2. The generalized pliability curve obtained by the time-concentration analogy agrees with the generalized pliability curve obtained by the time-temperature analogy within a significant time interval, which serves as an indication of the applicability of the time-concentration analogy in this time interval. However, for long times, the generalized pliability curve obtained by the time-concentration analogy lies lower, which is evidence of interaction of the plasticizer with the polymer, resulting in strengthening of the composition. Qualitatively, this correlates with the decrease in pliability of more highly plasticized compositions at corresponding states.

LITERATURE CITED


TRUE AREA OF CONTACT IN HETEROGENEOUS MATERIALS BASED ON POLYMERS

A. I. Sviridenok, M. I. Petrokovets, T. F. Kalmykova, and V. M. Ken'ko

Contactive interaction of heterogeneous materials and, particularly, the processes of contact-area formation feature several characteristics which are related to the specifics of the composition, the structure, and the physicochemical properties of the individual components of a composite material.

For the purpose of determining the role of the filler (its nature and concentration) in forming the area of contact in thermosecting polymers, the authors studied the true area of contact in model composites with polyvinyl furfural as the base material (TU 88-BSSR-04-74).

For the test objects were picked composites with cadmium oxide [All-Union State Standard (GOST) 11120-65], molybdenum disulfide (MV4-4TU, MKhRU 1082-54), and Taiga graphite as filler materials. The dispersion of the filler powder was within the 40-50-μ range. The various different modes of interaction between filler and binder were evaluated on the basis of the wettability of these powders by polyvinyl furfural.

The composites were prepared as follows. Appropriate amounts of filler powder were added to a 10% aqueous solution of polyvinyl furfural. The resulting mixture was placed on a microscope slide after the latter had been degreased with alcohol and dried at 353°K. The test specimens were then produced by direct pressing in a mold, this mold being heated to 453°K under a pressure of 100.0 MN/m² and held there for 180 sec.

The true area of contact was examined by means of an instrument operating on the principle of area measurement simultaneously with optical and ultrasonic waves reflected from the boundary between a glass prism and the test specimen. The optical waves were let in at the critical angle, corresponding to total internal reflection, and the ultrasonic waves were let in normally to the boundary between both bodies. Such a compound measurement greatly improved the sensitivity of the instrument.

The wide scatter of test values calls for a statistical analysis, its main purpose being to establish the significance of the differences between true areas of contact in composites with different fillers and fill factors. Such a statistical evaluation of test data was actually made by the method of three-factorial variance analysis [1]. Here we will show the
TABLE 1. Results of the Dispersion Analysis

<table>
<thead>
<tr>
<th>Scatter</th>
<th>Number of degrees of freedom</th>
<th>Dispersion</th>
<th>$F=S_{\text{rep}}/S_{\text{err}}$</th>
<th>Tabulated value of $F_{0.05}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>From factor N (load)</td>
<td>$n=1=3$</td>
<td>$S_N^2=536,72$</td>
<td>129,00</td>
<td>8,65</td>
</tr>
<tr>
<td>From factor A (fill factor)</td>
<td>$a=1=3$</td>
<td>$S_A^2=406,40$</td>
<td>97,80</td>
<td>8,65</td>
</tr>
<tr>
<td>From factor W (filler material)</td>
<td>$w=1=2$</td>
<td>$S_W^2=3,78$</td>
<td>1,10</td>
<td>3,6</td>
</tr>
<tr>
<td>Interaction A X N</td>
<td>$(a-1)(n-1)=9$</td>
<td>$S_{AN}^2=7,76$</td>
<td>1,87</td>
<td>3,0</td>
</tr>
<tr>
<td>Interaction N X W</td>
<td>$(n-1)(w-1)=6$</td>
<td>$S_{NW}^2=0,42$</td>
<td>0,90</td>
<td>2,7</td>
</tr>
<tr>
<td>Interaction A X W</td>
<td>$(a-1)(w-1)=6$</td>
<td>$S_{AW}^2=1,59$</td>
<td>2,62</td>
<td>2,7</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>$(a-1)(n-1)(w-1)=18$</td>
<td>$S^2_{\text{rep}}=4,16$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results of this variance analysis with the three factors being the load N, the kind of filler W, and the fill factor A.

The results are given in Table 1. The interaction dispersions $S_{WA}^2$, $S_{WN}^2$, and $S_{NA}^2$ characterize the variability with the factor of the first index letter varied and the other two factors held constant. The interaction serves as a measure of the degree to which one quantity depends on another. The hypothesis of a homogeneous full set was tested by comparing the dispersions $S_A^2$, $S_N^2$, and $S_W^2$ with the dispersion of reproducibility $S^2_{\text{rep}}$ according to Fisher's criterion. The effect of a factor was regarded as significant if the value of $F = S_{i}^2/S_{\text{rep}}^2$ (i = A, W, N) obtained by the processing of test data was larger than the tabulated value of $F_{0.05}(f_x, f_\text{rep})$. Inasmuch as were of particular interest the effects of the fill factor and of the filler material on the size of the contact area, the significance of differences between the mean values of the true contact area was checked with the aid of t-statistics (at the 5% significance level).

This statistical analysis of experimental data has shown that the percent filler content affects the size of contact area in the given composites significantly, while the effect of the filler material is less significant and largely depends on the magnitude of the load, which in turn indicates the significance of interaction (N X W) and mainly so at heavier loads. This seems to have to do with the different nature of interaction between the given filler materials and the adhesive, since the physicomechanical properties of such materials depend on the polymer wettability of the filler.

It would be of interest to determine the mechanism by which the filler affects the contact area. The many factors determining the process of contact formation can be tentatively divided into two groups: physicomechanical ones governing the nature of the contact and geometric ones associated with the microroughness of interacting surfaces. For a qualitative estimate of the effect of each factor, therefore, the physicomechanical properties of our test specimens were analyzed and microphotographs of contacting surfaces were taken.

Microprofile measurements with a model "Kalibr-VÉT" profilograph-profilometer (vertical magnification ×20,000 and horizontal magnification ×100) revealed that plasticity of the binder had caused a thin layer of polymer to be pushed to the surface during molding of the model specimens, the filling of micropores between filler particles and the roughness of the test specimens being determined by nonuniformities of the generating surfaces of the mold. Consequently, the surface roughness of test specimens was almost independent of the filler material and percent content. The reduction of the contact area with a higher fill factor, noted throughout the load range, was thus due to changes in the physicomechanical properties of the composites [2, 3]. The stress-relaxation characteristics of the model composites with cadmium oxide as filler, shown in Fig. 1 for illustration, indicate an increase in the modulus of elasticity upon addition of filler material.

The dependence of the relative size of the contact area on the fill factor in the model composites, over the entire load range in this study, is shown in Fig. 2. This trend of the true contact area seems to result from the structurizing action of fillers. Indeed, the model specimens can be regarded as two-phase systems. Near the filler-binder interface we see a lower molecular mobility and more limited possibilities for conformance between macromolecules so that the stiffness as well as the strength of the polymer binder increases. This trend becomes more pronounced with increasing filler content. The inverse proportionality between the relative contact area and the Brinell hardness of the given composites confirms our findings.

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