Mathematical model of adhesion junction of layers during coextrusion

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Abstract. Nine theories of polymer adhesion during coextrusion are researched. Two approaches to describing adhesion are presented – thermodynamic and molecular-kinetic ones. The factors, determining the durability of adhesion junction, are analyzed. The stages of adhesion connection formation are presented. The adhesion junction emergence model as a result of intermolecular interaction is described. As a result of calculations the following dependencies are got: the dependence of ply separation energy on the contact length of polyisobutylene adhesion junction of different molecular weight, the dependence of ply separation energy on molecular weight of polyisobutylene adhesion junctions got during different time, the dependence of adhesion durability on squared difference of polymer solubility parameters, the dependence of interdiffused zone width in the time.

1. Introduction

Adhesion is a physico-chemical process going on the surfaces of condensed phases with the formation of a new heterogeneous system [1], [2], [3]. Along with this an interphase zone with special physical and chemical properties is generated on the division boundary.

If to examine the genesis of conceptions of polymer adhesion nature, during several years about nine theories have been elaborated:

- a mechanical theory – it gives preference to the influence of substrate surface microrelief;
- an adsorptive theory – it gives preference to the influence of adhesive sorption;
- a chemical theory – it gives preference to the influence of valent interphase connections formation;
- a diffusion theory – it gives preference to the influence of polymer compatibility in the adhesion zone contact;
- a rheological theory – it gives preference to the influence of increasing boundary layers durability of polymers in contact;
- a microrheological theory – it gives preference to the influence of adhesive flowing into microdefects of the substrate surface;
- an electric theory – it reduces the problem to the emergence of a double electric layer on the surfaces in contact;
• an electrorelaxation theory – it takes into consideration the specificity of relaxation phenomena in polymers;
• a molecular theory – according to its authors’ opinion, it presents the development of the adsorptive conception.

2. Approaches to describing adhesion
Nowadays, there are two approaches to describing adhesion which have been elaborated by L. M. Pritykin and V. L. Vakula, thermodynamic and molecular-kinetic ones, each of which considers different aspects of the issue, reciprocally complementing each other. Thus, if the thermodynamic approach allows substantiating a general picture of the phenomenon and giving the interpretation in the energy aspect, then the molecular-kinetic approach offers a principle opportunity to reveal the concrete mechanism of adhesion junction formation, considering the chain structure of macromolecules.

In the thermodynamic approach the most attention is given to the phenomena of moistening and spreading [4], [5], [6]. In the frames of the molecular-kinetic approach to the adhesion, the issue connected with the distinction of polymer properties in the capacity and surface layers is of great significance; this requires getting an objective assessment of transitional and boundary layers characteristics [7]. While considering these issues by the molecular-kinetic theory, the main emphasis is made on taking into consideration the role of flexibility and mobility of macromolecules during polymer adhesion interaction; and the manifestation of rheological effects is of a paramount importance for analyzing polymer adhesion at the macroscopic level [8].

3. Factors, determining the durability of an adhesion junction
The durability of adhesion junctions is determined by different factors, the most important of which are: the chemical nature of the adhesive and substrate [9]; the conditions of the adhesion junction formation (the contact length, temperature and pressure) [10]; the ratio of the adhesion (in the thermodynamic sense of this term) and the friction [11]; the adhesion itself on the division boundary; cohesive durability of the adhesive and substrate; the character of the adhesive viscosity and elasticity on the deformation intensity in the process of its application; the deformation of the junction components till its destruction; the conditions of the trial (temperature, at which the splice destruction happens, a loading speed, the time of power action, etc.); inner tenses contributing to the destruction of an adhesion junction, which should be taken into consideration during researching multilayer materials destruction by ply separation [12].

The formation of adhesion connection in the system of adhesives – the substrate flows in two stages: the formation of the contact surface and the emergence of the connections between the adhesive and substrate. At the first stage the main role is played either by the rheological adhesive properties or by the macromolecular segments’ diffusion and their dependence on the conditions of application, i.e. temperature, tension and shift speed. These parameters can be varied in the researched process [13].

Besides, the state of the covered surface of its structural characteristics, influencing the formation of the contact adhesive-substrate, is of great importance. It is connected with the adsorptive phenomena, in particular with moistening, which is the necessary (but not sufficient) requirement of adhesion connections formation. During coextrusion the degree of polymer destruction, humidity and the cleanness of the granulated material in the loading bunker can influence the surface state of the interacting melts [14].

4. The model of an adhesion junction as a result of intermolecular interaction
The adhesion junctions, having appeared as a result of microrheological or diffusion processes, may have different nature: chemical interaction, intermolecular interaction [15].

The moistening improves along with the increase of temperature due to the complete molecular contact of adhesive and substrate [16]. This also explains the increase of durability of glue joint while
heating. As the temperatures grows, the process of establishing equilibrium interfacial angle speeds up, due to their heightened viscosity the mentioned process goes on at normal temperatures very slowly. The moistening speed increases while the adhesive’s viscosity lowers. The viscosity of the coextrudates can be varied in definite limits of the researched process [17].

The main supporter of the adhesion diffusion theory S. S. Voyutsky asserted that the adhesive interaction of polymers of the same (autohesion) or different nature is determined by the reciprocal diffusion of macromolecules over the division interphase boundary [18].

For this the macromolecules or segments of polymeric chains of the adhesive and substrate have to be sufficiently mobile and intersoluble [19]. The second requirement can be substituted by the condition of the solubility parameters equation of the mentioned above objects which is presented by the ratio

$$\delta_s = \left[ \frac{H - RT}{V} \right]^{1/2}$$

in which $H$ is a molar heat (enthalpy) of evaporation;
$R$ is a universal gas constant;
$T$ is a temperature ($^\circ$K);
$V$ is a molar capacity.

Therefore, a solubility parameter acts as an indicator of two components’ compatibility.

Voyutsky considered the influence of contact time, temperature, polymer nature, its molecular weight and viscosity on the durability of adhesion junctions as an experimental corroboration of the correctness of his assumptions [20]. He supposed that, as the dependence character of the last characteristics on some of the parameters listed above was similar to diffusion processes, the adhesion was a result of the diffusion.

These conceptions were supported by the quantitative models, developed by Vasenin. First, he scrutinized the first Fick’s law which establishes interconnection between the substance quantity $w$, diffusing in the time $t$ to the direction $x$ over the surface of a single area, which is normal to the concentration gradient $dc/dx$ and the time $t$:

$$dw = -D \frac{dc}{dx} dt$$

where $D$ is a diffusion coefficient.

However, this ratio can be directly applied only in the case of a steady-state diffusion, when the concentration in different points of the system does not change in the time. It is clear that this requirement is not met during the penetration of the adhesive polymer chain segments into the surface area of the substrate. The formation and decay of the diffused objects is described by the second Fick’s law. That is why Vasenin used these laws to determine the penetration depth of the diffuse molecule. First he made an assumption that the decrease of the diffusion coefficient during penetration into the surface area of the substrate during the time $t$ can be put down as follows:

$$D = D_0 \cdot B \cdot t$$

where $D_0$ is a constant, characterizing the mobility of macromolecules; $B$ is a constant, determining the speed of diffusion coefficient $D$ changes during the times (usually $B$ is 0.5).

Then he got an equation for the depth of penetration $l$:

$$l = \left( \frac{\pi DL^2}{R_t} \right)^{1/2}$$

where $R_t$ is a constant, characterizing the rigidity of macromolecules, the length of connections and valent angles in them. Further, he introduced a ratio for the quantity $N$ of molecular chains of an adhesive with the density $\rho$ and molecular weight $M$, which cross the interphase boundary:

$$N = \left( \frac{2 \cdot N \cdot \rho}{M} \right)^{1/2}$$
Finally, relying on the assumption of the proportionality of ply separation energy necessary for the destruction along the interphase area, the penetration depth, as well as the quantity of the chains crossing the N phases division boundaries, Vasenin wrote the formula:

\[
P = R_\beta \left( \frac{2Np}{M} \right)^{\gamma/2} D^{\nu/2} t^{\nu/4}
\]

where \( R_\beta \) is a constant, determining molecular characteristics of objects.

Or for two different polymers:

\[
P = 5.55v \left[ \left( \frac{2p_1}{M_1} \right)^{\gamma/2} D_{1}^{\nu/2} + \left( \frac{2p_2}{M_2} \right)^{\gamma/2} D_{2}^{\nu/2} \right] \cdot t^{1+\beta/2}
\]

where \( v \) is a frequency factor.

Recording the main parameters allowed using successfully the equation for the assessment of polyisobutylene adhesion. In figure 1 the energy \( P \) is presented as a function of the contact length \( t \) of polyisobutenes of various molecular weights. A good agreement between the experimental and calculating results is found out in case of proportionality between the values \( P \) and \( t \).

However, it is necessary to point out that the exact value \( D \) was impossible to find out, that is why an approximate value was got, which meets the requirements of the experimental data totality.

Figure 1. Calculated by the equation, the dependence of ply separation energy on the contact length \( t \) of polyisobutylene adhesion junction of different molecular weight \( M \): \( M_1 \) is 0.88·10\(^6\); \( M_2 \) is 1.2·10\(^6\); \( M_3 \) is 2.42·10\(^6\).

Figure 2. The dependence of ply separation energy on molecular weight \( M \) of polyisobutylene adhesion junctions got during different time \( t \): \( T_1 \) is 15 min., \( T_2 \) is 60 min., \( T_3 \) is 120 min.

It is noteworthy that if to take the diffusion coefficient equal to 10-14 cm\(^2\)/s, then according to the theory of Vasenin set forth above, it will take the segments about 100 hours to penetrate from one polyisobutylene phase to another at the depth of 10 mkm.

However, the researches show that the diffusion even for a much shorter distance, according to the theoretical considerations, may provide a substantial durability of an adhesion junction; thus, the increase of interpenetration depth from 1 to 2 nm may lead to strengthening of the system durability five-fold – nine-fold.

That is why it is important to provide a sufficient degree of the segments’ interdiffusion to form branched reticular structures.

There are direct evidences of the interdiffusion of compatible polymers. The radiometric researches proved the existence of macromolecules’ diffusion. It is ascertained that the diffusion coefficients are in the range between 10-11 and 10-14 cm\(^2\)/s, such values are sufficient to form a durable interphase surface between polymers as a result of their contact, which lasts only several seconds. It is
ascertained (figure 4) that the adhesion durability between polymers decreases with the growth of difference in the solubility parameters of two phases.

The researches, conducted to study the interdiffusion processes on the example of the system PS/PS, reveal that at the temperature higher than of the glass transition temperature, the width of the division surface increases in the time according to the classical law in proportion to the time \( d \sim t^{1/2} \).

5. Summary

The mathematical model of adhesion junction layers’ formation during polymers coextrusion on the basis of the intermolecular interaction theory is developed.

By doing experiments on the model, we got the dependence of ply separation energy on the contact length of polyisobutylene adhesion junction of different molecular weight: 0.88\( \times 10^{6} \); 1.2\( \times 10^{6} \); 2.42\( \times 10^{6} \), the rational diapason of contact time is 20-30 sec\( \times 10^{-3} \).

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