Indentation Studies in Plasticized Epoxy Polymers

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Synopsis

A class of plasticized epoxy polymers were subjected to indentation tests over a wide range of temperature and plasticizer percentage. Constant or continuously varying temperature tests were carried out under constant load, and the materials exhibited creep behavior according to the temperature and the amount of plasticizer. Thermal expansion properties were also studied, and glass transition temperature as well as thermal expansion coefficients a_1 and a_2 were determined for each individual material. Theoretical predictions were found valid under the present conditions.

INTRODUCTION

The significance of epoxy polymers for structural purposes appears to be steadily increasing. In particular, the range of application of this class of materials can be considerably widened by means of plastification. The latter offers welcome possibilities of modification of the mechanical behavior of epoxies in order to conform with specific requirements. Several systematic studies on the properties of these materials were carried out over wide ranges of plasticizer percentage and temperature. In particular, Theocaris,[1] by applying the time–temperature superposition principle, derived master curves for extensional or bulk[2] creep and relaxation compliances and moduli for a class of such materials. It was proved that, within the range from ambient to 135°C, the above curves are of simple sigmoidal form, consisting of a glassy region, in which the material behaves elastically, a transion zone, in which the viscoelastic behavior is intense, and a flat rubbery region.

The response of such materials toward surface pressure is of great interest for structural applications. It can be determined by means of a rigid indenter, pressed against the surface considered, by measuring a characteristic dimension of the resulting deformation.

With tough polymers, one can refer to indentation hardness, which is determined in a similar manner as with metals, i.e., by measuring a characteristic dimension of the remaining deformation created by a specific indenter pressed against the surface with a specific force for a prescribed period of time. Examples of such standard methods are the D785-65 (Rockwell hardness of plastics and electrical insulating materials) and D2240-68 (indentation hardness of rubber and plastics by means of a durometer) ASTM methods.[3] Hardness test results cannot, in general, be directly related to any fundamental mechanical property of the material tested, such as mechanical moduli, etc., although such a possibility would be most welcome, as hardness tests are fast and easy to perform.

With plastics, particularly at higher temperatures or with high amounts of plasticizer, i.e., close to or within the transition zone, the problem grows more complex as time-dependent phenomena interfere and the deformation caused

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by an indenter under load, exhibiting creep recovery, renders measurements hardly accurate.[4] Ball indentation hardness tests, being a most convenient method, are being thoroughly investigated.[5]

With elastic materials, such as epoxy polymers in their glassy state, the depth of indentation produced by a practically rigid ball indenter can be related to the respective load by means of the Hertz contact theory,[6] provided that the specimen considered is sufficiently thick, compared with the indenter radius, to simulate an elastic half-space.

A similar theory can be applied for a cylindrical, flat-ended indenter[7] for frictionless contact. The presence of friction, particularly with flat-ended indenters, constitutes an important complexity, and this problem was also investigated[8] for curved-profile or flat-ended rigid indenters.

As far as elastic layers of finite thickness are concerned, the indentation problem was treated for a general axisymmetric rigid die,[9] and solutions were given for spherical, parabolic, or flat-ended indenters. A partial extension for elastic spherical indenter was also given.[10]

With viscoelastic materials, very complex situations arise, and elastic solutions can be applied, by means of the correspondence principle, in limited cases only.[11]

A particular case in which such treatment is possible is with incompressible materials such as rubbers, elastomers, or polymers in the rubbery state. Due to the simplicity of the resulting expressions, determination of Young's modulus from indentation tests appears to be possible. Such an application[12] derives Young's modulus by means of inversion of the expressions obtained by Vorovich and Ustinov.[9] The effect of thickness of thin rubber sheets under the action of spherical rigid indenters was also studied experimentally.[13] A direct analytic solution of the problem of indentation of almost incompressible thin films by a rigid flat-ended indenter was obtained[14] and experimentally verified for thin layers of swollen gelatine.

The thermomechanical analyzer (TMA) appears to be a very convenient instrumentation for the determination of the indentation behavior of polymeric materials, particularly at high temperatures. Such an investigation was undertaken by Hwo and Johnson,[15] who determined Young's modulus of elastomeric materials from indentation measurements.

In the present work, a conventional thermomechanical analyzer was used to determine the depth of indentation under the action of a rigid, cylindrical, flat-ended indenter of a class of cold-setting, plasticized epoxy polymers as functions of time and temperature. The load applied was sufficiently small, and no deformation remained after its removal and the viscoelastic recovery of the specimen. In fact, the materials exhibited creep, by which an elastic deformation component, developing at zero time, could be determined, as well as a time-dependent component, depending on the viscoelastic properties of the materials tested.

At temperatures higher than the ambient, thermal expansion occurred; and with measurements on a temperature scale, a separate series of tests to determine the latter was necessary, since the algebraic sum of linear thermal expansion and indentation was recorded on the instrument. In fact, the transition zone and the rubbery region of the materials were investigated, and experimental results were in good agreement with existing theories when certain fundamental requirements were fulfilled.
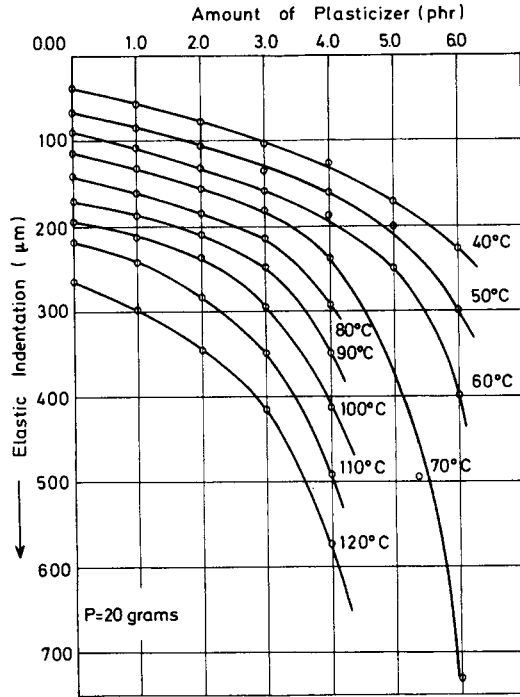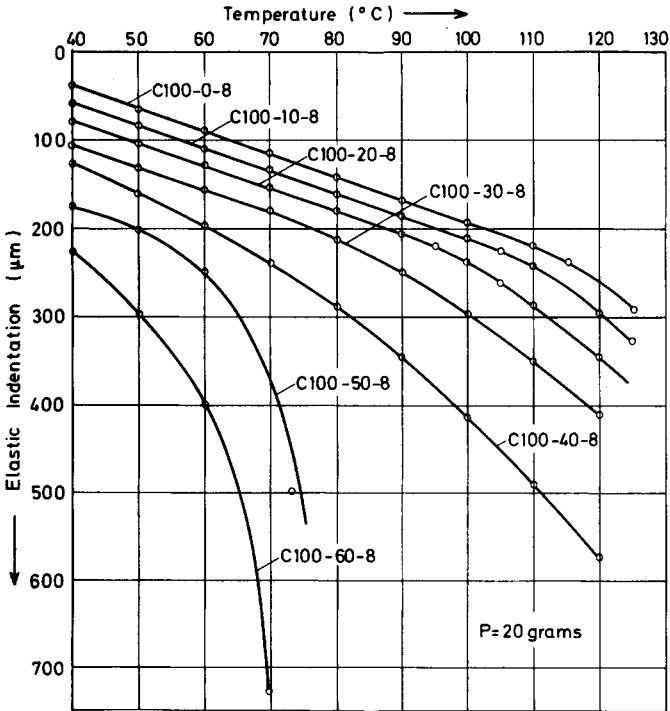
Fig. 1. Elastic or instantaneous component of indentation vs (a) plasticizer percentage for various temperature levels and (b) temperature for various degrees of plastification.
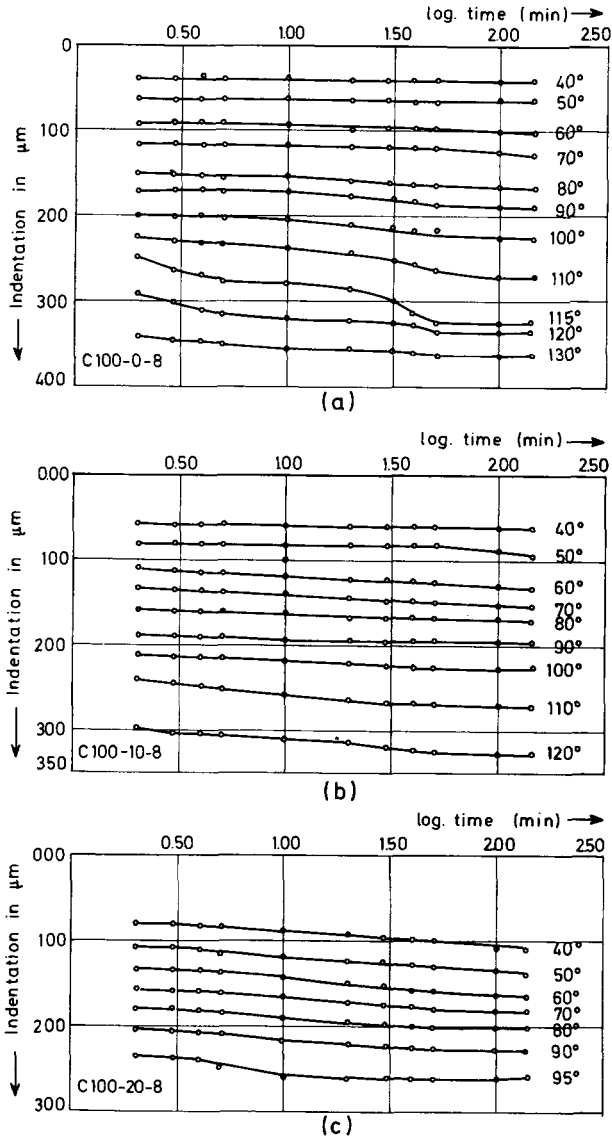
Fig. 2. Indentation vs logarithmic time for various constant temperature levels and each individual material.

EXPERIMENTAL

The present materials were derived from a system based on diglycidyl ether of bisphenol A resin (Epikote 828, Shell Co.) as prepolymer, with an epoxy equivalent of 185–192, a molecular weight between 370 and 384, and a viscosity of 15,000 cP at 25°C. As curing agent, 8 phr by weight triethylenetetramine was employed, i.e., a highly reactive primary aliphatic amine capable of curing diglycidyl ethers at room temperature.

As plasticizer, a polysulfide of the Thiokol LP-3 type was used, i.e., a primary plasticizer completely compatible with the resin considered. This plasticizer has a molecular weight of 1000, 2% crosslinking, a specific gravity of 1.27, and a viscosity of 700–1200 cP at room temperature.

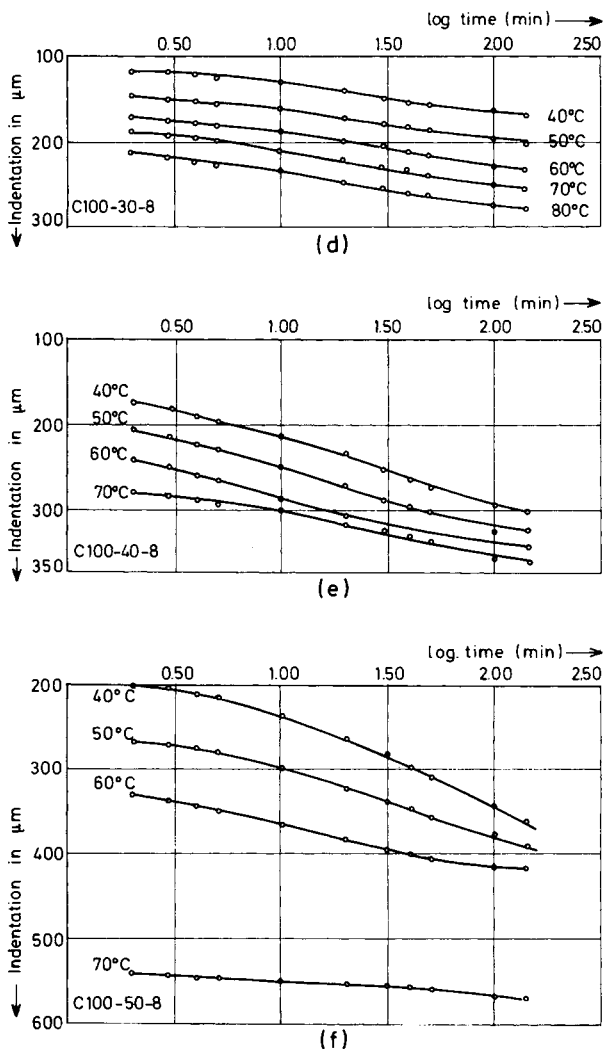Polysulfides of low molecular weight and of the general structure HS—S—SH

Fig. 2. (Continued from previous page.)

react with the epoxy groups to cause chain extensions but not crosslinking, and hardeners must therefore be added in the amounts required. However, in the presence of a primary aliphatic amine, the reactivity is increased, so that low amounts of plasticizer (up to 40 phr) reduce the pot life, which for higher amounts increase rapidly.[16]

The materials investigated in this work are denoted by $C100\text{-}P\text{-}8$, representing amount of prepolymer, plasticizer, and curing agent, respectively, where P (amount of plasticizer in phr) assumes the values 0, 10, 20, 30, 40, 50, and 60, while C stands for cold-setting.

The materials were produced as follows: The prepolymer was heated up to 30°C to decrease viscosity. Proper amounts of curing agent and plasticizer were then added, and the mixture after being stirred thoroughly was put in a vacuum chamber for degassing. Subsequently, it was put in a Plexiglas mold of suitable capacity. The pot life, i.e., the gelation time, was of the order of 15 min at 25°C.
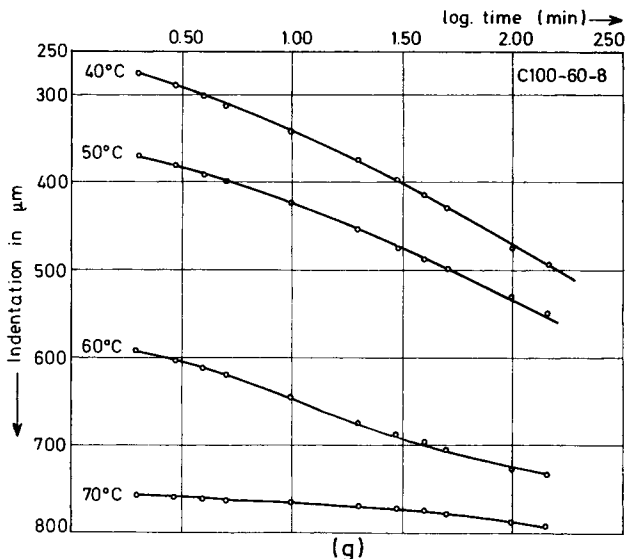
Fig. 2. (Continued from previous page.)

The molding was removed 24 hr later and subjected to thermal processing, aiming not only at complete curing but also at producing stress-free specimens. Temperature was raised at 5°C/hr from ambient to 100°C, maintained constant for approximately three days, and then decreased at 1°C/hr back to ambient.

Specimens about 3 mm thick with smooth surface of approximately 8 mm² were cut from the moldings. The specimens were tested on a du Pont 900 differential thermal analyzer combined with a du Pont 941 thermomechanical analyzer (TMA). A systematic description of the instrument can be found, for example, in Hwo and Johnson.[15] The indentation probe used for the TMA was a flat-ended quartz rod with diameter 0.833 mm, adjusted to act in a direction normal to the specimen surface (i.e., vertically). A constant axial load was applied to the probe, and the displacement of the probe was recorded as a function of time or temperature. The probe used for the TMA for measuring the linear thermal expansion was also a flat-ended quartz rod, but with diameter 2.5 mm, adjusted and loaded in the same manner.

RESULTS

For each particular material, the following tests were performed.

Constant Temperature Tests

A load of 20 g was applied, and indentation was recorded as a function of temperature. Several temperature levels were used from 40°C up to temperatures corresponding to well within the rubbery state of each particular material. Sufficient time was allowed for each particular test piece to reach a state of thermal equilibrium, so that pure indentation at the temperature considered was recorded without being affected by the thermal expansion of the material under testing.

At time $t = 0$, i.e., at the moment of application of load, an instantaneous in-
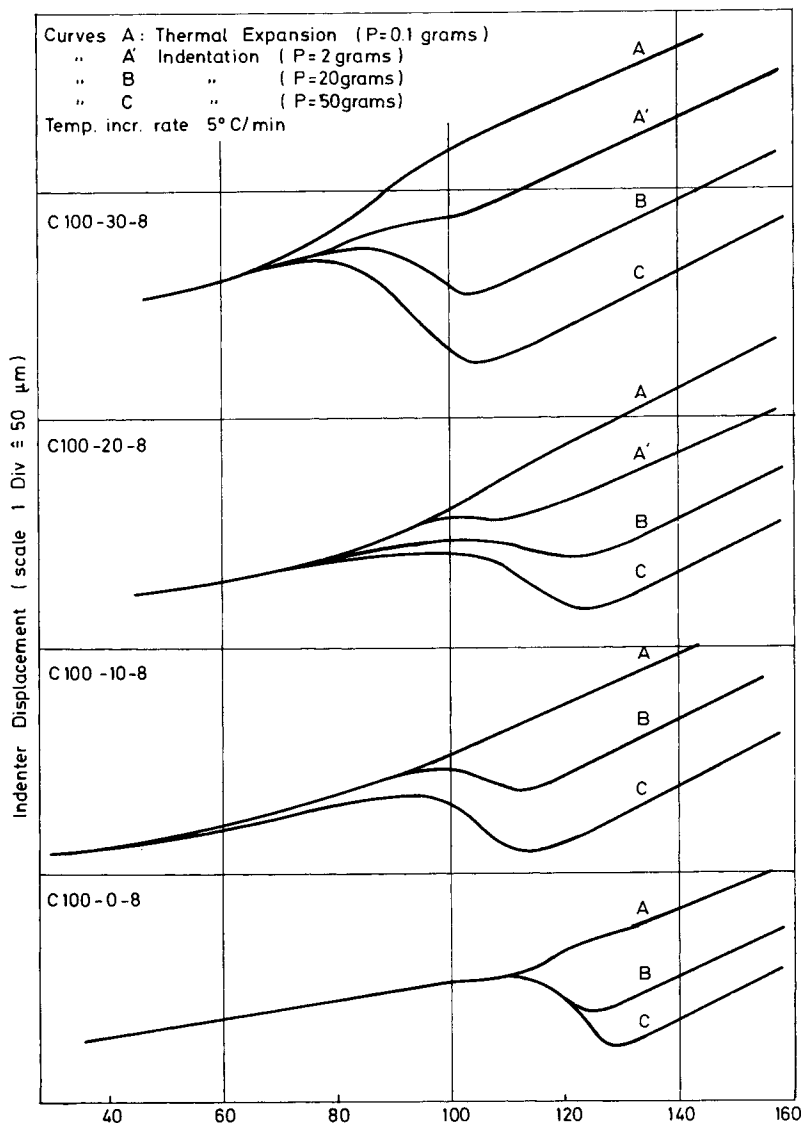
Fig. 3. Indentation curves for various loads and thermal expansion curve with continuously varying temperature for each material.

dentation was recorded, being, in other words, the elastic component of indentation; while in the sequence, normal creep behavior was exhibited.

The elastic component of indentation is presented in Figure 1. In Figure 1(a), the component is plotted against plasticizer percentage and for various temperature levels, while in Figure 1(b), it is presented as function of temperature for various amounts of plasticizer. With increasing temperature or plasticizer percentage, the elastic component increases rapidly, the effect of the plasticizer being more intense than the effect of temperature.

The time-dependent components of indentation at various temperature levels for each particular material are presented in Figures 2(a)–2(g) plotted on a
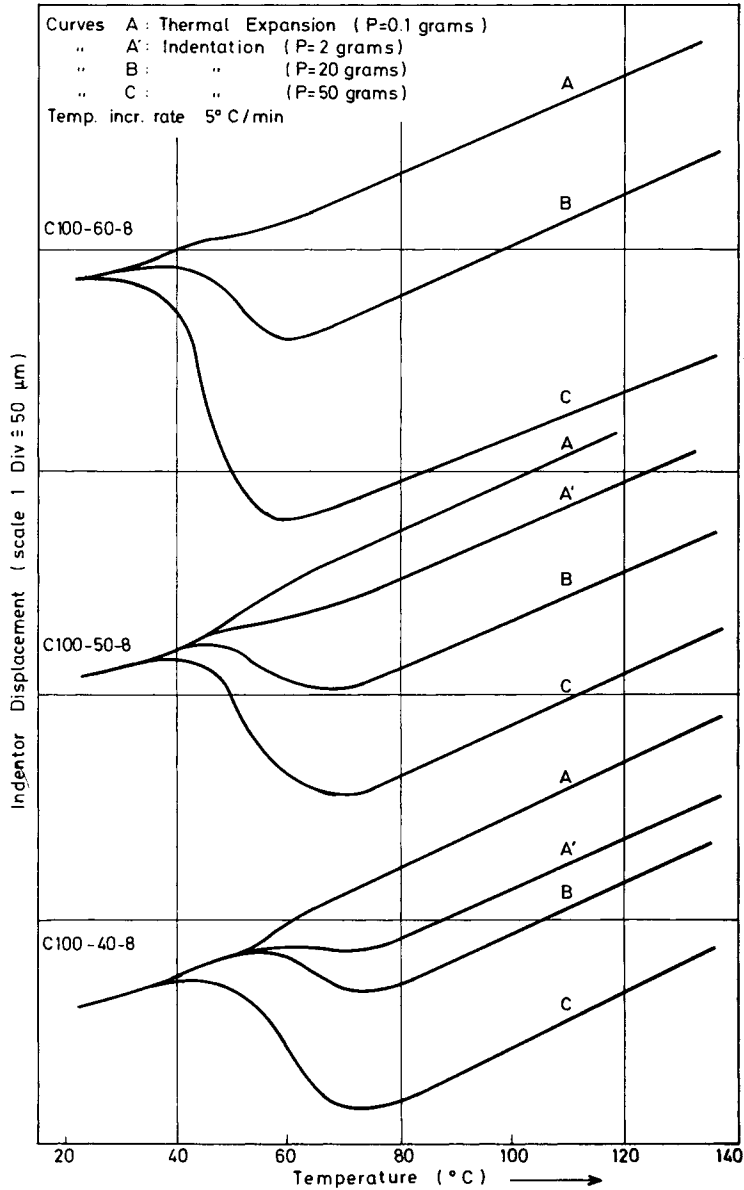
Curves A : Thermal Expansion (P=0.1 grams)
„ A′: Indentation (P= 2 grams)
„ B : „ (P=20 grams)
„ C : „ (P=50 grams)
Temp. incr. rate 5° C / min

Fig. 3. (Continued from previous page)

logarithmic time scale. The individual curves for each material have the same form as the respective curves derived from creep tests. At low temperatures and/or low degrees of plastification, the materials exhibit quasi-elastic behavior, i.e., hardly any time-dependent indentation occurs. Within the transition zone and, in particular, at the glass transition temperature T_g, the time dependence reaches a maximum, while it rapidly decreases when the material enters its rubbery state until it practically vanishes and the elastic component acquires its maximum.

The form of the above curves may give rise to thoughts that a time–temperature superposition could be possible and that master curves of indentation over a wide range of time could be constructed. However, although the present materials are usually considered as typically linear, it is obvious that due to the complexity of the phenomenon, no such attempt should be undertaken without careful consideration.

Varying Temperature Tests

The test piece is loaded at ambient temperature, and subsequently the temperature is increased at constant rate (5°C/min in the present case). Indentation is then recorded as function of temperature. However, it is obvious that no pure indentation is recorded, as the test piece with increasing temperature, exhibits steadily thermal expansion which should be algebraically subtracted from the indentation values recorded. For each individual material, indentation tests with 20- and 50-g loads and in some cases with 2-g loads, too, were carried out, as well as separate thermal expansion measurements. These were performed with the special large-area, flat-ended quartz tip of the du Pont 941 thermomechanical analyzer, under the same temperature rate (5°C/min) and a load of 0.1 g. The recordings for each particular material were brought on the same scale, as it is presented in Figure 3, where curves A correspond to thermal expansion (load 0.1 g) and curves A', B, and C correspond to indentation with loads of 2, 20, and 50 g, respectively. All four curves practically coincide in the first portion of the glassy region of the materials, where, under the small loads applied, very small indentations occur and, in any case, cannot be distinguished, since they are counterbalanced by thermal expansion. However, as the curves approach the transition zone, they separate and follow individual paths. Upon entering the rubbery region, all the curves become straight lines running in parallel.

The temperatures at which curves for all materials respectively acquire their maximum and minimum values usually differ by a nearly constant amount of about 16°C. The maximum slope for each curve occurs between the respective maximum and minimum and actually corresponds to the glass transition temperature.

As already stated, by subtracting thermal expansions from the indentation recordings, the pure indentation can be derived. These results appear in the plots of Figure 4, where the difference in the displacement of the tip of the indentation probe, which corresponds to pure indentation, is plotted against temperature for two different loads. Again, the form of the resulting curves reminds one of the possibility of constructing master curves by time–temperature superposition.

From the thermal expansion curves, the following data have also been derived: (a) The glass transition temperature T_g, which is presented in Figure 5 plotted against plasticizer percentage; T_g decreases with increasing amount of plasticizer linearly up to 40 phr and at a reduced rate thereafter. (b) Thermal expansion coefficients a_1, corresponding to temperatures T lower than the glass transition temperature T_g, and a_2, corresponding to temperatures higher than T_g. As one may conclude from the plots of Figure 3, a_1 is a weak function of temperature and can be considered as approximately constant. On the contrary, a_2 is totally independent of temperature. Both quantities are presented in Figure 6 plotted

against amount of plasticizer. The latter appears to have a dramatic effect on a_1, at least up to 40 phr, which decreases at higher amounts. On the other hand, a_2 is very slightly affected in a linear manner.

Before comparing the present results with existing theoretical predictions, one should comment on their inadequacy of completely explaining the complex phenomena involved. In the glassy region, as already mentioned, indentation was in most cases very small to be considered. In the transition zone, the viscoelastic behavior can hardly be theoretically treated, in particular as friction also interferes. In the rubbery region, things are much more favorable, and, as stated in the introduction, simple expressions experimentally verified have been derived on several occasions.

The present results appear to be in good agreement with the theory developed by Joppling and Pitts[14] according to the formula
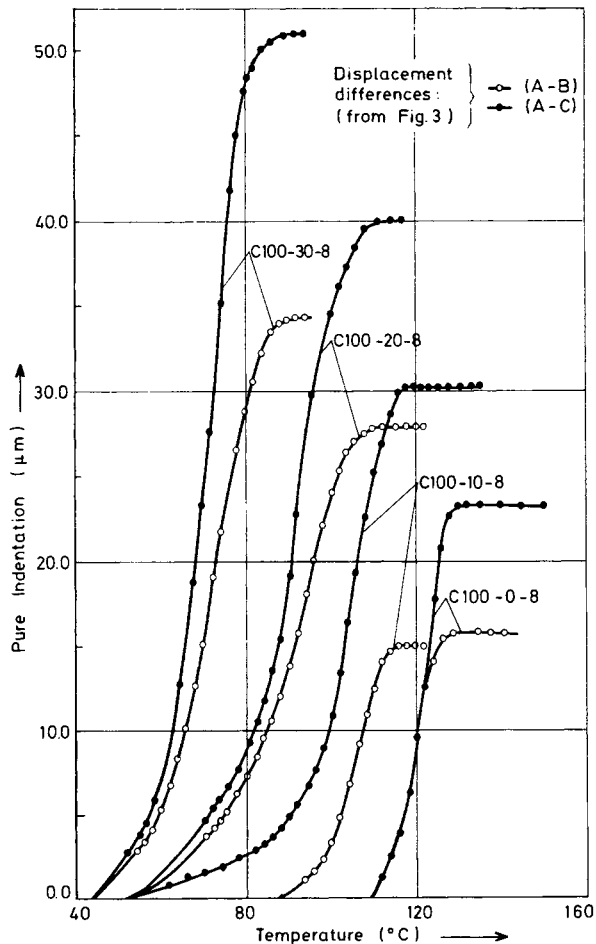
$$P = \frac{3\pi a r_0^4 G}{2z_0^3}$$

Fig. 4. Pure indentation variation with temperature for each material at different loads.
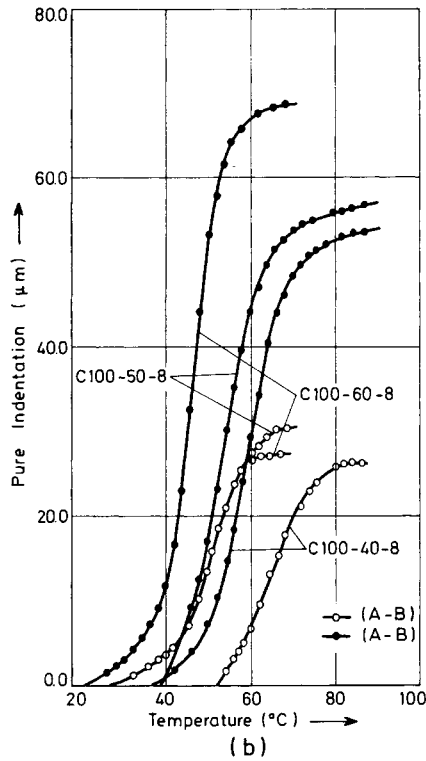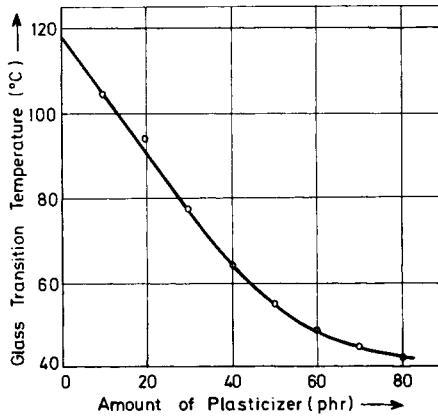
Fig. 4. (Continued from previous page.)

Fig. 5. Effect of plasticizer on glass transition temperature.

which is valid when there is no slip between the indenter and the test piece surfaces. This condition appears to be fulfilled, as the quartz probe under load adheres to the surface of the softened polymer at elevated temperature. In the above expression, P is the load in grams, a is depth of indentation, r_0 is the radius of the cylindrical indenter, G is the shear modulus of the material, and z_0 is the thickness of the test piece. To verify the present results by means of this formula,
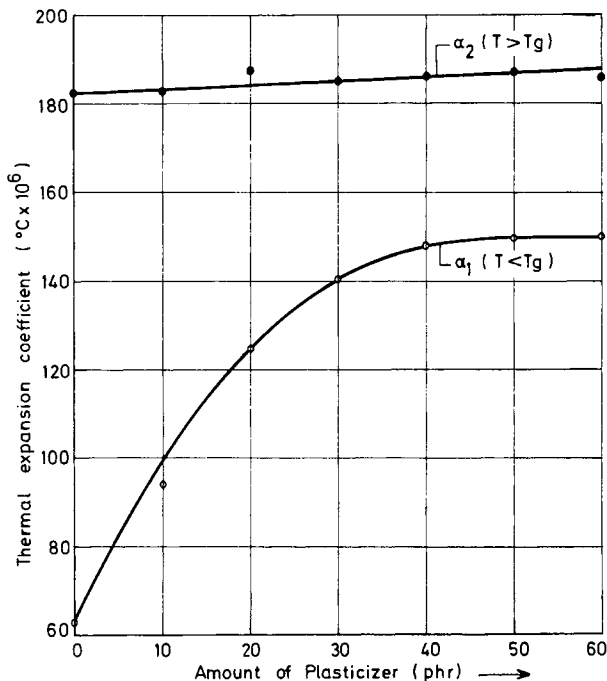
Fig. 6. Effect of plasticizer on thermal expansion coefficients.

measured values of the viscoelastic functions obtained by Theocaris[1,2] from creep experiments were used, and respective "theoretical curves" were constructed.

Indentation in the rubbery region, which is, as stated, purely elastic, is presented in Figure 7(a) plotted against plasticizer percentage. Theory and experiment appear to be in good agreement.

As an additional check, a "theoretical curve" was derived based on the instantaneous moduli, i.e., at time $t = 0$, at the glass transition temperature of each individual material. These values were compared with the elastic or instantaneous indentation occurring under the conditions of the present experiments. Again, a fair agreement between the two sets of values exists. It is worth noting that this "elastic indentation component" is small and does not depend on the amount of plasticizer [Fig. 7(b)].

CONCLUSIONS

Indentation studies were conducted on a series of plasticized epoxy polymers derived from a basic prepolymer with various degrees of plastification over a wide range of temperatures. The work was carried out by means of a thermomechanical analyzer with a cylindrical, flat-ended quartz probe. Two sets of experiments were performed: isothermal experiments, by which indentation was recorded as function of time at various levels of constant temperature; and experiments with varying temperature at constant rate. Various loads were also used. In addition, thermal expansion was recorded under the latter conditions so that pure indentation could be assessed by subtraction.

Under constant load and temperature, the materials practically exhibit creep behavior of the same form as with tensile loading. The different regions of the
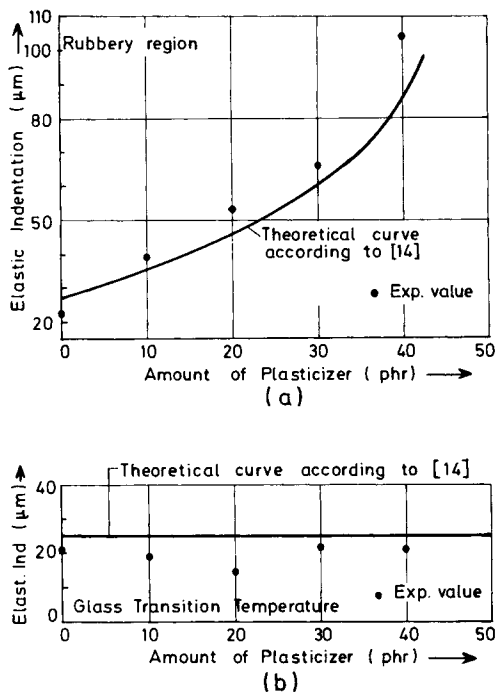
Fig. 7. Elastic or instantaneous indentation component as function of plasticizer percentage compared with theoretical predictions (a) in the rubbery region, and (b) in the transition zone.

state of the material are clearly distinguished, namely, the glassy region, the transition zone, and the rubbery region, according to temperature and amount of plasticizer. The form of the resulting curves appears to be convenient for the application of time–temperature superposition principle, which, however, should not be undertaken without careful consideration. As expected, the material responds quasi-elastically in the glassy region as well as in the rubbery region. In the transition zone, there is a small elastic or instantaneous component of indentation which is independent of the amount of plasticizer.

Under constant load and varying temperature, the material undergoes both thermal expansion and indentation, practically counterbalancing each other in the glassy region, but becoming distinct from each other upon entering the transition zone. Pure indentation curves were obtained plotted against temperature. Accurate determination of glass transition temperature T_g and thermal expansion coefficients was obtained for each particular material. T_g decreases linearly with increasing plasticizer percentage up to 40 phr, thereafter at a reduced rate. The thermal expansion coefficient a_1 at $T < T_g$ is strongly dependent on plasticizer percentage, while a_2, i.e., at $T > T_g$, only slightly depends on the latter.

Elastic or instantaneous indentation components were found in satisfactory agreement with theoretical predictions when certain fundamental conditions were fulfilled.

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