zone and working pressure is emphasized, which ensures the necessary viscous contact between the molten surfaces.

The conformational theory of polymer welded joints was formulated, proceeding from the results of investigations by Yu.S. Lipatov and PWI scientists [20]. The theory is based on the idea that the thermal movement of macromolecules occurs mainly due to conformational turns of molecular chains segments, not by translational movement of their ends. Therefore, polymer melting and solidification should be regarded as disordering and subsequent ordering by the conformational mechanism. Interpenetration of macromolecule fragments through the joint surface in polymer welding (interface “healing”) also occurs due to molecular conformational turns. Macromolecule diffusion by translational movement of their ends through the joint surface practically does not influence the “healing” process, because of short welding time and small number of free ends of molecular chains, compared to the number of segmental atomic groups, capable of conformation.

An assumption was also made that the number of spherulitization nuclei on the fusion surface has a determinant influence of the final crystalline structure of the polymer. In keeping with this statement, a criterion of formation of a sound butt welded joint of polymers was formulated. In Figure 9, *a*, an optimal number of crystallite nuclei is present along the fusion line. It results in formation of a continuous complete spherulitic structure of strength equal to that of the base polymer material. Figure 9, *b* shows the case when the thermo-physical conditions at butt joint formation promoted appearance of an excess number of spherulite nuclei. It results in formation of a large number of fine incomplete spherulites, and of the so-called transcrySTALLINE

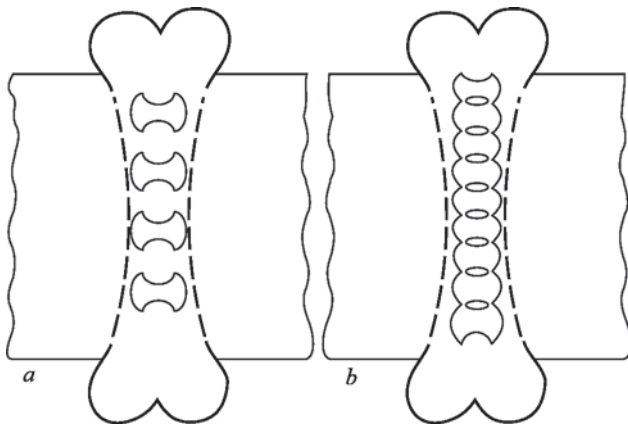


Figure 9. Formation of spherulitic structure along the polymer fusion line [20]

layer along the fusion line. Such a joint has lower strength and it fails along the weld line.

The recent studies performed at PWI, allowed complementing the conformational theory of polymer welded joint formation by new data [21, 22].

It is shown that the welded joint formation is influenced by two main factors — thermal energy T and force field P (external pressure and other factors) (Figure 10). Based on the results of comprehensive studies of the structure and properties of polymer welded joints it was assumed that in welding macromolecule orientation along the interface takes place in the thin melt layer with subsequent blurring of this surface due to rotational movements of macromolecule segments, i.e. change of their conformations in the transition layer volume [23]. The proposed concept does not deny the possibility of interdiffusion of polymer macromol-

ecules, in particular due to reptation. It is believed, however, that statistically the conformational rotational movements of macromolecule segments occur much more frequently, compared to the diffusion ones, so that they have a decisive influence on blurring of the interface for the short-term joining process (Figure 11), which polymer welding is in most cases [2]. The base of the process of macromolecule fragment movement in the melt at thermal motion is exactly the vacancy (hole) mechanism. Presence of such vacancies in the polymer crystalline structure is envisaged by the closest to reality Hosemann paracrystalline model [24].

In keeping with this model, the polymer structure contains voids, amorphous regions, single-crystals, fragments of straightened chains and other formations. After melting or transition into a viscous state the voids remain on the molecular level, similar to some folded or disordered formations capable of conformational transformations. Figure 12 shows a model of gradual disappearance of the interface in polymer welding by vacancy-conformational principle. At the stage of wetting and contact of the molten surfaces ($t = 0$) the number of vacancies is the greatest exactly near the contact plane. After some time ($t > 0$), the vacancies on the interface are gradually filled owing to thermal motion of molecular segments (conformations), moving in-depth of the material. If the polymer material is in the molten state for some minimal time required, vacancy distribution in the melt will become almost uniform, and the interface will be “blurred” and will disappear. After solidification of the homogeneous melt layer a strong tight welded joint forms. We will call this minimum time T_g the homogenization time.

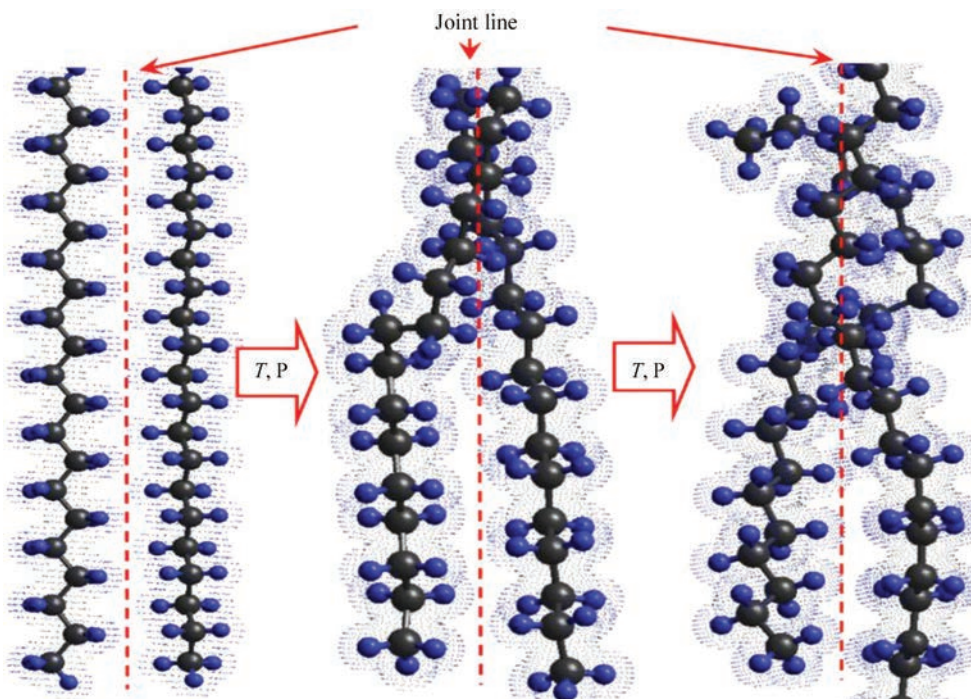


Figure 10. Process of segmental mobility with the change of macromolecule conformations under the impact of thermal and force fields in welding [23, 24]

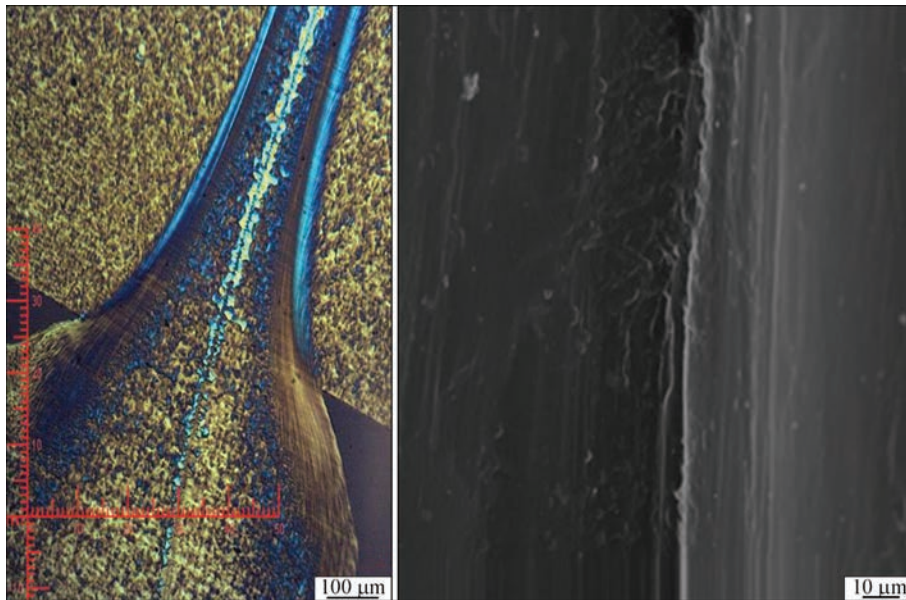


Figure 11. Optical and electron micrographs of polymer welds [25]

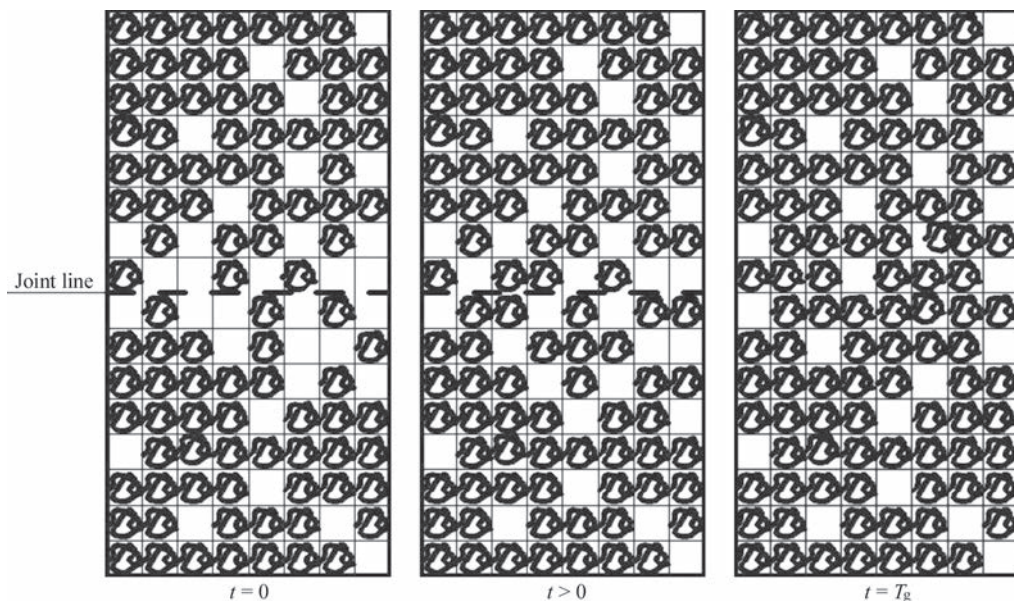


Figure 12. Model of transition layer homogenization on the interface in polymer welding by vacancy-conformational principle

We believe that the terms “healing”, and “sealing” for the process of disappearance of the interface between the melts of contacting polymers of one type are insufficiently accurate. In reality, even though incomplete but still equalizing of volume-spatial properties of molecular structure of molten polymer takes place, macromolecule fragment distribution becomes more uniform and homogeneous. That is why, the process occurring in the thin layer of the transition zone should be regarded as equalizing of the melt properties. i.e. “homogenization”.

It was noted above that in order to produce a crystalline formation at polymer melt cooling, individual molecular chains should have the ability to move in the melt relative to their neighbours. Macromolecular chain movement can have two forms: conformational

turns of individual parts of the molecule relative to its own chemical bonds, and translational movement of the chain relative to the common molecular tangle. Both the movements can be regarded as the phenomenon of self-diffusion, initiated by the thermal processes.

Note that the proposed model of the transition layer homogenization on the interface in polymer welding by the vacancy-conformational principle can be complemented by development of a mathematical model for determination of the appropriate modes of welding diverse polymer materials.

CONCLUSIONS

1. It was determined that the process of welding plastics is the gradual disappearance at the molecular level of the gap between the parts being joined and the formation of a transition layer (welded seam) between them, the

structure of which is strong, but significantly different from the structure of the main polymer material.

2. Nowadays there are several theories as to the nature and mechanisms of the process of plastics welding. Each of them has indirect experimental substantiation, but is not of a general nature. Therefore, at present continuation of investigations of the structure and properties of plastics welded joints is timely, in order to obtain fundamental data for complementing the theoretical fundamentals of polymer material welding.

3. A question which remains to be debatable is the possibility and mechanism of diffusion of molecular chain fragments, which is a decisive point for understanding the process of polymer welding. It is obvious that “homogenization”, i.e. equalizing of properties, will be a more accurate definition for the process of “blurring” of the interface in polymer welding, instead of the common definition of “healing”.

4. The currently available models of polymer welded joint formation are based on different physical phenomena — mutual adhesion of the substrates, macromolecule diffusion and melt rheology. We believe that the most realistic is the theory of polymer welded joint formation due to conformational transformations of macromolecule fragments. In development of the conformational theory, being elaborated by PWI Scientific School, a model was proposed of homogenization of the transition layer on the interface in polymer welding by the vacancy-conformational principle.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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