THERMOPHYSICAL ANALYSIS OF PLASTICIZED EPOXY COMPOUNDS

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A study has been made concerning the effect of dibutylphthalate and thiocol plasticizers in various concentrations on the structure as well as the thermophysical and the mechanical properties of grade ÉD-5 epoxy resin. It is shown that the entire complex of analyzed thermophysical properties changes appreciably, depending on the kind and on the concentration of the plasticizer. Conclusions are drawn pertaining to the mechanism of epoxy resin plasticization by these two additives at various concentration levels.

Epoxy resins are now used increasingly in the most diverse sectors of the national economy. In pure form, however, their applicability is largely limited by their considerable brittleness and low rate of stress relaxation, which are due to strong intermolecular forces and rigid chains in the stereo-lattice formed during hardening [1, 2]. For this reason, some plasticizer is, as a rule, a necessary ingredient of all epoxy compounds used in practice [1-4]. The presence of a plasticizer tends to eliminate the said drawbacks. By the proper selection of additives, it becomes possible to achieve in epoxy resin compounds any plasticization mode known in polymers: interstructural, molecular, or hybrid [5]. Depending on the plasticization mechanism, the structure of an epoxy resin changes in a different manner and, accordingly, its entire complex of physicomechanical properties.

Epoxy resins are most commonly plasticized with dibutylphthalate (DBP) and with low-molecular polysulfide rubbers (thiocols) [3, 4]. At present the various properties of epoxy compounds with DBP and thiocols are known rather thoroughly, but the mechanism of epoxy resin plasticization with these additives is not yet entirely understood. While most authors agree that the plasticization of epoxy resin with DBP is interstructural in nature [1, 3, 6], it is somewhat difficult to explain this mechanism in the case of thiocols. According to [6], for instance, thiocols do not form chemical bonds with the resin or the number of such bonds is too small to produce a stereostructure, and the plasticizing action of these additives is due only to reduced intermolecular forces between unbonded segments of neighboring macromolecules. This is the explanation which the authors of [6] offer for the appreciable deterioration of the most essential properties of hardened epoxy resins with the said type of additives. Meanwhile, data are given in [3, 4] which indicate an improvement in some physicomechanical properties of epoxy-thiocol compounds. It has been shown in [7] that thiocols combine with epoxy resins rather easily in any proportion. Since it has not been possible to separate the original products from their mixture by any known selective solvent, hence the authors of [7] conclude that epoxy resin groups interact with the mercaptan groups of the thiocol and form an epoxy-thiocol copolymer. However, as the authors have pointed out here, such an interaction could not be confirmed by any physical method. In a later study the same authors have attempted to discover a chemical interaction between epoxy resins and thiocols by the method of nuclear magnetic resonance. Even this method has not yielded an answer to the problem. An NMR line was obtained characteristic of two-component systems. The authors of [7, 8] explain such a divergence between the results of chemical analysis and physical testing methods by the fact that, while thiocols interact with epoxy resins, only very few links are formed as a result and they cannot be detected owing to the low sensitivity of the physical methods.

This brief survey brings out some ambiguities in the available data pertaining to the properties of epoxy resins and the mechanism of their plasticization with thiocols. For this reason, a further study of this problem is very important.

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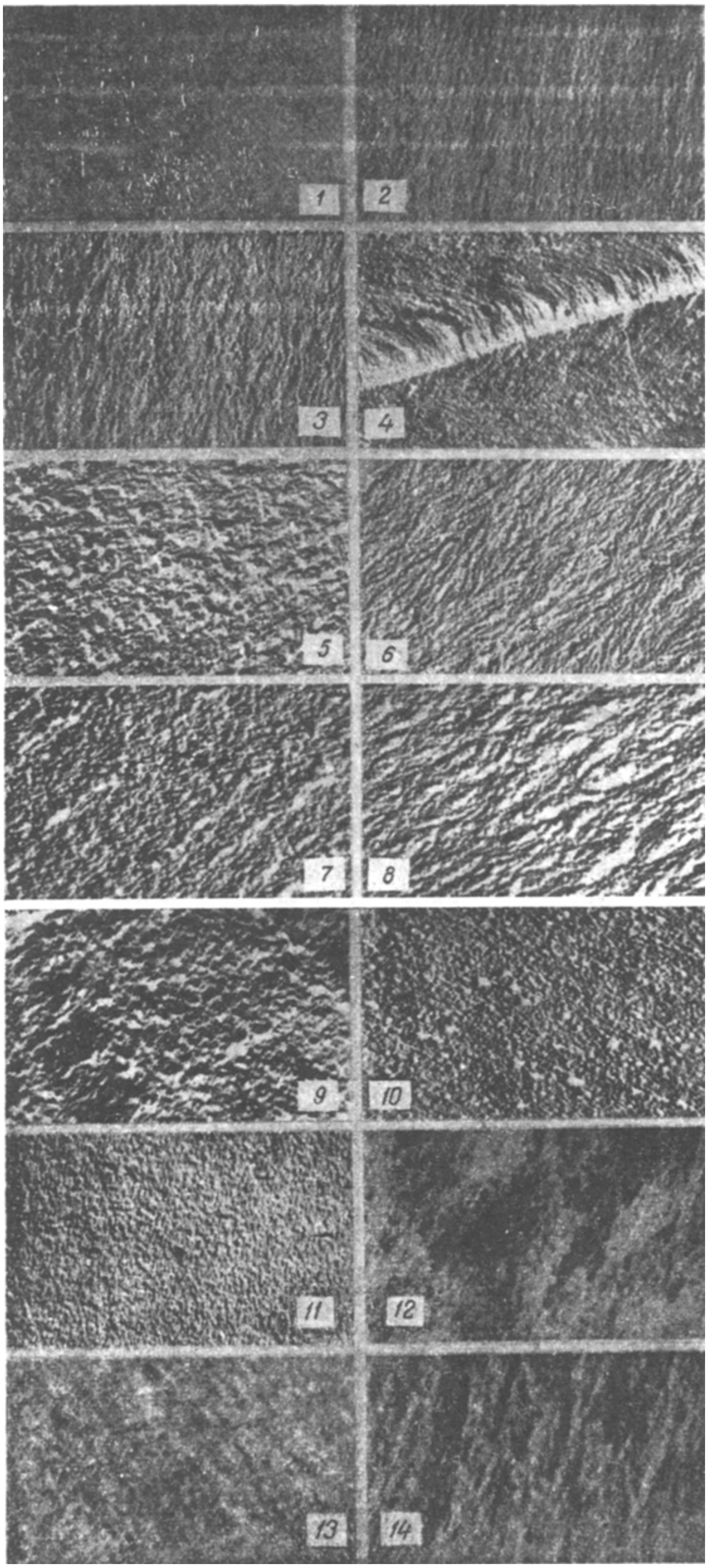

Fig. 1. Electron microphotographs of etched specimen sections: pure ED-5 (1), ED-5 + thiocol 3 weight parts (2), 5 weight parts (3), 7 weight parts (4), 10 weight parts (5), 15 weight parts (6), 20 weight parts (7), 25 weight parts (8), 30 weight parts (9), pure ÉD-5 (10), pure ÉD-5 (11), ÉD-5 + DBP 10 weight parts (12), 15 weight parts (13), 20 weight parts (14). Magnification ×3000 (1-9), ×23,000 (10-14).

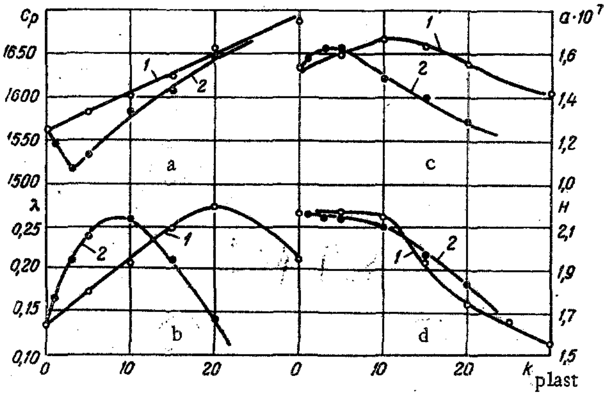

Fig. 2. Specific heat c_p (J/kg · °C) (a), thermal conductivity λ (W/m · °C) (b), thermal duffusivity a (m^2/sec) (c), microhardness (kgf/mm^2) (d) of ÉD-5 epoxy resin, as functions of the thiocol (1) and the DBP (2) concentration k_{plast} (weight parts).

It has been emphasized in [8] that implantation of rubber, which forms flexible crosslinks, will improve the elasticity of a system while insignificantly reducing its strength. Moreover, the final properties of the structured products are then determined by the diversity of structures of the copolymers resulting from such an implantation. This latter circumstance indicates that methods of structural analysis may yield some information about the mechanism of polymer plasticization by one or another additive.

The authors have studied the effect of various thiocol and DBP quantities on the epoxy resin structure, by analyzing the electron microphotographs of etched patterns on plasticized specimens and by microhardness tests. It has been shown in [9] that electron microscopy yields a wealth of information, if simultaneously other properties of these systems are examined. Upon the request by the authors of [9], we studied the thermophysical properties of filled epoxy compounds. According to this study, the results of thermophysical measurements correlate closely with the results of electron microscope measurements as well as with the results of mechanical and other measurements made on aid filled epoxy compounds. For this reason, in order to establish the applicability of physical methods to our problem, we not only examined the structures of plasticized epoxy compounds but at the same time also measured the complex of thermophysical properties: the specific heat (c_p), the thermal conductivity (λ), the thermal diffusivity (a), and the glass transition temperature (T_G). We have found, furthermore, that data on the thermophysical properties of epoxy compounds are of great practical importance in their own right, inasmuch as they lead to certain conclusions concerning the mechanism by which thiocols and DBP plasticize epoxy resins.

In our study we used the same grade ÉD-5 epoxy resin, grade PÉPA hardener, thiocol and DBP plasticizers as in [10, 11]. The specimens were prepared and hardened by the method shown in [10-12]. The etched sections on specimens were photographed from reverse replicas through a model UÉMV-100V electron microscope. The temperature dependence and the concentration dependence of the thermophysical properties were measured as follows: the specific heat c_p by the method in [13], the thermal conductivity λ by the methods in [12, 14], and the thermal diffusivity a by the method in [15]. The hardness of the test materials was measured on a model PMT-3 microhardness tester. The measurement error did not exceed 5% for λ, 3% for c_p and a.

Electron microphotographs of the ÉD-5 + thiocol system are shown in Fig. 1. The pictures indicate that under a ×3000 magnification the supermolecular structure of pure ÉD-5 resin cannot be resolved. A gradual increase in the thiocol concentration results in a buildup of the structural polymer components, until with 7-10 weight parts of thiocol the globular epoxy resin structure becomes distinctly visible. This agrees with the conclusions made in [7, 8] concerning the increased flexibility and mobility of chains in such systems. The higher flexibility and the correspondingly higher mobility of epoxy resin chains result from the formation of more flexible crosslinks during the interaction between functional groups of thiocol and epoxy resin according to the scheme suggested in [8]. A higher mobility of chains, according to [5], is in turn necessary for the transition from small monomolecular to polymolecular globules of epoxy resin and their subsequent agglomeration. All this is brought out on the photographs.

Thus, epoxy resin systems with a thiocol concentration of 10-15 weight parts represent an epoxy-sulfide copolymer with a single stereolattice and large supermolecular globular formations. For comparison, picture 10 in Fig. 1 shows an electron microphotograph of pure resin, magnified 23,000 times. Evidently, the 3000 times magnified globules of epoxy-sulfide are as large as 23,000 times magnified globules of pure resin, i.e., epoxy resin has been plasticized here by the molecular mechanism. This explains why at low thiocol concentrations one often notes an increase in the values of some physicomechanical properties of such systems [3, 4]. As the thiocol concentration in epoxy resin is further increased (20 weight parts and more), the distinct features of individual globule aggregates vanish (picture 7 in Fig. 1), while the structural components of the polymer become separated by whole "micropools" of thiocol (pictures 8, 9 in Fig. 1). Apparently, implantation of thiocol into the functional groups is accompanied

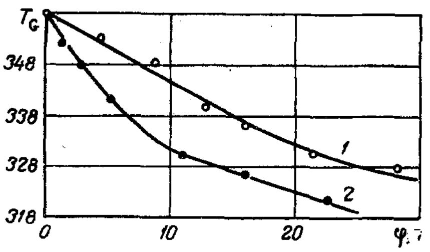

Fig. 3. Glass transition temperature T_G (°K) of ÉD-5 epoxy resin, as a function of the thiocol concentration (1) or the DBP concentration (2).

by its spreading between the supermolecular polymer formations and a consequent weakening of intermolecular forces between them. The appearance of such a microheterogeneous system results in intensive disintegration of the specimen structure, as the electron microphotographs also indicate. Evidently, in this case epoxy resin is plasticized by thiocol according to the hybrid mechanism.

This analysis applies also to the variation of the specific heat c_p of plasticized systems with an increase in the concentration of plasticizers (Fig. 2a).

According to Fig. 2a, the specific heat of epoxy resin systems first decreases slightly, as DBP is added in concentrations up to 5 weight parts. A further increase of the DBP concentration results in a higher specific heat, as in the case of epoxy resin with thiocol. Such a change in the specific heat of epoxy resin systems at low concentrations of DBP indicates that plasticization here is interstructural. In hardened epoxy resin this DBP, being an interstructural plasticizer, is unbonded from the polymer macromolecules which form the stereolattice and, as a result, the main role of the plasticizer is now to overcome spatial barriers, i.e., to act as a "lubricant" [16]. Apparently, the certain mobility thus acquired by the supermolecular structures causes their repacking into an arrangement where the mobility of macromolecules combined into these structures contributes less to the total specific heat c_p. This certain mobility acquired by the supermolecular formations does not compensate for the reduction in the total mobility of macromolecules, however, which is manifested in the lower specific heat c_p of such systems.

The electron microphotographs in pictures 11-14 (Fig. 1) show etched specimen sections of pure resin and of resin with DBP. According to these pictures, an increase in the DBP concentration from 10 to 20 weight parts results in a "distention" of globules, their merger and enlargement. It is also evident here that supermolecular structures are separated by DBP interlayers, whose specific heat contributes already appreciably to the total specific heat of the system. An accumulation of DBP in such systems, with this effect on the supermolecular structure of epoxy resin, results in a disintegration of the specimens manifested by a different trend of the specific heat c_p with increasing DBP concentration. Unlike for epoxy-DBP systems, the specific heat versus concentration curve for epoxy-thiocol systems rises over the entire range of thiocol concentrations. The increase in the specific heat at low concentrations must be associated with the said increase in the mobility of kinetic polymer chains and in the number of the degrees of freedom, which is attributable to the penetration of more flexible thiocol chains into the stereolattice and the resulting higher flexibility of the latter. At high concentrations the specific heat of this thiocol plasticizer also contributes more to the total specific heat c_p of the system. According to Fig. 2a, the trend of the specific heat versus concentration curve within the range of DBP concentrations is almost analogous to that curve for the epoxy + thiocol system. At 20 weight parts of DBP (picture 14 in Fig. 1) this corresponds to the disappearance of any distinct ordered epoxy resin structure and to the maximum disintegration of specimens. Evidently, at high concentrations of DBP its plasticizing effect on epoxy resin does not differ in any way from the plasticizing effect of thiocol on epoxy resin.

These data obtained by electron microscopy and specific heat (c_p) measurements are augmented by the results of thermal conductivity (λ) and thermal diffusivity (a) measurements. As can be seen in Fig. 2b, c, at low concentrations of either plasticizer, the conditions of heat transfer in the polymer improve. In systems with thiocol this can be explained by a higher segmental mobility of macrochains, due to their higher flexibility [17]. The reason for the higher thermal conductivity and thermal diffusivity in epoxy resin systems with DBP is, apparently, the reduced thermal contact resistance at the interfaces between supermolecular structures. Located between epoxy resin globules, the thin DBP interlayers act as "contact lubrication" between the latter and thus improve the conditions of heat transfer within the specimens. A further increase in the concentration of either plasticizer reduces the thermal conductivity and the thermal diffusivity, which agrees with the electron microscope measurements indicating a significant disintegration of specimen structures when the concentration of plasticizers is high.

Thus, the results of electron microscope and thermophysical measurements indicate that within the low-concentration range (up to 10% volume) there occurs molecular plasticization in epoxy resin systems with thiocol and interstructural plasticization in epoxy resin systems with DBP. Within the high-concentration range both additives plasticize epoxy resin by a similar hybrid mechanism (inasmuch as DBP does not interact with resin, the term "hybrid plasticization" should be interpreted here as a purely external effect of DBP penetration into and subsequent disintegration of the upper layers of globules).

This is also confirmed by the microhardness tests (Fig. 2d). At low thiocol concentrations in epoxy resin the microhardness of the system varies little, indicating a chemical interaction between the components with a formation of a single strong stereolattice. The addition of DBP to epoxy resin in even small quantities results in a gradual decrease in the specimen hardness. This confirms that plasticization of epoxy resin by DBP is interstructural. The latter, located between supermolecular formations of epoxy resin, weakens the bonds between them and, therefore, the lower hardness has to do with an easy breakdown of contacts between globules and a subsequent weakening of the entire system due to the shear deformation caused by penetration of the indenter during a hardness test. The further trend of these curves corresponding to systems with plasticizers indicates that the effect of DBP and of thiocol on the microhardness of epoxy resin is almost the same.

The hypotheses concerning the said plasticization mechanism are confirmed also by curves of the glass transition temperature T_G as a function of the plasticizer concentration (Fig. 3), this temperature being defined as the mean temperature over the range of fast rising specific heat on the $c_p(T)$ curve [18]. As the plasticizer concentration increases, T_G shifts toward lower temperatures in both cases but otherwise the trend of the $T_G(\varphi)$ curves for DBP and thiocol respectively is not the same. For thiocol, this lowering of the T_G point within the range up to 15% volume of plasticizer is described by the equation $\Delta T_G = 1.3\varphi$, with ΔT_G denoting the drop of T_G and φ denoting the volume fraction of thiocol. For DBP this lowering of the T_G point is more significant and, within concentrations up to 10% volume, is related to the molar fraction of plasticizer n according to the equation $\Delta T_G = 100n$. At high concentrations of both thiocol and DBP the trend of the T_G point is similar and described by the same equation $\Delta T_G = 0.25\varphi$. This tells that the plasticization mechanism is in this case the same. At high concentrations of thiocol in the system there forms an excess of it which has not reacted with the resin and, therefore, behaves like DBP in somewhat lowering the glass transition temperature T_G and somewhat raising the specific heat c_p.

Thus, our study has demonstrated the feasibility of determining what the mechanism of polymer plasticization is by thermophysical methods; it has been shown here that no single answer can be given concerning the mechanism of epoxy resin plasticization by any one additive, unless the concentration of the latter in the given polymer is also specified; it has been found that at plasticizer concentrations in epoxy resin up to 10%, the plasticization is molecular in the case of thiocol and interstructural in the case of DBP. At higher concentrations of these plasticizers in epoxy resin the plasticization mechanism is a hybrid one.

NOTATION

c_p	is the specific heat at constant pressure;
λ	is the thermal conductivity;
a	is the thermal diffusivity;
H	is the microhardness;
T_G	is the glass transition temperature;
k_{plast}	is the weight concentration of plasticizer;
φ	is the volume concentration of plasticizer;
n	is the molar concentration of plasticizer.

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