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Statistical aspects of the strength evolution at interfaces of compatible dissimilar amorphous polymers with radically different glass transition temperatures

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Using the Weibull's and the normal probability methods and a series of tests for normality, a statistical analysis of the distributions of adhesive strength σ developing at the contact zone of the samples of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has been performed. The contact has been carried out in the region of the glass transition temperature T_g of PS corresponding to the region $T < T_g - 100^\circ$C for PPO. The most correct type of the σ distribution has been determined. The compliance with the null hypothesis of the normal probability for the arrays of the σ distributions has been analyzed. A new approach has been proposed that allows for a correct comparison of the σ dispersion within the framework of various statistical methods of analysis.

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

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1. Introduction

When two specimens of identical or different polymers are in contact, with time t their coupling (adhesion) may occur, but only in the case when the segments of polymer chains of a single specimen diffuse through the contact zone and produce new physical bonds with the segments of chains in the other specimen in a nanometer-thick ultrathin layer [1–3]. Manifestation of this physical phenomenon — self-healing of interfaces — is related to formation of new Van der Waals bonds between the segments of chains that occurred as a result of their mutual diffusion, and also topological intermolecular nodes of engagements to entanglement of chains. It should also be underlined that the implementation of such scenario of events development at the molecular level in the polymer–polymer interfaces is only possible at temperatures T that are not below the glass transition temperature T_g, when rotation-translation movement of segments is activated [4]. Therefore, the observation of adhesion between polymers at $T \ll T_g$ [5,6], for example, even at $T < T_g - 120^\circ$C [6], seems rather unexpected. However, due to the effect of glass transition temperature decrease in the near-surface layer T_g^{surf} with the thickness of the order of diameter of the statistically rolled coil of macromolecule (units — dozens of nanometers depending on the chain flexibility and length) compared to T_g of specimen volume T_g^{bulk} [7,8], the rotation-translation mass transfer of segments in this layer may be activated at $T < T_g^{\text{bulk}}$, too, if the condition $T_g^{\text{surf}} < T < T_g^{\text{bulk}}$ is complied with.

In this context the greatest interest is presented by the study of interfaces of heterogeneous polymers with outlying T_g, since intensities of the molecular mobility at this temperature T in different polymers vary dramatically. One of the few interfaces suitable for this purpose is the interface of polystyrene (PS)–poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). First, this is a pair of thermodynamically compatible polymers, which is a favorable factor for mutual diffusion and formation of a mechanically stable adhesive joint (AJ). Second, the difference between the T_g^{bulk} PS and PPO values exceeding 100°C [6], is huge, which makes the considered system dramatically asymmetric from the point of view of molecular mobility.

It is known that the general approach to the study of the kinetics of adhesion strength evolution σ in polymer–polymer interfaces, including at $T < T_g^{\text{bulk}}$, is the analysis of dependences of mean strength value $\sigma(\sigma_{\text{av}})$ on temperature and time t [1–6]. At the same time the recent papers [9–12] showed that more detailed analysis of this phenomenon with involvement of a combination of statistical methods makes it possible to produce an additional valuable information broadening the ideas on the self-healing mechanisms of polymer-polymer interfaces under the conditions of the limited segmental mobility and their destruction. Since the statistical aspect of this process for PS–PPO interface was not studied, the objective of this paper is to do the statistical analysis of the process of PS–PPO interface adhesive strength evolution at $T \ll T_g^{\text{bulk}}$ PPO. To solve the task presented, for the first time a wide circle of graphic methods (Weibull and normal probability plots) and tests for normality (Kolmogorov–Smirnov, Shapiro–Wilk, Lilliefors etc.) were used [13–15]. These tests were selected, since they are generally recognized and standard, are widely

The results of tests for normality for distributions of adhesion strength of PS–PPO interfaces

T, °C	Test type		Statistics of test	Parameter of normality p	Solution at level 5%*
90	of Kolmogorov–Smirnov		0.17052	0.75161	+
100			0.23353	0.24002	+
90	of Shapiro–Wilk		0.89988	0.09477	+
100			0.83212	0.00448	–
90	of Lilliefors		0.17052	0.20000	+
100			0.23353	0.01050	–
90	of Anderson–Darling		0.54143	0.13634	+
100			1.25353	0.00207	–
90	of K-square of D.Agostino-K squared	Omnibus	3.75114	0.15327	+
90		Skewness	1.82121	0.06858	+
90		Kurtosis	0.65904	0.50987	+
100		Omnibus	3.61008	0.16447	+
100		Skewness	1.89515	0.05807	+
100		Kurtosis	−0.13593	0.89188	+

* Note: „+“ and „–“ mean that „normalcy may not be rejected“ and „normalcy is rejected“, accordingly.

used for statistical analysis, and are also included into the available software suites (for example, OriginLab).

2. Experimental part

High-molecular amorphous PS (Dow Chemicals) and PPO (General Electric) were used with the number average molecular weight 81 kg/mol (PS) and 23 kg/mol (PPO) and weight-average molecular weight 230 kg/mol (PS) and 44 kg/mol (PPO). Specimens (films with thickness of 0.1 mm) of PS and PPO were produced using the method of melt extrusion. Values T_g^{bulk} for PS and PPO specimens measured by method of differential scanning calorimetry, made 103 and 216°C, accordingly. PS and PPO films were maintained in contact at $T = 90$ and 100°C for 10 min under the conditions of low-baric contact (under contact pressure of 0.8 MPa). The contact area was $5 \times 5\,\text{mm}^2$. Mechanical tests of AS PS–PPO were conducted on universal breaking machine Instron, model 5565, at room temperature and tensile speed of 10 mm/min.

3. Results and discussion

Figure 1 provides results of mechanical measurements for two series of PS–PPO interfaces formed at various temperatures, $T = 90$ and 100°C, in the ascending order of value σ. One can see that even under conditions if short-term ($t = 10$ min) contact of PS and PPO specimens at T in the field T_g^{bulk} PS, i.e. even under such extremely low T to T_g PPO as $T = T_g^{\text{bulk}} - 126$°C, a mechanically stable AS PS–PPO is formed, besides, increase of T from 90 to 100°C causes increase in value σ. Such behavior seems typical with account of intensification of the process of mutual diffusion of segments via the interface with increase of T — key factor of interface self-healing [1–6].

Let us analyze the produced arrays of experimental data given in Figure 1, using graphic methods (see Figure 2 and Figure 3) and tests for normality (see Table). Curves of normal probability (see Figure 2, *a* and Figure 3, *a*) are compared to the corresponding Weibull curves (see Figure 2, *b* and Figure 3, *b*) at $T = 90$ and 100°C in Figures 2 and 3, accordingly. As it follows from comparison of Figure 2, *a* and Figure 2, *b*, at $T = 90$°C both curves are satisfactorily approximated with linear dependence, however, the description under Weibull model (see Figure 2, *b*) seems to be more correct. Under increase of T to 100°C the linearity in Weibull coordinates stays (see Figure 3, *b*), while the

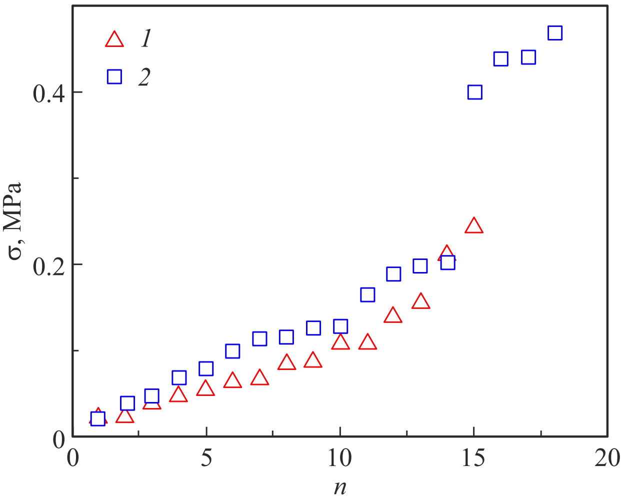

Figure 1. Dependences of adhesion strength in ascending order on measurement number for PS–PPO interfaces after their self-healing for 10 min at $T = 90$°C (*1*) and 100°C (*2*).

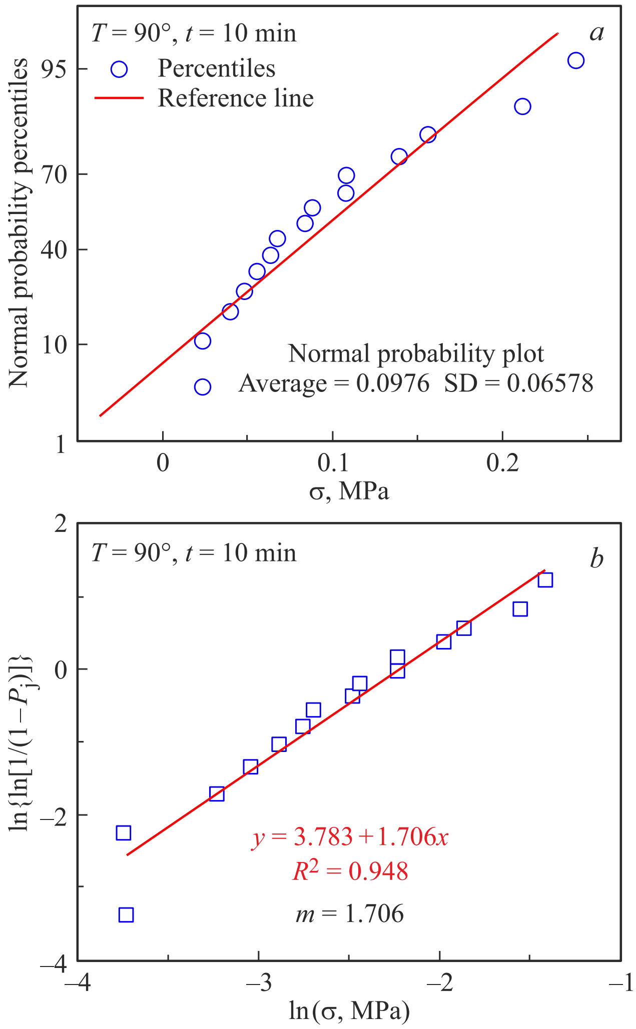

Figure 2. Approximation with distributions of normal probability (a) and Weibull (b) for PS–PPO interfaces strength after their self-healing for 10 min at $T = 90°\mathrm{C}$; P_j — total probability of break; in formula of linear dependence x — $\ln(\sigma, \mathrm{MPa})$, y — $\ln\{\ln[1/(1-P_j)]\}$.

linearity in coordinates of normal probability is problematic (see Figure 3, a). This result is confirmed by results of tests for normality (see Table) — Shapiro–Wilk, Lilliefors and Anderson–Darling tests at $T = 100°\mathrm{C}$ predict normalcy failure. Accordingly, the Weibull model is more correct for description of distribution σ, which is due to quasi-brittle nature of PS–PPO interface damage in connection with low values σ.

Let us compare statistical parameters produced when two independent methods are used. For correct comparison, it is necessary to reduce the criteria of experimental data spread to a single type, i.e. to express them in the same units. Since standard deviation (SD) defined from normal probability curves has strength dimension, MPa, and Weibull module value m is dimensionless, let us normalize SD by σ_{av}, having received dimensionless parameter $(\mathrm{SD}/\sigma_{\mathrm{av}})$. And taking into account the fact that SD increase indicates larger data spread, where as increase of m — the opposite trend, its decrease, it can be naturally assumed that the correct comparison of the analysis results of two different methods is only possible when comparing dispersion parameters $\mathrm{SD}/\sigma_{\mathrm{av}}$ and $1/m$. Using values $\mathrm{SD} = 0.06578$ MPa, $\sigma_{\mathrm{av}} = 0.0976$ MPa and $m = 1.706$ at $T = 90°\mathrm{C}$, and $\mathrm{SD} = 0.14795$ MPa, $\sigma_{\mathrm{av}} = 0.18656$ MPa and $m = 1.337$ at $T = 100°\mathrm{C}$, produced as a result of graphic analysis of data presented in Figures 2, a, 2, b, 3, a and 3, b, we receive $\mathrm{SD}/\sigma_{\mathrm{av}} = 0.674$ and $1/m = 0.586$ at $T = 90°\mathrm{C}$ and $\mathrm{SD}/\sigma_{\mathrm{av}} = 0.793$ and $1/m = 0.748$ at $T = 100°\mathrm{C}$. Ratio of these parameters $(\mathrm{SD}/\sigma_{\mathrm{av}})/(1/m)$ at $T = 90$ and $100°\mathrm{C}$ is 1.15 and 1.06, accordingly, i.e. is close to unity. Accordingly, the approach proposed by us for the first time to review the parameters of dispersion identifies their statistical identity, despite the difference of basic principles of normal distribution (equally probable

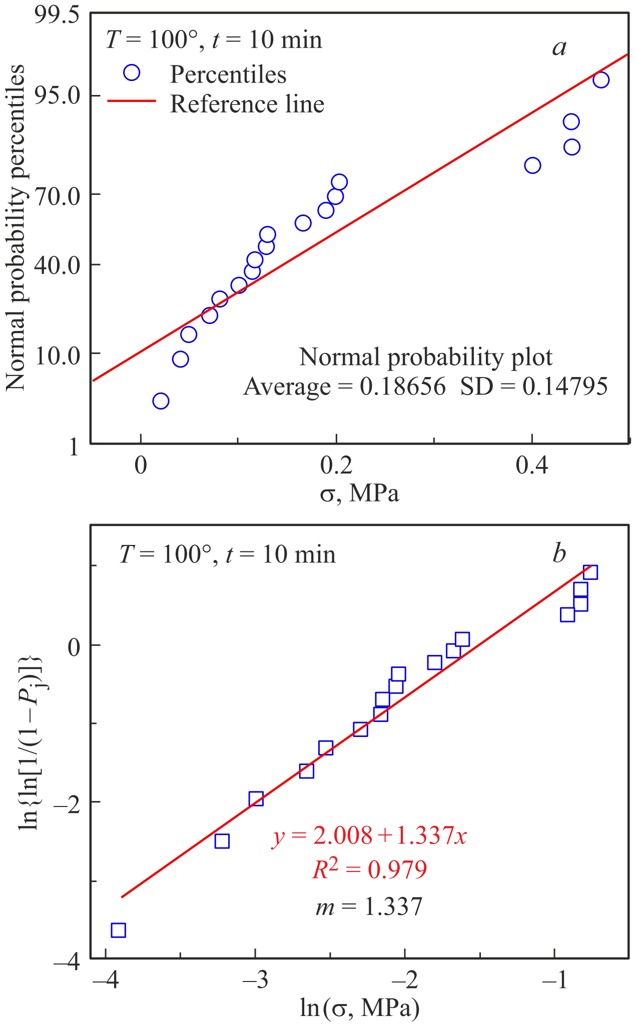

Figure 3. Approximation with distributions of normal probability (a) and Weibull (b) for PS–PPO interfaces strength after their self-healing for 10 min at $T = 100°\mathrm{C}$; the legend is same as in Figure 2.

nature of damage) and Weibull distribution (critical role of surface cracks and weak interfaces) [9–18].

To conclude, we would note the multiple number of existing normalcy tests (for example, in paper [14] 50 such tests are analyzed), to which one can refer the method of small sample data distribution [19]. Some of them may be considered in the future to find out further details of evolution statistics of polymer-polymer interface adhesion strength. However, in this paper the main attention was paid to classic and generally recognized methods of normal distribution and Weibull distribution and normalcy tests (Kolmogorov–Smirnov, Shapiro–Wilk, Lilliefors, Anderson–Darling and K-square D'Agostino tests).

4. Conclusion

For the first time the analysis of statistical distributions of adhesion strength of PS–PPO interfaces formed under conditions of extremely low molecular mobility in PPO specimen, for their compliance with the normal distribution and Weibull distribution. It was shown that the Weibull model was more correct for description of the adhesion strength distribution of PS–PPO interface at temperature equal to T_g^{bulk} PS and much lower T_g^{bulk} PPO, which is caused by quasi-brittle nature of its fracture. For the final conclusion relative to the compliance of the distributions of adhesive strength of PS–PPO interfaces it is necessary to involve the Gaussian probability density function, and to increase the number of arrays of experimental data due to substantial expansion of temperature-time intervals of AJ PS–PPO formation. This work is currently being completed, and its results will be considerd in the nearest future.

Conflict of interest

The author declares that he has no conflict of interest.

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