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Statistical regularities of the early stages of the self-healing process of interfaces of incompatible high-molecular-weight solids

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Using a number of statistical methods (normal probability plots, probability density function histograms, and a series of the standard tests for normality), an analysis was made of the conformity of the strength distribution σ of the polystyrene (PS)–poly(ethylene terephthalate) (PET) interface at the initial stages of self-healing to the normal distribution. The contact of PS and PET samples with the glassy bulk was carried out at a temperature of 74 °C, which is the lower temperature limit for the origination of σ between these thermodynamically incompatible polymers. The revealed features of compliance with the null hypothesis of normality and the data dispersion depending on the contact duration are discussed.

Keywords: amorphous polymers, interfaces, adhesion, strength, statistics.

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1. Introduction

A fundamentally important aspect of the contact interaction between high molecular weight solids is the occurrence of adhesive strength σ. Indeed, the manifestation of this physical phenomenon is possible only if segments of polymer chains of one sample can diffuse through the interface and form new intermolecular Van der Waals bonds with molecular groups of chain segments of another sample [1,2]. As a result, the concentration of such bonds per unit contact area increases in the ultrathin interfacial nanoscale layer, and, as a result, a mechanically stable adhesive joint (AJ) is formed. In the absence of mutual diffusion, the intersurface interaction is provided by exceptionally weak dispersive forces between electrically neutral molecular groups, the action of which is clearly insufficient to keep polymer samples in mechanically stable contact.

Naturally, the implementation of such a scenario at the molecular level is possible only on devitrified surfaces, when large-scale rotational translational movement of segments is activated [1,2]. In other words, the nucleation of σ implies the activation of this mode of molecular motion. Moreover, even if the polymer volume is in a glassy state, segmental mass transfer through the interface is also possible. However, for this purpose, the surface layer of the sample with a thickness of the order of the diameter of a statistically folded chain coil (several nm) must be in a highly elastic state, which must be preserved at the interface. This effect is observed at temperatures T, much lower (even by 100 K) than the glass transition temperature T_g of the polymer bulk (T_g^{bulk}), if this T exceeds the T_g of the near-surface layer ($T_g^{surface}$) [3–9].

Most pairs of chemically dissimilar polymers are thermodynamically incompatible [10]. Therefore, the interfaces of such polymers are of the greatest interest. These include the polystyrene (PS)−polyethylene terephthalate (PET) interface. Upon contact of PS and PET, mutual repulsion of molecular groups of different chemical structures occurs, which, at first glance, does not allow the formation of mechanically stable PS−PET AJ. Nevertheless, due to the minimization of the total surface energy of the system by doubling the total area of its free surface (four surfaces of two samples before contact and two surfaces after bringing the samples into contact), adhesion is realized by activating the interface self-healing process. Its driving force is the thermodynamically advantageous elimination of the discontinuity of the medium in the contact zone due to mutual segmental diffusion [1]. In addition, the existence of PET in both an amorphous and semi-crystalline state is of interest from the point of view of the influence of the crystallinity factor on the nature of statistical behavior at the interfaces of amorphous PS−crystalline PET and amorphous PS−amorphous PET.

One of the most widely used approaches for analyzing the degree of self-healing of polymer-polymer interfaces is to establish the kinetic laws of the evolution of the arithmetic mean σ (σ_{av}) versus the contact time t. However, for a better understanding of the mechanisms of self-healing and fracture of such interfaces, it is also very informative to identify statistical patterns in the distribution σ [11–15]. In this context, the PS−PET interface was studied only within the framework of the Weibull model [11,16]. However, an analysis of the correspondence of the σ distribution to the most commonly used normal [17–19] distribution for this interface, especially under the conditions of the occurrence of σ, was not carried out.

Thus, the purpose of this work is to find out the correspondence of the statistical distribution σ for the

Results of normality tests for the adhesive strength distributions of the PS–PET interface

t, min	Type of test	Statistics of test	Parameter of normality p	Parameter $p \geq 0.05^*$
30	Kolmogorov-Smirnov	0.15256	1	+
240		0.13563	1	+
30	Shapiro–Wilk	0.9311	0.45875	+
240		0.95378	0.71325	+
30	Lilliefors	0.15256	0.2	+
240		0.13563	0.2	+
30	Anderson–Darling	0.33489	0.43108	+
240		0.2098	0.80635	+
	D'Agostino K-square:			
30	Generalized	3.42281	0.18061	+
30	Peak asymmetry	1.32722	0.18444	+
30	Peak brightness	1.28891	0.19743	+
240	Generalized	0.43868	0.80305	+
240	Peak asymmetry	0.43939	0.66038	+
240	Peak brightness	−0.4956	0.62018	+

Note. „+“ in the last column means that the hypothesis of normality cannot be rejected.

amorphous interface of the PS–PET at the occurrence of σ to the normal distribution.

2. Experimental part

High-molecular-weight PS and PET with weight-average molecular weight 230 kg/mol and 15 kg/mol, respectively, were selected as model objects of the study. The PS and PET samples (amorphous films 0.1 mm thick) were obtained by extrusion and melt pressing, respectively. The T_g^{bulk} values of PS and PET measured by differential scanning calorimetry were 103 and 81 °C, respectively. PS–PET AJ was formed at $T = 74$ °C — the lowest T, at which adhesion of PS and PET was observed — with short-term ($t = 30$ min) and long-term ($t = 4$ h) contacts. The contact area was 5×5 mm. Mechanical tests of the formed AJ were performed using the Instron-5565 universal testing machine at room temperature and a tensile velocity of 10 mm/min. The number of parallel measurements for each t was $n = 10$. Within the framework of the used statistical algorithm of the Origin program, at $n = 10$, the values of the probability parameter p were calculated for all standard normality tests. The calculation indicates that $n = 10$ is sufficient to correctly determine p.

3. Results and their discussion

Figure 1 shows the values of σ in ascending order for a series of n measurements for PS–PET interfaces formed at $T = 74$ °C during $t = 30$ min and $t = 4$ h. It can be seen that the adhesive strength of the interface under study varies from 0.03 to 0.07 MPa at $t = 30$ min and from 0.04 to 0.09 MPa at $t = 4$ h. In other words, increasing t by one decimal order leads to a noticeable increase in the value of σ. This behavior seems logical given the intensification of the process of mutual diffusion of segments with an increase in t — one of the key factors, along with T, influencing the process of self-healing of polymer-polymer interfaces [1–4,6,8]. Despite the fact that the measured strength values appear to be very low, they exceed the lower strength level $\sigma = 0.02$ MPa of the beginning of the formation of a mechanically stable adhesive bond [20], confirming the diffusion coupling mechanism of PS and PET under the conditions studied.

Let's perform a statistical analysis of the data in Figure 1 using normal probability graphs (Figure 2, *a, b*), Gaussian

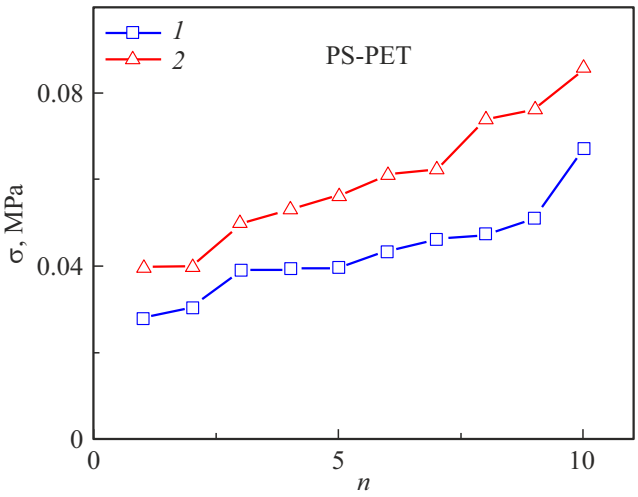

Figure 1. Dependences of adhesive strength in ascending order on the measurement sequence number for the PS–PET interface after self-healing at $T = 74$ ° for 30 min (*1*) and 4 h (*2*).

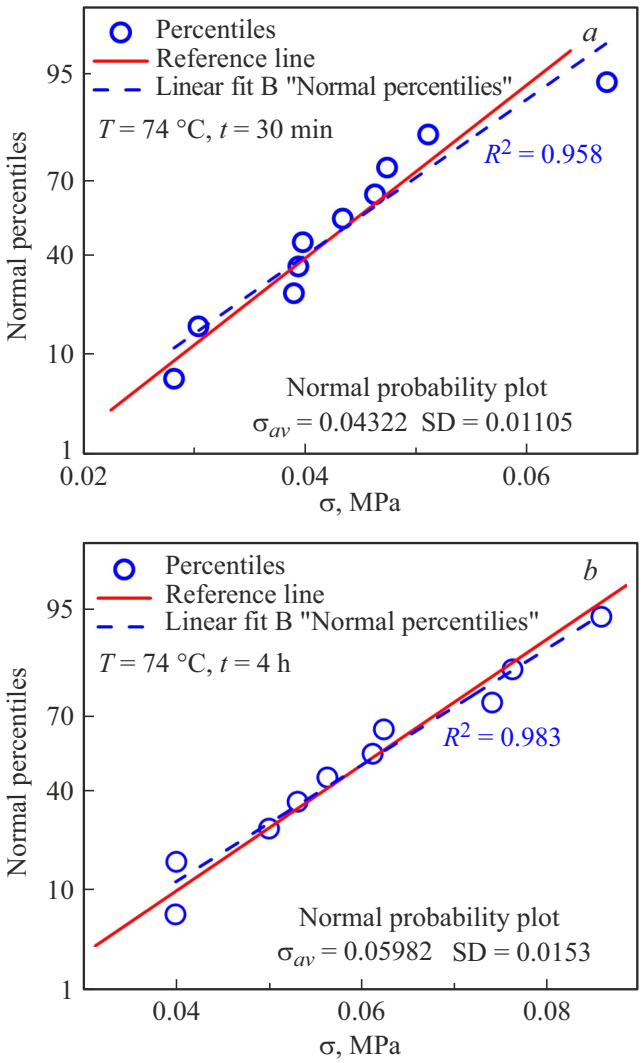

Figure 2. Normal probability graphs based on the basic (solid) lines generated by the Origin program for the PS–PET interface after self-healing at $T = 74°$ for 30 min (a) and 4 h (b). The dotted lines show the results of the analysis of the generated dependencies using the least squares method, which make it possible to determine the value of R^2.

histograms (Figure 3, a, b), and tests for normality (see the table). As follows from the comparison of the data in Figure 2, a and b, both experimental graphs are satisfactorily approximated by linear dependencies close to the graphs of the normal distribution with sufficiently high values of the coefficient of determination R^2. However, the approximation of the data with a normal distribution for $t = 4$ h with $R^2 = 0.983$ (Figure 2, b) seems to be more correct than for $t = 30$ min with $R^2 = 0.958$ (Figure 2, a). On the other hand, an analysis of the same data using histograms of the probability density function PDF(σ) shows that the approximation using the standard Gaussian function for $t = 30$ min (Figure 3, a) is more correct ($R^2 = 0.597$) compared to a very conditional approximation for $t = 4$ h (Figure 3, b) with a low value of $R^2 = 0.159$.

Let's analyze the experimental data using the third approach — tests for normality [17–19] (see the table). As can be seen, all the tests performed indicate the validity of the null hypothesis H_0, and even the minimum value of the normality parameter $p = 0.17$ significantly exceeds the significance level $p = 0.05$ — the minimum generally accepted value p, starting from which H_0 is fair. It also follows from the table that the values of p for $t = 4$ h are either equal to the corresponding values of p for $t = 30$ min (Kolmogorov-Smirnov and Lilliefors tests), or noticeably they are exceeded (Shapiro-Wilk, Anderson-Darling, and D'Agostino's K-squared tests). Thus, all three methods used to study the compliance of the adhesive strength distribution in the early stages of self-healing of the PS–PET interface with a normal distribution have shown their suitability. However, two methods (normal probability plots and normality tests) revealed a more correct distribution for long-term contact ($t = 4$ h), and one (Gauss histograms) — for short-term ($t = 30$ min).

The similar, rather complex nature of the statistical behavior at the polymer-polymer interfaces at the initial stages

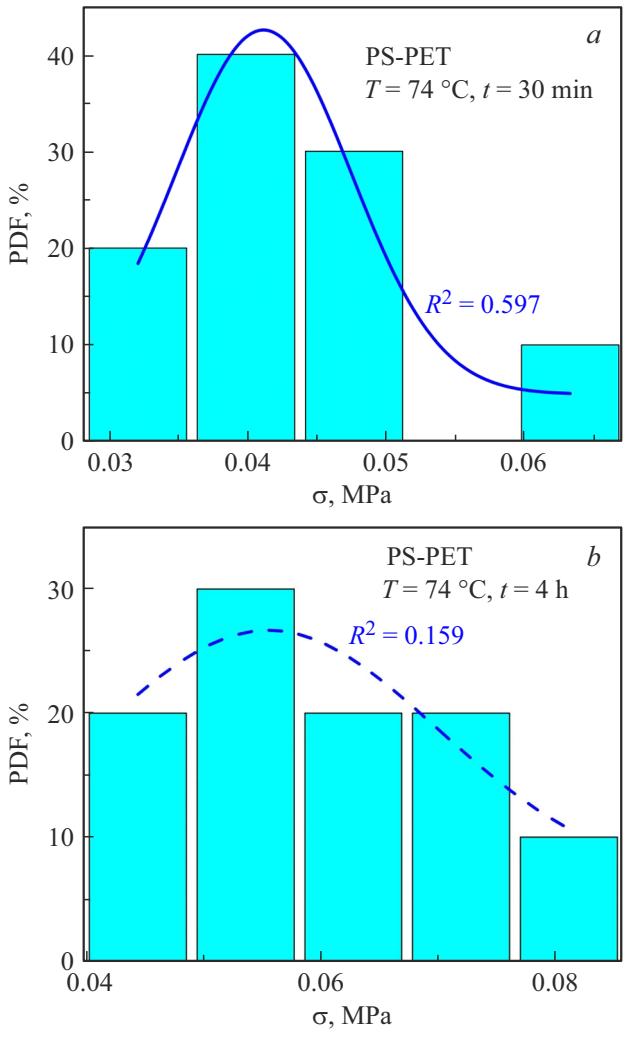

Figure 3. Gaussian histograms for the PS–PET interface after self-healing at $T = 74°$ for 30 min (a) and 4 h (b).

of self-healing is confirmed by the data in Refs. [12–15]. In particular, it was noted that there may be no direct correlation between the results of normality tests and the shape of Gaussian histograms for σ distributions. So, in most cases, when observing H_0, the Gauss histogram did not have the shape of a bell curve. We also note that due to the overestimated values of p defined in the Kolmogorov-Smirnov test, the use of this test to analyze the adhesive strength of polymer-polymer interfaces seems impractical, especially considering the fact that for interfaces PS–PS, PS–poly(2,6-dimethyl-1,4-phenylene oxide), polymethylmethacrylate–polymethylmethacrylate [12–15] the values of p exceeded the critical significance level $p = 0.05$ in all cases.

Within the framework of our proposed approach, we compare [13] the dimensionless parameters of the variance the σ values, determined from the graphs of normal probability (standard deviation normalized by σ_{av}, SD/σ_{av}), with the values of the reciprocal of the values of the Weibull modulus $1/m$, using the values of m from Ref. [11]. Using the values SD = 0.01105 MPa, $\sigma_{av} = 0.04322$ MPa (Figure 2, *a*), $m = 4.69$ [11] at $t = 30$ min and SD = 0.0153 MPa, $\sigma_{av} = 0.05982$ MPa (Figure 2, *b*), $m = 4.53$ [15] at $t = 4$ h gives SD/$\sigma_{av} = 0.2557$, $1/m = 0.2132$ at $t = 30$ min, and SD/$\sigma_{av} = 0.2558$, $1/m = 0.2208$ at $t = 4$ h. The ratio of SD/σ_{av} to $1/m$, which is 1.20 and 1.16 at $t = 30$ min and $t = 4$ h, respectively, is close to unity which indicates the statistical identity of SD/σ_{av} and $1/m$, despite the difference in basic principles underlying on the basis of these analysis methods.

Conclusion

This study is a first detailed statistical analysis of the distribution of adhesive strength at the temperature of its interdiffusion occurrence on an incompatible PS–PET interface within the normal distribution. In all the standard normality tests used, the validity of the null hypothesis has been established. Using classical normal probability graphs and Gauss histograms, a complex pattern of statistical behavior of σ was revealed depending on the duration of contact. This requires further research on self-healing of the PS–PET interface in the wider ranges of t and T, which are currently being completed. The statistical identity of the variance parameters σ in the Weibull and Gauss models has been confirmed.

Conflict of interest

The authors declare that they have no conflict of interest.

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