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Structure and Properties of Networks in Heat-resistant Polymers

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Methods are discussed for obtaining networks in heat-resistant polymers, including cross-linking at terminal groups, the use of reactive oligomers together with heat-resistant polymers capable of interacting with them, polycyclotrimerisation, etc. The influence of the chemical structure of the network and the frequency of branch points has been traced on the dynamic mechanical properties of the polymers and also on the stress relaxation and creep under static conditions. Network parameters and strength properties are compared, and methods of controlling the mechanical properties of network systems possessing enhanced heat-resistance are discussed. A list of 75 references is included.

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I. INTRODUCTION

The preparation and properties of heat-resistant polymers based on network systems have been the object of persistent attention by research workers. This is due to the great difficulties often encountered in producing articles from linear heat-resistant polymers, as a consequence of the high temperatures and pressures in their processing by the usual methods (hot extrusion, injection moulding) necessitated by the high softening points and great viscosities of the systems. However, the initial compounds for the preparation of network systems (oligomers of aromatic structure, mixtures of linear thermostable polymers with reactive oligomers) can easily be converted into a plastic state, and the required materials obtained from them by heat-treatment or other methods.

Several processes are now available for obtaining network systems based on heat-resistant polymers: oligomers containing aromatic rings and reactive terminal groups can be cross-linked; heat-resistant linear polymers containing reactive groups in the chain can be mixed with reactive oligomers, and the mixture then heat-treated; and oligomers containing aromatic units between reactive groups can undergo cyclotrimerisation. The chemical structure of the chain segments between branch points, of course, has a substantial influence on the properties of the heat-resistant network system; formation of a supermolecular structure at different stages of network formation is also important.

A vast amount of research work, summarised in a monograph[1], has been devoted to traditional network systems. The present Review is concerned with the structure and properties of network heat-resistant polymers. Such systems have the characteristic methods of preparation enumerated above (which, however, have much in common with methods for obtaining traditional networks) and exhibit specific effects of network structure on polymer properties. In the case of networks constructured of flexible macromolecules forming the internodal segments heat-resistance can be enhanced only by substantial increase in the density of cross-linking. However, the polymer material then loses its valuable qualities: brittleness, cracking, etc. appear. A high degree of cross-linking is not necessary to obtain heat-resistant materials based on rigid macromolecules, for the chemical structure of the internodal segments then has the greatest influence on properties. Furthermore, a feature of networks based on aromatic compounds is their capacity of order, evident in signs of crystallinity at high degrees of conversion.

II. INFLUENCE OF CHEMICAL STRUCTURE ON MOLECULAR MOBILITY OF NETWORKS

Heat-resistant polymers are extremely interesting materials for the investigation of relaxation transitions, since they exist in a vitreous state over wide temperature ranges, within which many transitions can be detected. Completely aromatic polymers provide unique opportunities for the study of molecular motions, in particular those responsible for transition ranges and relaxation effects. In ordinary linear aromatic polymers relaxation processes arise from rotational movements of chain segments and also of various polar radicals. In completely aromatic polymers the rotational mobility of the molecules is considerably restricted by resonance and steric effects (e.g. barriers to rotation due to *ortho*-substitution), so that mobilities other than rotational must be expected.

Great attention has recently been paid to the study of relaxation transitions in heat-resistant polymers[2-13]. Fundamental research on transitions in heat-resistant aromatic polymers[2] has involved study of the relaxation properties of poly(phenylquinoxalines) over the wide temperature range from −200 to 500 °C. Far less study has been made of the dynamic mechanical properties of network systems based on heat-resistant polymers. Most heat-resistant aromatic polymers can be cross-linked simply by holding isothermally at high temperatures. The density of cross-linking and hence the dynamic mechanical characteristics can be varied within wide limits by controlling the time and/or temperature of cross-linking.

Investigation of the influence of the previous thermal history on the dynamic characteristics of polyquinoxaline and poly(phenylene oxide) films has shown[2,5] that heating in helium at 400 °C gradually displaces the temperature dependence of the modulus of elasticity E' to higher temperatures, and shorter times of heating in air yield similar results. This change in modulus is explained[2,5] by pyrolytic cross-linking during heating in an inert atmosphere, which in air is accompanied by oxidation.

Linear poly-(2,2'-*p*-phenylene-6,6'-bis-3-phenylquinoxaline) has been cross-linked[14] by isothermal heating at 425–490 °C, with the kinetics monitored by the variation in the glass point T_{gl}. The influence of the molecular mass and nature of terminal groups on dynamic properties was examined in three specimens differing only in these characteristics. The apparent activation energy of cross-linking is independent of them and has the same value (60 kcal mole^{-1}) as the activation energy of thermal breakdown of the polymer (which was determined from measurements of the isothermal weight losses). However, the rate of change of the glass point resulting from heating at these temperatures is a function of both molecular mass and type of terminal groups. It was also observed that the isothermally cross-linked polymer undergoes a sharp decrease in mass at a higher temperature than its linear analogue, and leaves a larger carbon residue at 800 °C.

The same workers have investigated[15] the thermomechanical properties of poly(phenylimide-quinoxaline), which differs from the polyphenylenephenylquinoxaline only in the presence of an imide group in the chain. In the present case, unlike the former, no difference between rates of change of glass point is observed after specimens containing different terminal groups have been heated. Comparison of such rates in specimens of the two types of polymer showed that, despite the identical activation energies, formation of cross-links is far more intense in the polymeric imide derivatives. This implies an additional mechanism of formation of cross-links, probably involving opening of the imide ring.

The density of cross-linking can be varied also by introducing reactive side-groups. An investigation[16] of the mechanism of the hardening of linear poly(phenylenequinoxalines) containing and not containing such groups led to the conclusion that their presence promotes more rapid change in glass point. An accompanying kinetic examination of cross-linking in poly(phenylamide-quinoxalines) of high molecular mass showed that isothermal holding in nitrogen at temperatures from 380 to 420 °C produced an initial lowering of the glass point followed by a rise with increasing duration of heating. In some polymers of this type the fall in glass point during the initial stage of heating reached 16 deg. Such behaviour was attributed[16] to the superposition of two effects—random chain rupture and cross-linking—the former of which leads initially to a sharp decrease in mean molecular mass with a corresponding fall in glass point, whereas thermal cross-linking produces an almost linear rise in glass temperature. In polymers of low molecular mass random chain rupture has little effect on the glass point, change in which is due mainly to cross-linking. Therefore such polymers do not exhibit a minimum in the isothermal variation of glass point with time. It must be stressed that such minima have never been observed with poly (phenylenequinoxalines) or poly (phenylimide-quinoxalines), which possess greater resistance to chain rupture, so that cross-linking is dominant.

When isothermal heating is conducted above the glass point the time variation of the loss coefficient passes through a maximum. In all cases (heating below and above the glass point) an equilibrium state is established within a time depending on the hardening temperature. However, the resulting glass points do not remain the same, but rise significantly[16].

Comparison of the dynamic mechanical properties of hardened phenolic resins with those of poly(phenylenequinoxalines) showed[17] that not only the speed but also the absorption of sound is greater in the former, which is unexpected, since materials with a higher velocity of sound usually have lower absorption. It was therefore assumed[17] that some additional loss mechanism operates in phenolic resins. The absorption of sound depends significantly on the degree of hardening, and may serve for determination of the degree of cross-linking.

Oligo(phenylquinoxalines) containing vinyl terminal groups undergo thermal cross-linking far more readily than does the standard poly(phenylenequinoxaline) and form structures with a high frequency of cross-linking and high glass points[18]. On heat-treatment (in nitrogen at 350 °C) the glass point rises rapidly during the first 15 min, after which it remains almost unchanged.

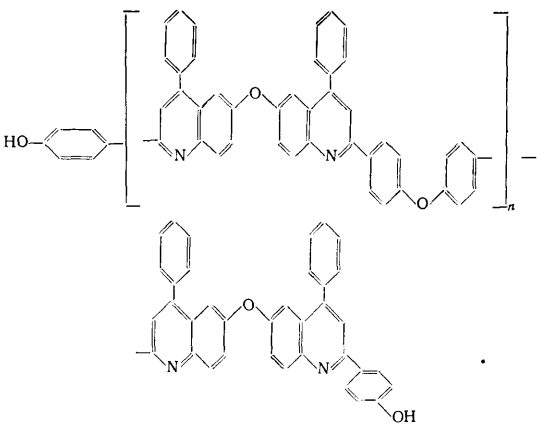
Oligo(phenylquinoxalines) containing acetylenic terminal groups are also used to form network heat-resistant polymers[19,20]. The oligomers dissolve well in organic solvents and have comparatively low softening temperatures. When such systems are heated at 200–300 °C they undergo cross-linking owing to polymerisation of the acetylenic groups; the process of cross-linking is extremely complicated and takes place by various mechanisms. Analysis of the influence of temperature and duration of hardening of oligo(phenylquinoxalines) on their properties must take into account the sharp rise in glass point on hardening, which slows down cross-linking. Thermogravimetric and mass-spectrometric examination of hardening of the oligomers and degradation of the hardened systems has shown[20] no evolution of volatile components in the temperature range of hardening (200–300 °C), and vacuum degradation beginning at 465 °C.

The cross-linking of poly(phenylene sulphide) when heated is assumed[21] to be accompanied by oligomerisation with increase in chain length. In air cross-linking is thought to be effected by oxygen bridges, but in an inert atmosphere through benzene rings and sulphide bridges. The cross-linking of poly(phenylene sulphide) by sulphur leads to a decrease in thermal stability, although the heat-resistance increases[22].

Several studies have been made[23–26] on the properties of thermostable polymers already cross-linked in course of preparation. Biphenylene units introduced into the macromolecular chain have been used[23] as hardening agents for polyquinolines. Cross-linking takes place without evolution of volatile products, but the resulting compounds possess enhanced heat-resistance. Hardening can be effected either thermally or in the presence of a rhodium catalyst, which appreciably lowers the temperature of cross-linking. Cross-linked poly(phenylquinoxalines) have been obtained[24] by introducing trisbenzyl into the reaction mixture. They have been used in the production of multicomponent materials containing graphite fibres.

Cross-linked polymers have been obtained[25] by the polycondensation of tetracarboxylic dianhydrides with polyfunctional amines. Under thermomechanical constraint these polymers behave similarly to other cross-linked systems that exhibit a rise in glass point with increase in concentration of the cross-linking agent.

Cross-linked polyphenylenes and poly(phenylquinolines) have been obtained[26] by the cyclotrimerisation of aryl cyanates. An example of the former is the condensation of di-*p*-acetylphenyl ether with di-*p*-amino-*m*-benzoylphenyl ether and *p*-hydroxyacetophenone to give the structure This prepolymer containing terminal hydroxyls was treated with excess of cyanogen bromide to convert it into the aromatic dicyanate, which was then transformed by heat-treatment into a cross-linked product. The temperature required for cross-linking rises with increase in the length of the segment between the cyanato-groups. Cross-linking raises significantly the glass point of the polymer (in relation to those of the prepolymers), although leaving it lower than for linear analogues (e.g. polyphenylene).



(I)

However, chemical cross-linking in heat-resistant polymers, which can be effected at relatively low temperatures (200–300 °C), yields materials having lower glass points (and hence lower operating temperatures) than have materials that have been thermally cross-linked at high temperatures[23, 24, 26]. Even with 100% content [sic] of cross-linking agent the materials exhibit thermoplasticity[24], but this is eliminated by additional heating at high temperatures (482–510 °C). Similar results have been obtained by the high-temperature afterhardening of compositions with lower contents (30–60%) of cross-linking agent.

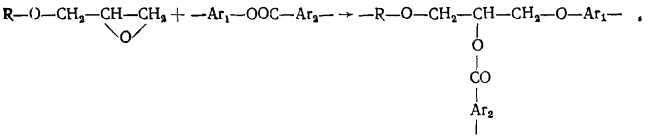
Calculated and experimental glass points for poly(phenylquinoxaline) have been compared[27, 28]. Formation of cross-links in this polymer by heat-treatment raises the glass point by 50–80 deg.

Investigation of the dynamic mechanical properties of polyamides has shown[29] that formation of a polymer network by irradiation[30] or chemical reaction[31] diminishes the mobility of the amorphous regions. As a consequence there is a loss of mechanical properties due to large amounts of the α-form. The glass transition of the polyamide is displaced to higher temperatures. The influence of density of cross-linking on local and segmental mobility of networks has been discussed in detail in the monograph[1].

The effect of isothermal heat-treatment of a polyimide on its dynamic mechanical properties has been studied[32, 33]. Heating at 500 °C raises the glass point from 350 to ~500 °C, whereas the relaxation transition in the vitreous state (with a maximum at ~150 °C) actually remains unchanged after heat-treatment. This suggests that here the density of cross-linking is sufficient to have an appreciable influence on the motion of the large chain segments involved in the glass transition but insufficient to affect the small-scale movements responsible for relaxation in the vitreous state.

An important achievement of the dynamic mechanical method for investigating relaxation transitions is to permit study not only of the properties of the final reaction products but also of the variation in such properties during the actual reaction. Recently several workers[34–39] have used measurements of dynamic mechanical properties to study the kinetics of hardening. Usually the phenomenon is investigated by estimating the degree of conversion of reactive groups by chemical analysis, infrared spectroscopy, or calorimetry. However, the sensitivity of these methods drops abruptly in the final stages of hardening (at high degrees of conversion) that generally are largely responsible for the optimum properties of cross-linked polymers.

The dynamic mechanical method has been used[39] to investigate the kinetics of the hardening of epoxy-polymers of heat-resistant aromatic systems. Such hardening is due to reaction of the epoxy-rings with ester links[40]. When a polyarylate serves as chemically active heat-resistant polymer, for example, its reaction with an epoxy-oligomer can be represented[41]:



The temperature at which reaction begins and the rate are significantly influenced by the chemical structure both of the epoxy-polymer and of the polyester. Reaction takes place also in the hardening of compositions containing traditional hardeners together with polyesters. The result is a polymer network possessing several interesting mechanical properties, as will be shown below.

A study has been made[39] of the influence of the composition of polymer networks on the temperature dependence of the modulus of eleasticity E' and tan δ. Fig. 1*a* illustrates the measured temperature dependence for a composition based on the polyarylate F-2 (a polyester of terephthalic acid and phenolphthalein)[42] and the cycloaliphatic epoxy-resin UP-612 (epoxide number 26–28) and containing various quantities of the hardener UP-607 (a polyanhydride of sebacic acid). Increase in the hardener concentration is accompanied by increase in the maximum values of tan δ, but a fall in the glass point, evidence of the plasticising effect of the aliphatic hardener. A sharp rise in tan δ, corresponding to softening of the system as a whole, occurs with all compositions in a similar temperature range. Fig. 1*a* shows also that introducing a larger quantity of hardener leads to formation of a more elastic network with a smaller modulus of elasticity. In order to assess the effect of the concentration of the epoxy-polymer on the temperature dependences, various quantities of UP-612 were introduced into a composition containing 50 parts by weight of UP-607 per 100 of F-2. Fig. 1*b* shows that tan δ_{max} increases with the concentration of the epoxy-polymer and that the corresponding temperature T_{max} rises. The slight increase can be attributed to the accompanying decrease in the proportion of the plasticising low-molecular hardener.

A characteristic feature of a polymer network formed by reaction between a polyarylate and an epoxy-polymer is a well defined difference in rigidity between cross-linked chains (polyarylate) and cross-linking bridges (epoxy-polymer). The network itself can be constructed in several ways—by formation of (i) an ordinary three-component network, (ii) so called interpenetrating networks as a consequence of the difference in reactivity between two macromolecular hardeners, and (iii) an intermediate system by partial interpenetration of networks accompanied by formation of chemical branch points—of which process (iii) is the most interesting. Interpenetrating networks form a complicated system[43–47] comprising two or more three-dimensional network polymers, not combined chemically but inseparable owing to the mechanical intertwining of chains consequent on the conditions of preparation. In the opinion of some workers[45] such systems must be regarded as a particular case of graft copolymers, in which the number of cross-links between macromolecules of each component far exceeds the number of grafts of one component on the other.

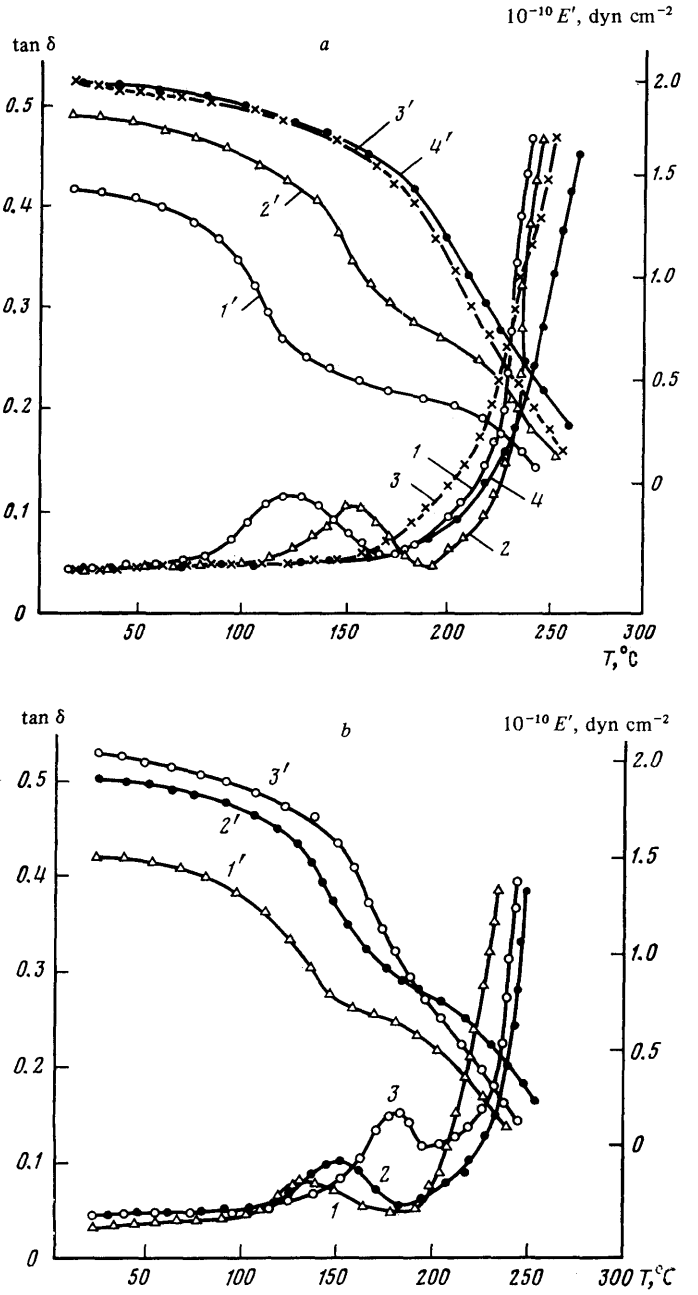


Figure 1. Temperature dependence of tan δ (unprimed curves) and E' (primed) for materials based on (parts by weight) 100 F-2: (*a*) with 100 UP-612 and different quantities of UP-607 hardener: 1,1′) 100; 2,2′) 50; 3,3′) 25; 4,4′) 0; (*b*) with 50 UP-607 and various quantities of UP-612: 1,1′) 50; 2,2′) 100; 3,3′) 150.

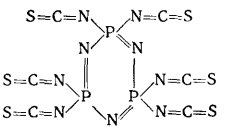
The synthesis of interpenetrating networks represents a new method for controlling the size and structure of different phase regions by varying the degree of cross-linking. Whereas many mechanical mixtures of polymers exhibit a tendency to form large (1–10 μm) phase regions, interpenetrating networks give a more uniform phase structure with smaller inhomogeneities. When the phase regions are very small (~100 Å), the classic concept of a sharp boundary separating two phases is inapplicable. A composite material having regions of ~100 Å is non-classical and varies continuously from point to point. In this case every local volume element makes its contribution to the glass point according to its composition and structure.

Materials comprising normally incompatible polymers forced into a single network possess a fairly broad region of high damping, which may cover the temperature range between the glass points of the individual components. Several vibration-absorbing materials having a wide (and controllable) useful temperature range for the damping of vibrations have been obtained[48–51] by preparing special compositions of interpenetrating networks, but they cannot be applied above ~100 °C. The temperature range of effective damping can be extended by the use of heat-resistant systems. In particular, a high-temperature vibration-absorbing material, exhibiting great absorption of mechanical energy over the range 160–220 °C, has been developed from networks of a polyarylate and epoxy-polymers[52,53].

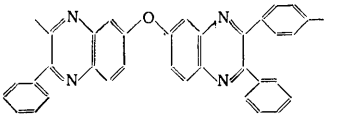
III. DYNAMIC MECHANICAL INVESTIGATION OF CHEMICAL CROSS-LINKING PROCESSES

Since hardening is a chemical reaction accompanied by conformational rearrangements of the polymer molecules, the dynamic mechanical method might be used to investigate not only the kinetics of hardening but also any solid-phase reaction in general. In this case, too, highly heat-resistant polymers provide unique opportunities for research. Indeed, owing to the degeneration of the relaxation transitions that are due to rotational mobility, and because of the high softening temperatures, heat-resistant polymers may have wide temperature ranges within which their intrinsic relaxation does not develop. This enables them to be used as matrices for the investigation of chemical changes in reactive substances introduced into them.

Chemical reactions of the relatively simple compound—hexaisothiocyanatocyclotriphosphazene



have been investigated[39] in a matrix of the poly(phenylquinoxaline)



Diffractograms obtained for the initial hexaisothiocyanate powder and for a film of the polymer modified with the former show that the crystalline hexaisothiocyanate undergoes complete amorphisation on introduction into the poly(phenylquinoxaline) matrix, which indicates excellent compatibility of the two compounds.

Application of the dynamic mechanical method to films containing different quantities of the hexaisothiocyanate shows (Fig. 2) a sharp increase in tan δ with rise in temperature, to reach a maximum at ~150 °C. Such behaviour of the films on heating is due to softening of the system followed by chemical formation of a network by polymerisation

of the hexaisothiocyanate. A higher content of the latter corresponds, of course, to a more intense maximum in tan δ observed at the given temperature. With decrease in the hexaisothiocyanate content the maximum gradually degenerates, and is not observed at all for the initial poly (phenylquinoxaline).

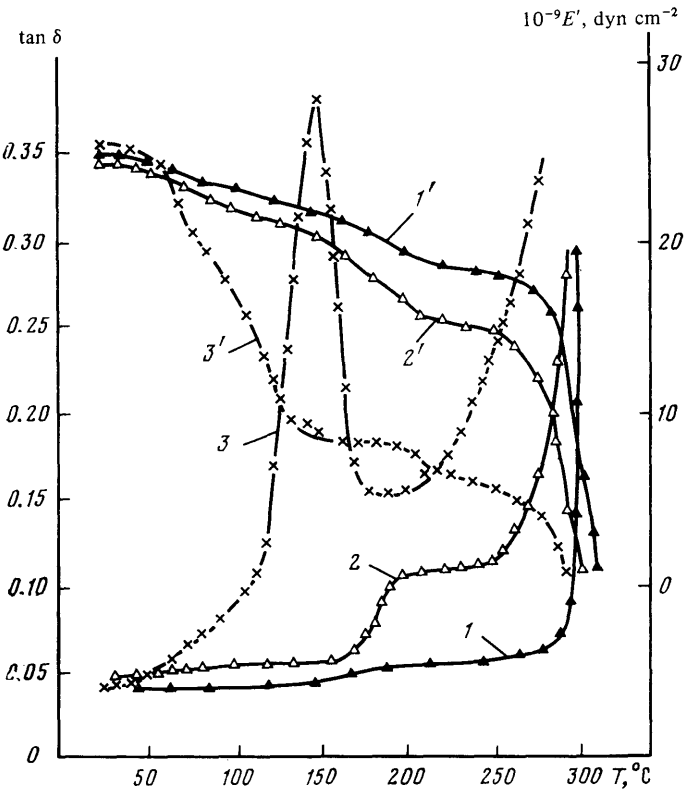


Figure 2. Temperature dependence of tan δ (unprimed curves) and E' (primed) for films obtained from mixtures of 100 parts by weight of poly(phenylquinoxaline) with different quantities of hexaisothiocyanatocyclotriphosphazene: 1,1') 1; 2,2') 10; 3,3') 50.

The characteristic temperature dependence of tan δ suggests[54] that by the dynamic mechanical method it is comparatively easy to study chemical processes occurring in the solid phase on heating: the sharp increase corresponds to the temperature range in which chemical reaction takes place; and the temperatures at which reaction begins, has its maximum rate, and in effect terminates can easily be determined (from respectively the start of the rise in tan δ, its maximum value, and the end of its decrease). The modulus of elasticity falls fairly sharply (which is to be expected of a system with great molecular mobility) in the temperature range in which the hexaisothiocyanate softens and formation of a network is only beginning. After reaction has proceeded sufficiently on heating to temperatures above that of maximum tan δ, the decrease in modulus of elasticity slows down. In this respect these systems differ in behaviour fundamentally from the usual linear and network polymers, which when heated pass from the solid (vitreous or crystalline) state to a hyperelastic or plastic state. In this case, too, a maximum is observed in the temperature dependence of tan δ, but the modulus of elasticity falls by a few orders of magnitude.

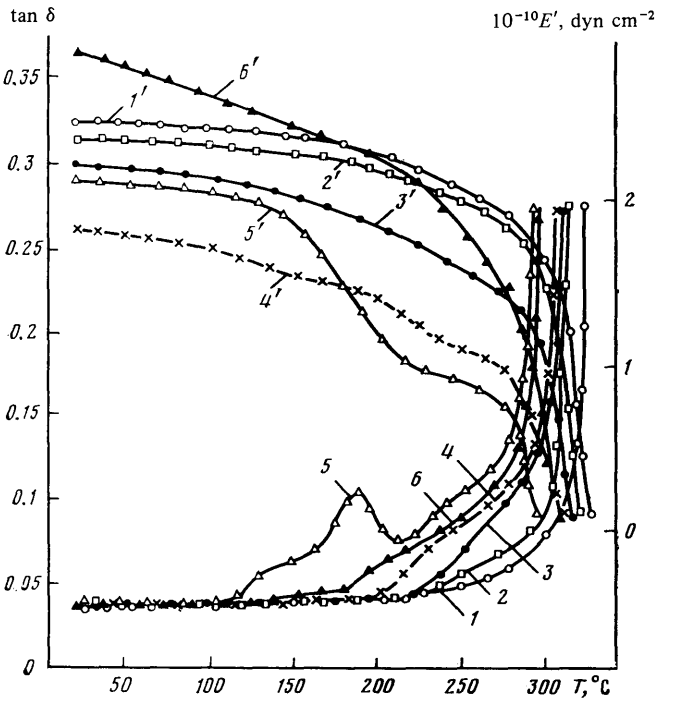


Figure 3. Temperature dependence of tan δ (unprimed curves) and E' (primed) for films, preheated at 180 °C for 30 h, of 100 parts by weight of poly(phenylquinoxaline) with different quantities of hexaisothiocyanatocyclotriphosphazene: 1,1') 1; 2,2') 10; 3,3') 25; 4,4') 50; 5,5') 100; 6,6') 100 additionally preheated at 280 °C for 4 h.

The dynamic mechanical results have been confirmed[54] by direct infrared-spectroscopic monitoring of the polymerisation of hexaisothiocyanatocyclotriphosphazene in a film of the poly(phenylquinoxaline). The variation in the characteristic absorption bands indicated both polymerisation of the hexaisothiocyanate with ring cleavage and reaction of isothiocyanato-groups with terminal amino-groups in the poly (phenylquinoxaline) to form thiourea links. The result is cross-linking of the polymer with a loss in solubility and a change in physicomechanical properties. This appears entirely probable, since ordinary poly(phenylquinoxalines) obtained from stoichiometric proportions of the reactants usually contain terminal amino-groups[55]. The hexaisothiocyanate is distinguished by great reactivity and readily interacts with compounds containing active hydrogen (amines, alcohols)[56].

Comparison of the results of infrared and thermomechanical spectroscopy on specimens that have been heated to different temperatures shows that heating lowers tan δ_{max} and shifts it slightly to higher temperatures. Heating at a relatively low temperature (120 °C) leads to some diminution in tan δ_{max}

in comparison with the initial specimen, but even when the temperature is raised only slightly (to 130–150 °C) the value decreases significantly, and at higher temperatures the maximum degnerates completely[54]. All this is consistent with the infrared results, and indicates a vigorous irreversible chemical reaction occurring in the range 140–160 °C. With rise in the temperature of preheating the sharp increase in tan δ following the maximum, which corresponds to softening of the specimens as a whole, takes place at increasingly high temperatures. This is evidence of the formation of a single network on opening of the phosphazotrien ring and interaction with the poly(phenylquinoxaline.)

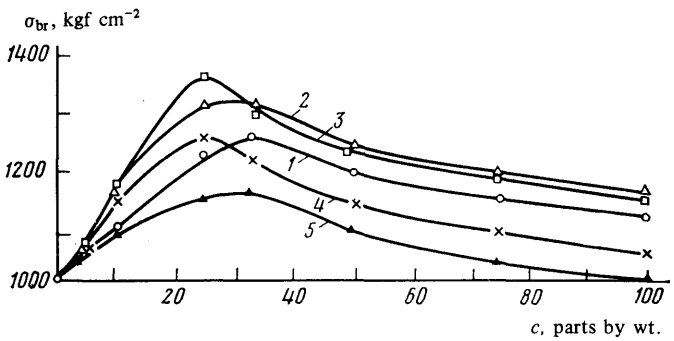


Figure 4. Effect of content c (parts by weight) of UP-612 on breaking strength σ_{br} of compositions, preheated at 200 °C for 20 h, of 100 F-2 with different quantities of UP-607: 1) 0; 2) 5; 3) 10; 4) 20; 5) 30.

Investigation of the effect of the hexaisothiocyanate concentration on the temperature dependence of tan δ for films heated at 180 °C for 30 h has shown (Fig.3) that, under otherwise similar conditions, the completeness of network formation depends on the quantity of hexaisothiocyanate added. When the latter is large (100 parts by weight) a well defined maximum is observed in tan δ with a peak at 180 °C; when the content is lowered (to 50 and below) the maximum degenerates almost completely, and the sharp rise in the temperature dependence occurs at ever higher temperatures. The presence of a clear maximum at 100 parts by weight indicates that under the above conditions (180 °C for 30 h) network formation is incomplete. Further heating of the specimen at 280 °C for 4 h results in complete disappearance of the maximum (Fig.3, curve *6*). This again confirms that the dynamic mechanical method permits the study even of extremely delicate chemical changes in the solid phase and reliable assessment of their completeness.

IV. STRENGTH PROPERTIES OF NETWORKS

Here we consider the changes in the strength and deformation properties of heat-resistant polymers accompanying formation of network systems and the influence of composition on the mechanical properties. It has been shown above that a network system can be obtained from an epoxy-polymer by the simultaneous introduction into the resin of a chemically active heat-resistant polymer of high molecular weight and traditional hardeners such as a polyanhydride of sebacic acid (UP-607) and tetrahydromethylphthalic anhydride. As a consequence of the presence of excess of the reactive polymer the portion thereof not involved in network formation remains as a free powder and serves as a filler. Such a chemically active macromolecular filler lowers significantly the specific gravity of the material, and produces sharp increases in thermal shock resistance and mechanical indices relative to a material containing an ordinary mineral filler[57]. Several compositions[58–61] have a density of 1.1 g cm^{-3}.

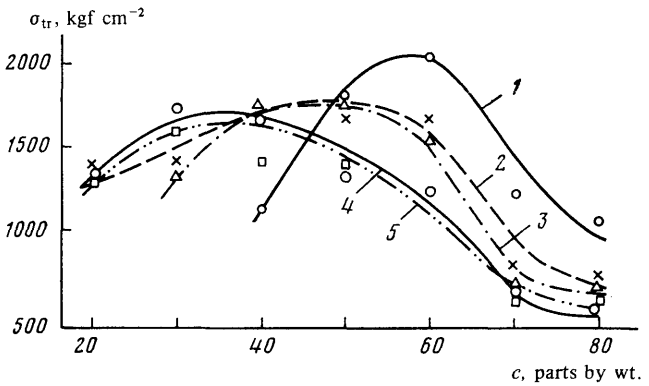


Figure 5. Dependence of transverse strength σ_{tr} on content c of UP-607 hardener for different contents of F-2 polyarylate: 1) 10; 2) 20; 3) 30; 4) 40; 5) 50.

Fig.4 shows the dependence[39] of the breaking stress σ_{br} of F-2 polyarylate network compositions containing various quantities of UP-607 hardener on the content of UP-612 polymer. All the curves pass through a maximum at a content of 25–33 parts by weight of the epoxy-polymer per 100 of the polyarylate. If the strenght of the polyarylate is 1020 kg cm^{-2}, the introduction of 33 parts by weight of UP-612 increases the breaking strength to 1260 kg cm^{-2} (curve *1*). Addition of a small quantity of the hardener (5–10 per 100 parts by weight of UP-612) produces a further improvement in strength properties (curves *2* and *3*). When the hardener content is increased to 20 parts by weight and above, the strength properties of the materials deteriorate (curves *4* and *5*). These compositions exhibit maximum specific elastic modulus at a UP-607 content of 40–60 parts by weight. Fig. 5 illustrates the variation in the transverse strength σ_{tr} for monolithic specimens of the same compositions[58]. The dependence of this property on the UP-607 content with various contents of F-2 polyarylate also passes through a maximum, at approximately 50% of UP-607.

It is noteworthy that the strength characteristics of the network systems exceed those of the polyarylate over very wide ranges of contents both of UP-607 and of F-2 polyarylate; this permits wide variation in the composition of the systems to obtain materials with other optimum mechanical properites, without fear of lowering the tensile strength[39,58]. In contrast to the above variation in breaking and transverse strengths, the compressive strength σ_c and the modulus of elasticity E' usually decrease monotonically with increase in the content of UP-607 hardener (Fig.6). Compositions containing a minimum quantity of UP-607 exhibit the highest values of these two properties, which is fully explicable,

since network formation by cross-linking with a more rigid system (F-2 polyarylate) will produce more rigid networks possessing a higher modulus of elasticity and greater static compressive strength. Introduction of a larger quantity of a flexible-chain oligomeric hardener will yield a more elastic network with a smaller modulus of elasticity and lower compressive strength. On the whole the mechanical properties on compression of networks based on heat-resistant polymers are quite high (Fig.6).

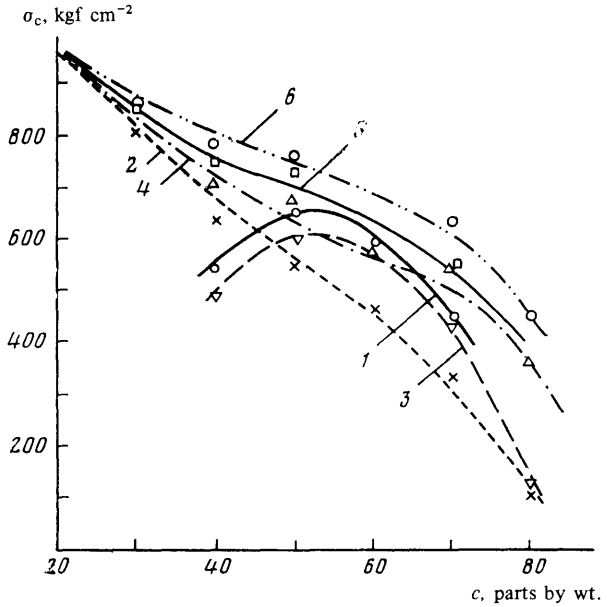


Figure 6. Dependence of compressive strength σ_c on content c of UP-607 hardener for different contents of F-2 polyarylate: 1) 10; 2) 20; 3) 0; 4) 30; 5) 40; 6) 50.

Data on mechanical properties have been obtained for other compostions based on UP-612 cycloaliphatic epoxy-polymer with UP-607 and tetrahydromethylphthalic anhydride as traditional hardeners and F-2 polyarylate, a polyimide of benzophenonetetracarboxylic acid and anilinephthalein, or an aromatic polyamide of terephthalic acid and anilinefluorene as chemically active macromolecular hardener–filler[61]. The results are essentially similar to those illustrated in Figs.5 and 6. Thus the introduction into compositions based on epoxy-polymers of chemically active aromatic polymers of high molecular weight, which act both as hardeners and as fillers, yields strong and light materials, capable of functioning over wide ranges of temperature and mechanical loadings.

Interesting results have been obtained[39] for the strength and deformation properties of a poly(phenylquinoxaline) alone and modified with a small quantity (20 parts by weight) of hexaisothiocyanatocyclotriphosphazene. Fig.7 shows that at low temperatures the modified polymer is slightly the stronger, but with rise in temperature loses strength more rapidly. At 150 °C, however, the decrease in breaking strength ceases owing to network formation, and at high temperatures (when this can be completed within the duration of the experiment) there may even be some increase in strength, with the modified specimen becoming stronger than the unmodified. At comparatively low temperatures the former breaks down at smaller deformations, but with rise in temperature to 220–230 °C the pattern reverses abruptly: at high temperatures the modified poly(phenylquinoxaline) exhibits extremely large (up to 200%) elongations at rupture, which is not usually characteristic of heat-resistant polymers. Hence the modification of poly(phenylquinoxaline) by the addition of a small quantity of hexaisothiocyanatocyclotriphosphazene tends to improve the deformability of the system at high temperatures.

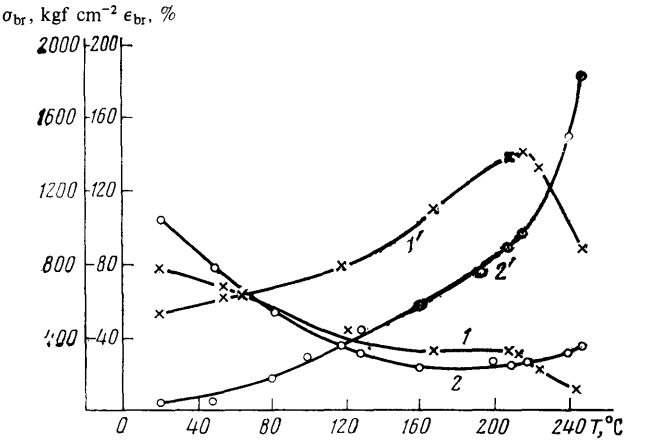


Figure 7. Effect of modification with hexaisothiocyanatocyclotriphosphazene temperature dependence of breaking strength σ_{br} and elongation at break ε_{br} for poly(phenylquinoxaline): 1) unmodified σ_{br}; 1') unmodified ε_{br}; 2) modified σ_{br}; 2') modified ε_{br}.

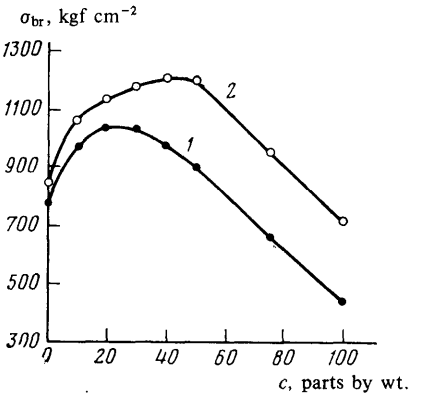
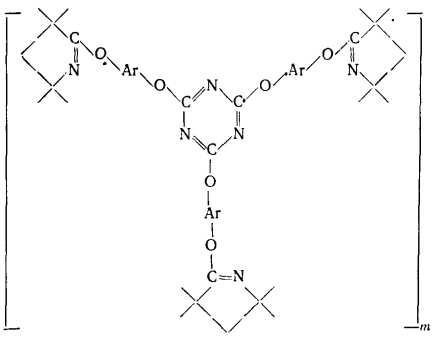


Figure 8. Dependence of breaking strength σ_{br} on content c of hexaisothiocyanatocyclotriphosphazene in modified poly(phenylquinoxaline) films: 1) initial; 2) after heating.

An increase in strength is produced[39] also by heating at 150 °C for 2 h poly(phenylquinoxaline) films modified with different quantities of hexaisothiocyanatocyclotriphosphazene (Fig.8). As already noted, this is due to the polymerisation of the hexaisothiocyanate occurring under these conditions, with formation of a network system. With such heat-treatment the strength of the initial poly(phenylquinoxaline) changes little (from 780 to 830 kg cm^{-2}), but an appreciable increase in breaking strength (to 1200 kg cm^{-2}) is produced at a higher temperature (280 °C for 10 h). The probable cause is formation of a network system by thermal cross-linking of the polymer molecules, but this is accompanied by a sharp decrease in deformability.

An interesting recent development in heat-resistant systems is investigation of the preparation and properties of networks formed by the polycyclotrimerisation of various arylene dicyanates[62,63] to give network aromatic polycyanates having the structure



This process is characterised by great selectivity and a quantitative yield of a highly cross-linked polycyanate. Hence the resulting network is very regular, and monolithic specimens are distinguished by improved properties in comparison with ordinary network polymers.

It is of interest to examine in greater detail the influence of the chemical structure of the initial dicyanic esters on the properties of the network polycyanates[64]. In the case of dinuclear aromatic dicyanates the nature of substituents attached to the central carbon atom has a significant effect on the properties of the networks. Table 1 shows the structure of the initial esters together with several parameters for the corresponding polycyanates. Since mechanical and other properties depdend also on the crystallinity of the specimens, Table 1 includes appropriate characteristics.

The first striking fact is that polymers of dicyanates containing identical small substituents attached to the central carbon atom (I–III in Table 1) have abnormally high resilience (23–25 kgf cm cm^{-2}). However, the presence of identical aromatic substituents attached to this atom (IV–VI), and also large planar groups (VII–IX), produces an appreciable diminution in resilience for moulded specimens of the polycyanates. In the latter cases, however, the transverse strength of the polycyanates is increased appreciably.

In the absence of a bonding sp^3 carbon atom between the benzene rings, as in the polycyanate (XII) from *pp'*-biphenylylene dicyanate, the resulting material has comparatively low specific resilience (6 kgf cm cm^{-2}). Diminishing the distance between branch points to single phenylene groups (polycyanates from *m*- and *p*-phenylene dicyanates) again produces a considerable improvement in resilience and transverse strength.

X-Ray examination indicates that most of the polycyanates obtained are amorphous polymers. In several cases, however, when identical small substituents (hydrogen, methyl) are attached to the central carbon atom, and also in polycyanates formed from dicyanic esters of resorcinol, quinol, and biphenyl-*pp'*-diol, slightly and moderately ordered structures are formed. Thus the presence of a rigid three-dimensional network in these polymers is not an obstacle to the appearance of ordered structures. A slightly ordered crystalline structure is observed also in the polycyanate from 10,10-diphenylanthr-9-one *pp'*-dicyanate, which contains large planar groups attached to the central carbon atom.

Table 1. Physical properties of polycyantes from dicyanic esters of various aromatic diols[64].

No.	Aromatic dicyanate*	Specific elastic modulus, kgf cm cm^{-2}	Transverse strength $10^{-3}\sigma_{tr}$, kgf cm^{-2}	Density (20 °C), g cm^{-3}	Mol. mass of chain unit	Volume of chain unit, A^3	Packing coeff. *K*	X-Ray results
(I)	$NCOC_6H_4—CH_2—C_6H_4OCN$	23	1.22	1.307	750.78	655.81	0.688	cryst., moderate order
(II)	$NCOC_6H_4—C(CH_3)_2—C_6H_4OCN$	25	1.40	1.235	834.95	769.63	0.686	amorphous, signs of cryst.
(III)	$NCOC_6H_4—C(CF_3)_2—C_6H_4OCN$	24	1.46	1.528	1158.80	858.79	0.682	amorphous
(IV)	$NCOC_6H_4—C(H)(C_6H_5)—C_6H_4OCN$	10	1.59	1.255	979.08	891.85	0.689	amorphous
(V)	$NCOC_6H_4—C(CH_3)(C_6H_5)—C_6H_4OCN$	17	1.85	1.229	1021.16	943.93	0.684	amorphous
(VI)	$NCOC_6H_4—C(C_6H_5)_2—C_6H_4OCN$	5	1.62	1.220	1207.37	1118.53	0.681	amorphous
(VII)	3,3-Di-*p*-cyanatophenylphthalide	6	2.02	1.322	1105.06	934.63	0.673	amorphous
(VIII)	9,9-Di-*p*-cyanatophenylfluorene	5	1.54	1.269	1207.37	1080.73	0.688	amorphous
(IX)	10,10-Di-*p*-cyanatophenylanthr-10-one	6	1.69	1.288	1285.36	1134.90	0.685	cryst. slight order
(X)	*m*-$NCOC_6H_4OCN$	18	1.92	1.414	480.41	388.33	0.688	amorphous, signs of cryst.
(XI)	*p*-$NCOC_6H_4OCN$	12	1.73	1.431	480.41	388.33	0.697	cryst., slight order
(XII)	$NCOC_6H_4—C_6H_4OCN$	6	1.47	1.319	708.70	615.13	0.689	cryst., moderate order

* With the exception of polymer (X) all the phenylene groups were *para*-substituted.

V. RELAXATION PROPERTIES OF NETWORKS UNDER CONDITIONS OF STATIC CONSTRAINT (STRESS RELAXATION AND CREEP)

Investigation of stress relaxation in heat-resistant aromatic polymers under both isothermal and non-isothermal conditions and study of the mechanical applicability of the systems under conditions of stress relaxation over wide ranges of temperature and deformation have been conducted for a relatively long time and have been quite widely discussed[65-68]. In the present Review, therefore, attention will be concentrated mainly on the most recent studies of static relaxation properties.

A detailed investigation of the relaxation properties of networks based on epoxy-oligomers and heat-resistant aromatic polymers[58-60] has enabled the influence of the chemical structure of the network on the heat-resistance to be identified and the boundaries of possible application of the materials to be determined. Both binary systems (epoxy-resin–aromatic polymer) and ternary systems (with addition of a hardener) have been studied. Relaxation properties have been examined under non-isothermal conditions with uniaxial compression by a method[68,69] permitting determination of the ranges of stress and temperature within which the polymer retains distinct hardness and can function as a structural material. The boundary of the operable region is drawn through the maxima of relaxation curves obtained with a linear temperature rise at a specified rate for compressed specimens whose deformation remains constant during an experiment.

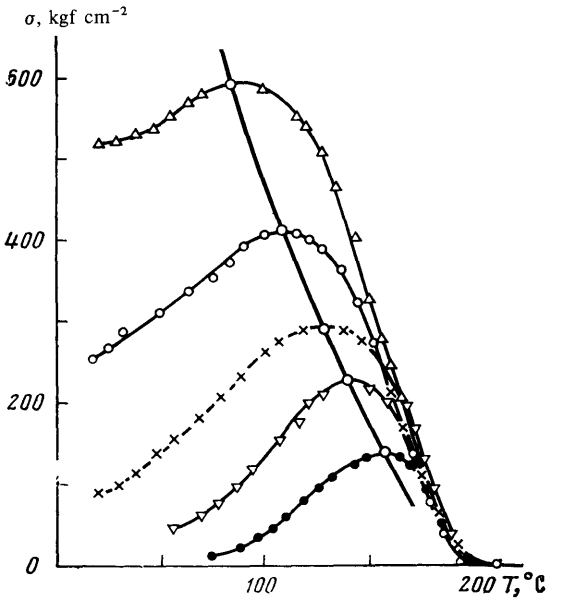


Figure 9. Region of applicability of composition containing (parts by weight) 100 UP-612 + 60 F-2.

Hardening an epoxy-oligomer with a chemically active aromatic polymer leads to a significant broadening of the region of mechanical applicability, with respect both to stress and especially to temperature. For example, the solid material formed by reaction between an epoxide and a polyarylate possesses far greater heat-resistance than do the usual hardened epoxy-resins. Such a material can be used at significantly higher temperatures than can an ordinary composition hardened with a traditional hardener.

A similar result has been obtained[58] for binary compositions containing UP-612 cycloaliphatic resin and F-2 polyarylate. The composition for which results are illustrated in Fig. 9 possesses the largest range of application, with respect to both temperature and stress, among all the solid compositions studied.

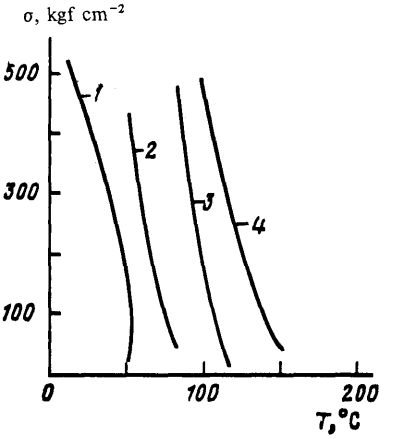


Figure 10. Curves bounding regions of applicability of various compositions (parts by weight): 1) 100 Ed-16 + 60 UP-607; 2) 100 ED-16 + 40 F-2; 3) 100 Ed-16 + 50 F-2; 4) 100 ED-16 + 60 F-2.

In order to trace the effect of the quantity of polyarylate on heat-resistance curves bounding the region of applicability have been obtained for a composition based on ED-16 epoxy-resin hardened with a polyanhydride of sebacic acid. With increase in the quantity of polyarylate these curves (Fig. 10) are regularly displaced to higher temperatures, and are situated substantially to the right of the curve for an ordinary solid composition. Thus introduction of a polyarylate into an epoxy-resin increases the heat-resistance of the composition, which may function at higher temperatures under greater loads.

As has already been noted, the introduction of a heat-resistant aromatic polymer into an epoxy-resin with the aim of obtaining a network does not prevent simultaneous use of a traditional hardener. Networks formed by the interaction of three components have special features. As example Fig. 11 shows the region of applicability of a solid composition comprising a polyarylate, ED-16 epoxy-oligomer, and a polyanhydride of sebacic acid as the traditional hardener. Introduction of a polyarylate into a ternary composition appears to give two regions of applicability, characterised respectively by (i) comparatively low temperatures and high stresses and (ii) high temperatures and low stresses. The region corresponding to high stresses remains approximately the same whether or not the heat-resistant polymer (polyarylate) is present: there is merely a slight

rise in the temperature limits. However, in the presence of the polyarylate the composition based on the epoxy-resin can withstand at high temperatures far larger loads than can the usual compositions. The height of the "loop" (i.e. the stress) then increases with the quantity of polyarylate added[58].

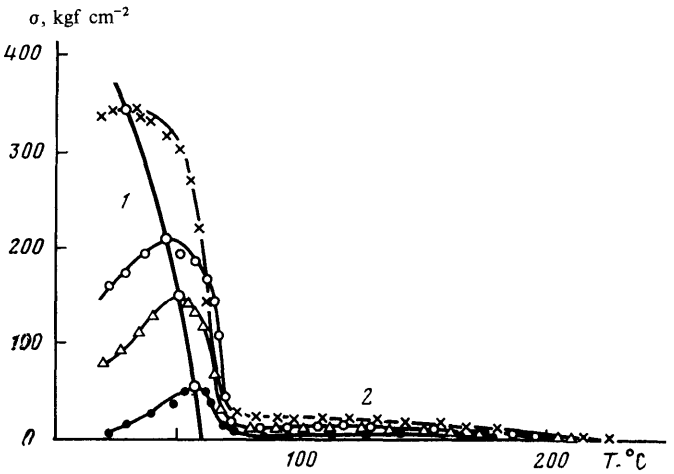


Figure 11. Region of applicability of composition comprising (parts by weight) 100 ED-16 + 40 UP-607 + 50 F-2.

These results have been attributed[58] to differences in flexibility among the chain segments between branch points in the network formed by hardening of an epoxy-resin with a mixture of a traditional hardener and a polyarylate. When such a network is heated in a stressed state for determination of the region of applicability, stress relaxation will occur primarily by the appearance of molecular mobility in the flexible chain segments of the epoxy-resin. Since these are present in every composition, acceleration of relaxation processes will develop, of course, at approximately the same temperatures in composite materials differing in composition. At high temperatures, however, at which stress relaxation is complete in the usual compositions, the presence of polyarylate fragments in the present case prevents complete relaxation right up to 220 °C: slight stress is retained in the material.

A similar result is obtained when other heat-resistant aromatic polymers are introduced into compositions based on epoxy-resins of diverse structure. Two regions of applicability are evident: the high-temperature region may extend to 300 °C; the low-temperature region (at high stresses) remains almost the same as in the absence of heat-resistant aromatic polymers[61].

Thus the investigation[58-61] has shown that solid compositions based on epoxy-resins can be obtained without the use of traditional hardeners by introducing into the resin chemically active heat-resistant polymers (polyarylates, aromatic polyamides, polyimides, etc.). Such a process produces a significant extension to higher temperatures of the region of mechanical applicability of the composition. Introduction of aromatic polymers into an epoxy-resin does not prevent use of ordinary hardeners, and the properties of the material can be controlled by varying the composition of such a ternary system[61].

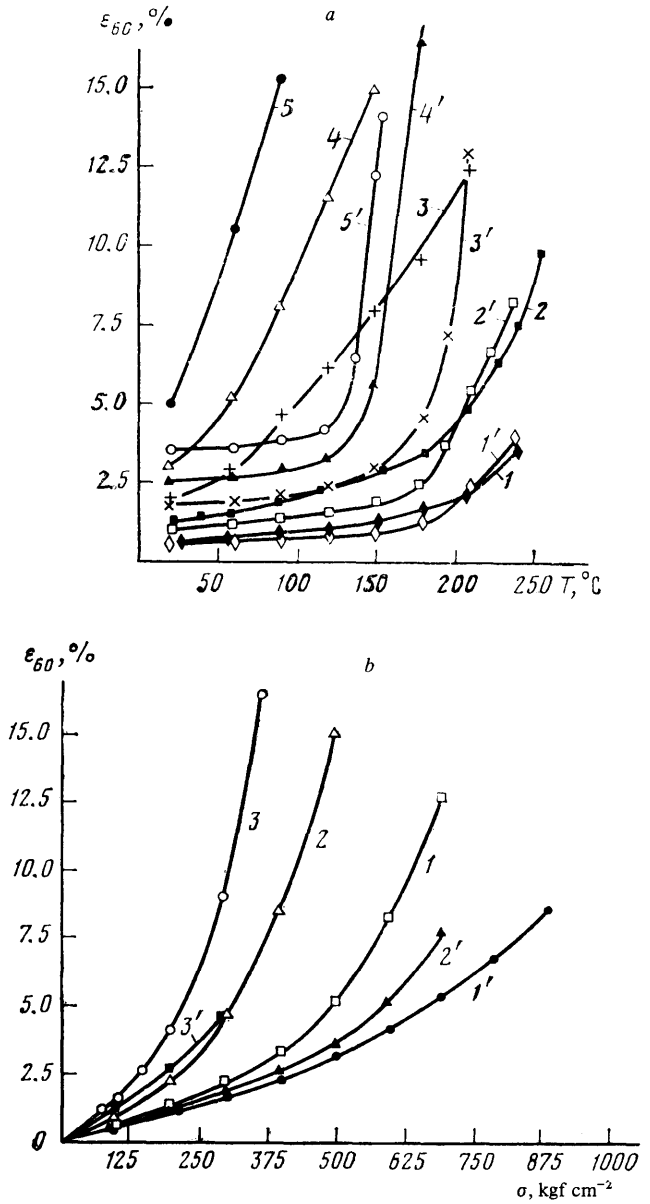


Figure 12. Dependence for initial and preheated polyarylate (respectively unprimed and primed curves) of deformation ε_{60} developed during 60 min of creep: (*a*) on temperature under stresses σ (kgf cm^{-2}): 1,1′) 100; 2,2′) 200; 3,3′) 300; 4,4′) 400; 5,5′) 500; (*b*) on stress at various temperatures *T* (°C): 1,1′) 20; 2,2′) 90; 3,3′) 150.

A considerable number of studies has been made on creep in network systems based on heat-resistant polymers. Such investigation is of fundamental interest, since it helps to reveal the limits of stress, temperature, and duration within

which deformation in the polymer material does not exceed a specified value. It may even be claimed that the study of creep is more importanat than the investigation of stress relaxation for assessing the mechanical applicability of polymer materials, since in most cases their working conditions tend to develop creep (with variable or constant loading and temperature). Measurements of creep must be made over all temperature and stress ranges possible for a given specimen in order completely to characterise the region of its applicability. The possible range of stresses is determined by the ability of the polymeric material to creep without disintegration; the possible temperature range is determined in the case of heat-resistant solid plastics by the glass point.

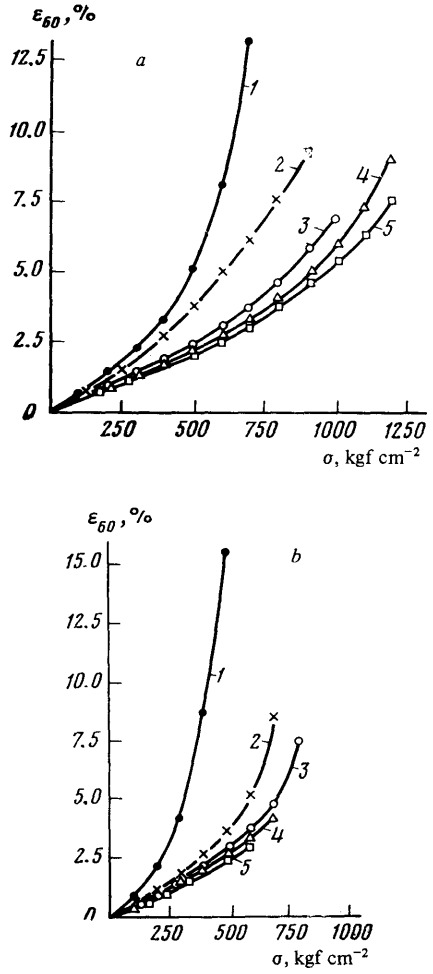


Figure 13. Dependence of ε_{60} on σ at (*a*) 20 °C and (*b*) 90 °C for 100 parts by weight of a polyarylate alone and in network systems containing various quantities of an epoxy-polymer: 1) 0; 2) 0 (preheated); 3) 10; 4) 20; 5) 33.

Detailed investigation of creep in the initial heat-resistant polymers and derived network systems[39,54,70] has shown that such polymers are characterised by very slight dependence of deformation on temperature over a very wide range. This experimental finding is illustrated by Fig.12, which shows the creep deformation ε_{60} developed during the process lasting 60 min for initial and heated polyarylates and for network systems. With various constant stresses the variation in ε_{60} is small over a fairly wide temperature range (depending on the stress), and only near the softening point does the creep begin to increase rapidly. This is especially characteristic of the heated polyarylate, which exhibits a far smaller tendency to creep than does the original specimen. Diffractograms[70] show that the reason for such behaviour is that the specimen becomes more ordered as a result of heating.

The influence of stress on creep is readily seen from Fig.12, in which is plotted the dependence of ε_{60} on mechanical stress at various constant temperatures. These curves show that the deformation increases appreciably with stress throughout its range, and here, too, a heated specimen exhibits far less tendency to creep than does the initial specimen.

Investigation[39,70] of the creep of film specimens containing various quantities of UP-612 epoxy-polymer and heated to form a cross-linked network of chemical bonds has revealed a generally smaller tendency of the network specimens to creep. In several cases the curves for the latter are almost horizontal lines: i.e. deformation does not develop with time. This result has considerable practical value, since undeformable materials, which do not change their shape with time under the influence of quite large stresses, can be obtained on the basis of networks of a polyarylate with an epoxy-polymer. A similar conclusion can be reached from a series of creep curves for initial and network specimens obtained under different mechanical stresses at a constant temperature[70].

To summarise the results and present them more vividly Fig.13*a* illustrates the stress dependence of ε_{60} (at 20 °C) for initial and heated polyarylate and for derived network specimens containing various quantities of UP-612. The network specimens exhibit a far smaller tendency to creep even than the heated polyarylate at the same stress throughout the range investigated. The best results are obtained with specimens containing 20–50 parts by weight of UP-612 per 100 of the polyarylate. The above tendency is maintained with rise in temperature, but the curves representing the stress dependence of ε_{60} are closer together (Fig.13*b*). This is entirely reasonable, since with rise in temperature the presence of a less heat-resistant material in the network should tend to increase creep, although, as noted above, network specimens undergo less deformation in all cases.

Thus the investigation of creep in an initial polyarylate and in network polymers based on the polyarylate and epoxy-polymers has shown that, as a consequence of the formation of a network of chemical bonds, heating diminishes substantially both the magnitude and the rate of creep. Almost complete cessation of the development of deformation with time under the influence of very large stresses can be achieved by varying the composition.

Fig.14 shows correlated logarithmic pliability curves plotted on the principle of temperature–time equivalence by displacement along time axis with $T_0 = 20$ °C selected as reference temperature. Three series of curves are included, representing respectively the behaviour under creep conditions of initial and heated polyarylate and of a network formed by interaction with UP-612 epoxy-polymer. Curves obtained at different constant stresses for initial and heated polyarylate specimens are evidently not superposable. The greater the applied stress, the greater the pliability. All this clearly indicates non-linear mechanical behaviour of

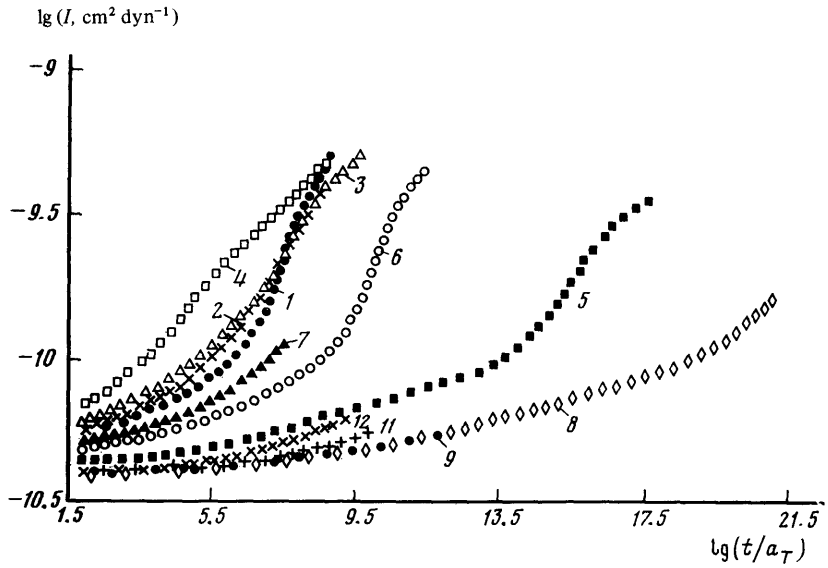


Figure 14. Correlated pliability curves (reference temperature $T_0 = 20$ °C) for initial and preheated polyarylates and a network polymer containing 33 parts by weight of an epoxy-polymer per 100 of the polyarylate, obtained under different stresses (kgf cm^{-2}): 1) polyarylate 200; 2) polyarylate 300; 3) polyarylate 400; 4) polyarylate 500; 5) preheated 200; 6) preheated 300; 7) preheated 400; 8) network 200; 9) network 300; 10) network 500; 11) network 600; 12) network 900.

polyarylates over wide ranges of stress and temperature. However, the network system exhibits quite different behaviour: the correlated curves practically coincide over a wide stress range, especially for short durations. Only at high stresses (600–900 kg cm^{-2}) do the curves begin to diverge towards an increase in pliability (at comparatively short durations). Another feature of the network system is lower pliability than for initial and heated polyarylate throughout the correlated curve.

Another feature of Fig.14 is that plots of $\lg I$ against $\lg (t/a_T)$ obtained for relatively small stresses, where I is the pliability, t the time, and a_T the displacement factor, consist of two segments having different slopes. The first is gently sloping, which indicates a low rate of creep within the given range of $\lg (t/a_T)$ values, corresponding to a definite range of comparatively low temperatures. The second segment has a greater slope, indicating compartively rapid creep. The principle of temperature–time equivalence can be used to determine the temperature range of the transition between these two sections of relatively slow and rapid creep. As has been established for a polyarylate, this temperature range, in which creep undergoes abrupt acceleration, coincides precisely with that in which stress relaxation is sharply accelerated.

Thus investigation of the creep of heat-resistant systems has yet again confirmed the advisability of subdividing the temperature range of the vitreous state into two subranges with different rates of relaxation. When polymeric materials are used under non-isothermal conditions, it must be borne in mind that a rapid increase in the rate of creep will be observed on passing from one subrange to the other, which may lead to an unacceptable change in shape of the material.

The course of the creep curves for the polymeric systems studied is well reproduced by the quantitative relation[71]

$$\varepsilon(t) = \sigma_0 I_\infty [1 - e^{-(t/\theta)^m}] + \frac{\sigma_0}{\eta} t,$$

where the product of the applied constant stress σ_0 and the equilibrium pliability I_∞ gives the equilibrium deformation $\varepsilon_0 = \sigma_0 I_\infty$, while θ is the time lag, m a constant characteristic of the material, and η the viscosity coefficient of the system. All the creep curves obtained for the initial F-2 polyarylate and its derived network systems have been calculated[70] by means of this equation from statistical least-squares processing of experimental results. The calculations show that the parameters m, θ, and η have a strong scatter, so that a regular temperature and stress dependence cannot be established. Only for the equilibrium pliability I_∞ is a smooth dependence observed.

A detailed investigation has been made[64] of the heat resistance of highly cross-linked polycyanates prepared from dicyanic esters of various aromatic diols. Fig.15 shows as example the temperature limits of the heat-resistance of several polycyanates as a function of the mechanical stress. A striking feature is the similarity between the non-isothermal stress-relaxation curves (broken) and curves bounding the region of applicability for highly cross-linked systems—polycyanates and linear heterochain polymers (with a polycarbonate as example).

Replacing an isopropylene by a fluorene group in the chain segments between branch points increases the heat-resistance of the polymer throughout the temperature and stress ranges investigated. An appreciable shift is also observed in the maximum temperature of applicability, at

which the stress in the specimen relaxes completely to zero. Replacing a *para*-substituted dinuclear dicyanate residue by a mononuclear *meta*-radical between the branch points in the polymer network lowers the heat-resistance of the polycyanate with respect both to temperature and to stress[64]. Introduction of a 1,2-carborane instead of a 9,9-fluorene bridge between the phenylene groups of the cyanate also lowers the heat-resistance of the polycyanates (Fig. 15).

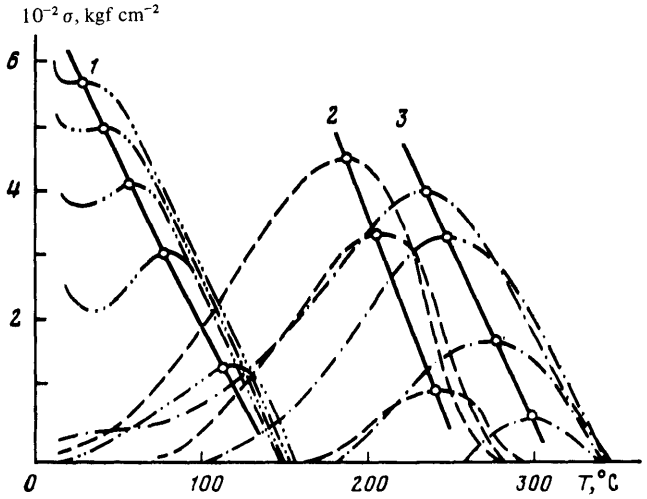
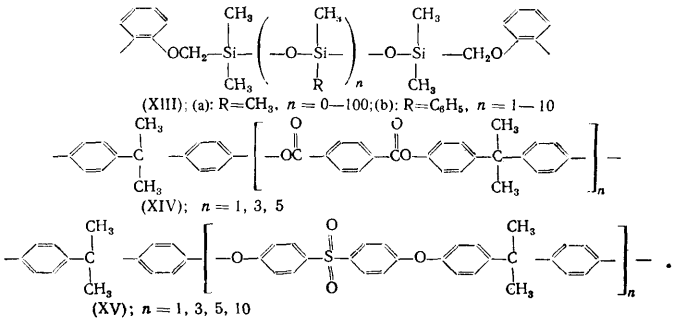


Figure 15. Regions of applicability of 1) a polycarbonate from 2,2-diphenylpropane-*pp'*-diol; 2) polycyanate (II); 3) polycyanate (VIII).

Thus the structure of the initial aromatic cyanate exerts a significant influence on the properties of the resulting polycyanates, although the latter are dense networks. Even small changes in the structure of the segments between branch points in such a dense network lead to appreciable changes in the properties of monolithic specimens of the polycyanates.

Still greater variation in properties can be achieved by varying the chemical nature of the segments between branch points in the dicyanates. Dicyanic esters of oligosiloxanes, oligo(arylene sulphoxides), and oligoarylates of various lengths have been used[72] as initial compounds for network formation. It is interesting that linear macromolecular analogues of these segments find wide application. The segments between the branch points[72] had the structures



Depending on the chemical structure and also on the number n of repeating units monolithic specimens of the network polycyanates had properties varying from rubberlike with large reversible deformation and a low modulus of elasticity to vitreous with a high modulus. Analysis of the equilibrium modulus in the rubberlike state showed that the distance between network branch points in the polycyanates corresponded almost exactly to the chain lengths in the initial oligocyanates, evidence of a process with high selectivity and a network with few defects. It is therefore possible to analyse the effect of the chemical structure of the internodal segments on the properties of the network polycyanates.

Table 2. Parameters in the Kohlrausch equation for network polymers.

n	Gel fraction, %	ε, %	E_∞ (kgf cm^{-2})	E_0 (kgf cm^{-2})	τ_p, min	k	$10^{-7}\eta$, P
Polymer (XIIIa)							
5	96	20	16.0	5.50	23	0.70	6.3
25	95	50	2.3	0.12	18	0.52	1.88
50	95	50	1.7	0.12	14	0.42	0.51
70	92	50	1.0	0.08	8	0.33	0.41
Polymer (XIV)							
1	96	30	19.3	9.17	32	0.83	$5.11\cdot10^9$
3	95	30	13.2	3.84	28	0.17	$6.03\cdot10^{10}$

The investigation[72] has shown that stress relaxation in the polycyanates is well described by the Kohlrausch equation with parameters depending very characteristically on the chemical structure of the network. Comparison of polycyanates based on oligosiloxanes and on oligoarylates with small values of n shows that such parameters as E_∞, E_0 and τ_p have closely similar values (Table 2). The main difference between these polymers lies in the fractional power of the time ($k = 0.70$ and 0.17) and in the viscosity ($\eta = 6.3 \times 10^7$ and 6.03×10^{10} P respectively). Such a substantial difference in the viscosities of the polymers is attributed to the chemical structure of the internodal segments. In the region of the hyperelastic state polymers with oligoarylate segments probably exhibit considerably greater intermolecular interaction and rigidity than do network polydimethylsiloxanes[72].

Comparison of the relaxation properties of polycyantes based on oligo(arylene sulphoxides) and on oligoarylates does not reveal such an important difference (at equal values of n). However, a network polycyanate based on the former type of oligomer has the larger relaxation modulus.

Great selectivity of the polycyclotrimerisation of arylene dicyanates, which governs many physical and chemical properties of the resulting polycyanates, distinguishes it favourably from that of other groups having multiple bonds (–N:C:O, –C⋮CH), which is accompanied by numerous side-reactions such as dimerisation, polymerisation in the chain, etc.[73,74]. As a consequence of the great selectivity of cyclotrimerisation of –O.C⋮N groups in arylene dicyanates and its nearly quantitative completion the resulting highly cross-linked polymers possess several properties marking them off from well known cross-linked polymers, e.g. greater specific resilience, which is not typical of highly cross-linked systems.

Under certain conditions several polycyanates form partly crystalline structures[72], which is probably also related to the regularity of their chemical structure, confirmed by calculations of the density of packing of macromolecules in the final monolithic polycyanates. The density of packing of the chain was assessed from the molecular packing coefficient defined by the formula

$$K = \frac{N_A \sum_i \Delta V_i}{M/d},$$

in which ΔV_i is the van der Waals volume of the ith atom in the repeating unit, M the molecular mass of the unit, d the density, and N_A Avogadro's number.

Calculations have shown[64] that packing coefficients for network polycyanates differing in aromatic structure lie in the range 0.673–0.697 (Table 1). The mean packing coefficient for monolithic specimens of linear polymers is 0.681. Hence network systems based on aromatic polycyanates exhibit as high a density of packing of macromolecules as do linear systems. When polysiloxane segments are introduced between network branch points, the packing coefficient decreases rapidly, especially with increase in chain length between these points[72]. This is a feature also of linear polydimethylsiloxanes.

The process of formation of the supermolecular structure of polycyanates at various stages of synthesis—from the initial monomer to a regular network with almost 100% conversion of functional groups—has been examined[75] in order to find the reasons for the improved mechanical indices (especially on impact). In the early stages the specimens were liquids, which were frozen down to −150 °C to fix the structure instantaneously after which relicas were sputtered at −190 °C. The initial monomer comprised finely crystalline structures, which on heating underwent changes as a consequence of polycyclotrimerisation. In the early stages of this reaction sharply bounded regions of globular structure, with globules of mean size 500 Å, appeared on the background of the characteristic structure of the monomer. With further polycyclotrimerisation the whole surface consisted of globules, whose size gradually diminished with increase in the degree of conversion of cyanato-groups. In the very last stage of polycyclotrimerisation fibrillar structures appeared. This may be the reason for the characteristic mechanical properties of aromatic polycyanates.

The relaxation properties also change with the degree of conversion (and hence the supermolecular structure). In the comparatively early stages the stress-relaxation curves shift to higher stress values (the modulus of eleasticity and the equilibrium modulus increase). In the later stages, however, these moduli begin to decrease (i.e. the rigidity of the specimen diminishes under otherwise similar geometrical conditions). Thus there exists a definite relation between the chemical structure of a polycyanate (its degree of conversion), the supermolecular structure, and its mechanical properties.

* * *

From our discussion of the structure and properties of networks based on heat-resistant polymers we may conclude that the most promising trends in this field are the synthesis of network systems from reactive oligomers of aromatic structure, including polycyclotrimerisation, and the production of networks by chemical reaction between oligomers such as epoxy-resins and heat-resistant aromatic polymers containing in the main chain groups capable of interacting with reactive groups in the oligomers. The properties of the resulting network systems can be controlled within wide limits by varying the chemical structure of the segments between and also the density of branch points in the network. In the Reviewers' opinion the greatest interest attaches to densely cross-linked polymers based on polycyanates, in which the networks are almost completely free from defects; the formation of these systems is accompanied by substantial change in the supermolecular structure at various stages of conversion, resulting in extremely ordered structures with clear signs of crystallinity at high conversions. In the future it may be of great interest to obtain highly crystalline network systems with interesting sets of properties.

It is also necessary to seek quantitative relations between the chemical structure, the topology of the network, and the set of mechanical properties. It is important to calculate the number of branch points in a network formed of aromatic segments. Since the mechanical (relaxation) behaviour of network systems having aliphatic and aromatic segments differs greatly, only a few values of the equilibrium modulus of elasticity may prove insufficient for such calculation.

There thus remains several unresolved questions in the recent study of the preparation and properties of network systems based on heat-resistant polymers, associated with controlling their properties by varying both chemical and network structures. In view of the rapid development of this field, interesting new results may be expected in the future.

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