Compression Creep Behavior of a Highly Crosslinked Plasticized Polyester System

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Synopsis

The influence of plasticizer addition on behavior of highly crosslinked unsaturated polyester–styrene systems was investigated by measurement of their compression creep and creep recovery at different temperatures.   The correlation between the observed behavior of the investigated polymeric systems and their structures was explained by assuming the presence of supermolecular structures which change in the applied field of stress at different temperatures.   In a wide temperature range the plasticizer addition shows a similar effect to that of temperature increase on creep recovery of the investigated polymers.

INTRODUCTION

Much work has been done in order to investigate the influence of plasticizers on mechanical properties of linear and slightly crosslinked polymers,[1,2,3] but the correlation between the plasticizer addition and properties of preswollen polymer networks was studied only to a limited extent.[4–7] Recently a study of time dependence of tensile creep recovery in crosslinked epoxy resins was reported.[8]

In the present work the influence of plasticizer addition on behavior of highly crosslinked preswollen polymers was investigated by measurement of creep and creep recovery of the polymeric systems at different temperatures.   The presence of plasticizers during polymerization (preswelling) affects the structure of the polymers and consequently their rheological properties primarily owing to the influence of the plasticizer on the degree of crosslinking and to the dilution effects.

The materials used in this work were: Laminac 4116, a solution of about 70% of an unsaturated polyester of the maleic type in styrene, product of American Cyanamid Co., (average molecular weight of the polyester about 2000); Lupersol DDM, a 60% solution of methyl ethyl ketone peroxides and hydroperoxides in dimethyl phthalate, product of Wallace & Tiernan Inc.; and dioctyl phthalate (DOP), a product of Fluka G.M.B.H.

EXPERIMENTAL PROCEDURE

Samples of Laminac 4116 mixed with amounts of DOP ranging from 0 to 20 wt-% were polymerized by addition of 0.5% Lupersol DDM (calculated
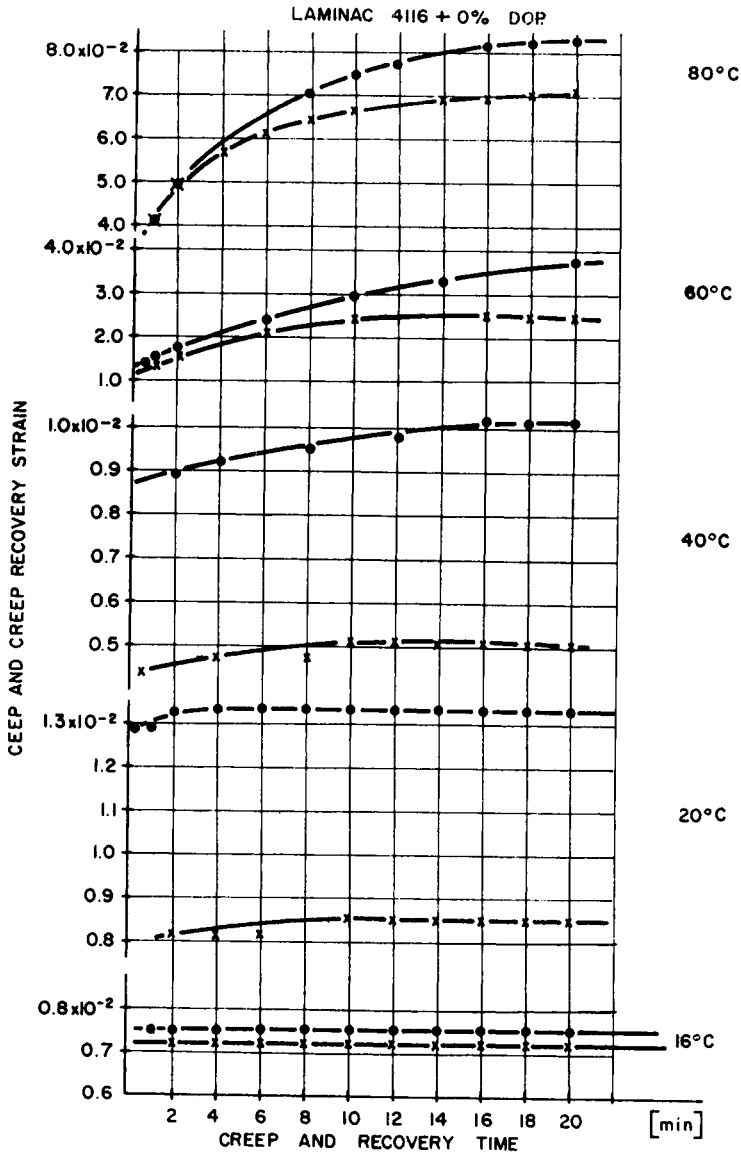
Fig. 1. Creep and creep recovery strain vs. time curves for unplasticized Laminac 4116.

on the basis of 0.5% Laminac) and heating for 3 hr at 60°C and for additional 3 hr at 100°C. The polymerization took place in aluminum Teflon-coated molds and test samples in the shape of cylinders (Φ10 mm × 8 mm) were prepared by machining of the polymerized materials. The test pieces were compressed between two parallel plates by application of a constant load (25 kg) in a modified Haake consistometer. Creep and creep recovery
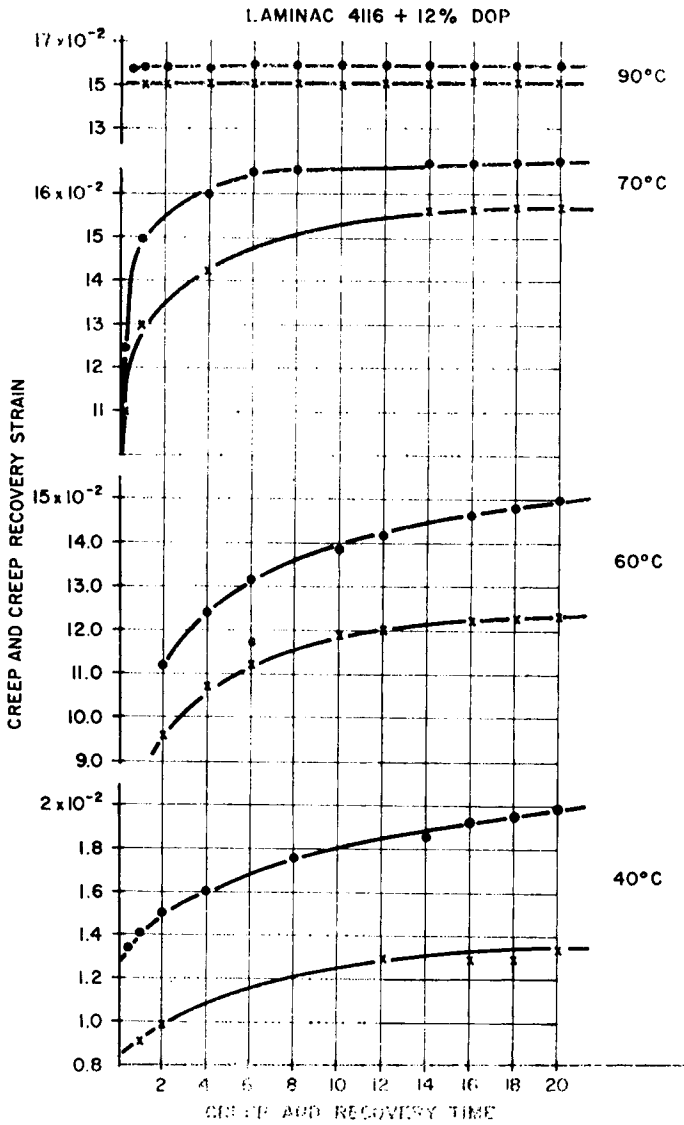
Fig. 2.   Creep and creep recovery strain vs. time curves for Laminac 4116 with 12%
DOP.

strains were measured simultaneously by use of a dial gauge and a differential linear transformer (LVDT)–Dytronic system.   Deformations of 10^{-3} mm were measured and the LVDT output was recorded.   The consistometer was thermostated with an accuracy of $\pm 0.2°C$.   Compression was applied for 20 min, then the load was removed instantaneously, and creep recovery was measured for another 20 min.   The load application and
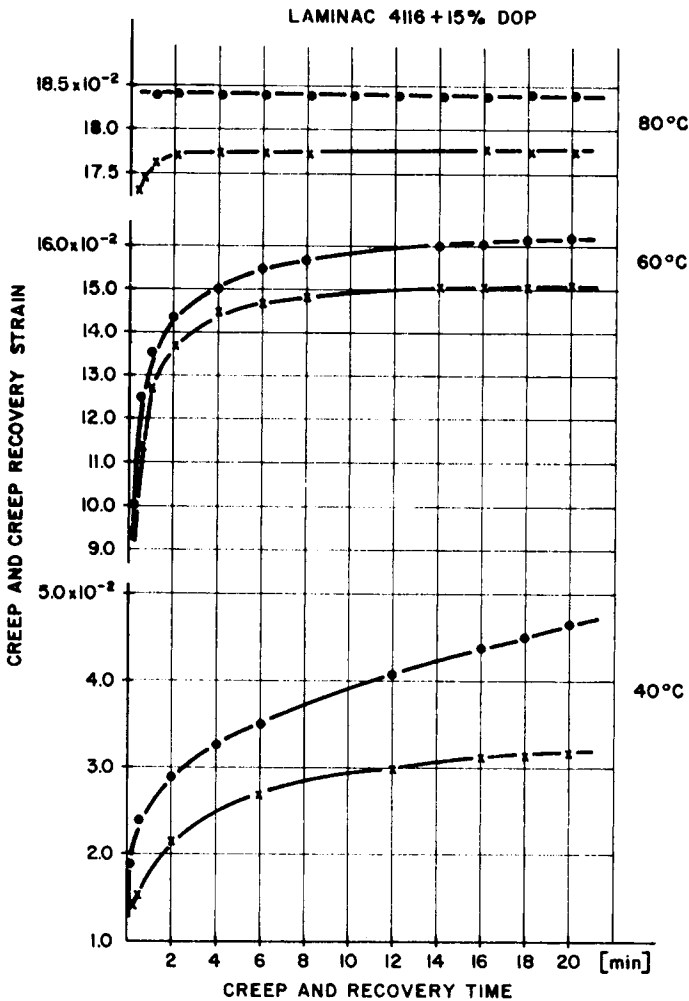
Fig. 3. Creep and creep recovery strain vs. time curves for Laminac 4116 with 15% DOP.

removal were done carefully in order to diminish inertia effects and recording of data was started 30 sec after the initiation of the creep and recovery experiments.

RESULTS

The average network chain molecular weight of the investigated polymers calculated from swelling measurements, according to the Cluff, Gladding, and Pariser method,[9] was 650–700. Some of the experimental results are shown in Figures 1 to 4, in the form of plots of creep and creep recovery strain versus time. In order to obtain a clear base for comparison of
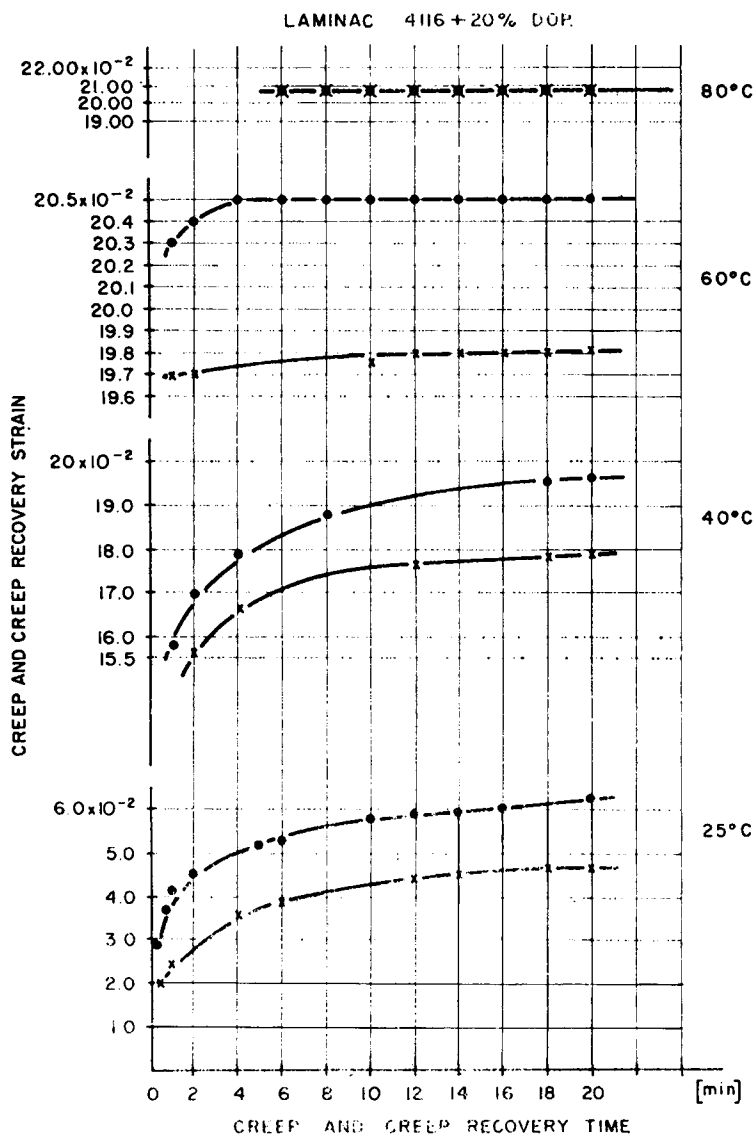
Fig. 4. Creep and creep recovery strain vs. time curves for Laminac 4116 with 20% DOP.

results, the creep recovery curves are shifted to $t = 0$, although the real time of experiment is $t_{c(20)} + t_r$ when $t_{c(20)}$ is the final time of creep loading (20 min) and t_r is the recovery time from the moment of load release. When values derived from subtraction of creep recovery strain from creep data are plotted against time, in most cases straight lines are obtained (Fig. 5). These lines are parallel to the time coordinate for low and high tempera-
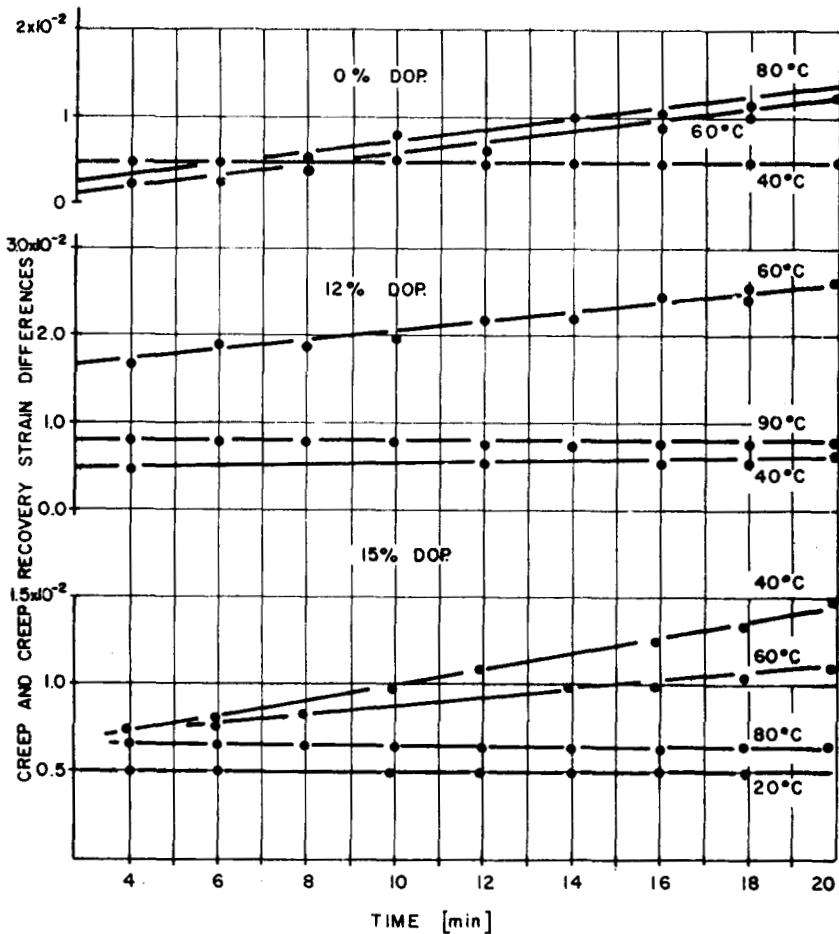
Fig. 5. Strain differences between creep and creep recovery vs. time curves for Laminac 4116–DOP systems.

tures, while for intermediate temperatures lines with different slopes were obtained.

Plots of the logarithms of creep recovery per cent, log $[1 - (\epsilon_{r(20)}/\epsilon_{c(20)})]$ $\times$ 100, 20 min after load release versus temperature are shown in Figure 6, where ϵ_c and ϵ_r are creep and creep recovery strains, respectively, measured as $\Delta l/l_0$. In the general form of the curves, three linear sectors with a clear minimum can be distinguished.

The regions of different rheological behavior of the investigated polymers obtained from measurements of their 10-sec compression deformation versus temperature under constant load (10 kg) at a constant rate of temperature increase of 1°C/min are shown in Figure 7. It can be seen that the minimum appearing in Figure 6 represents the behavior of the polymers in the glassy region. From intersections of slopes characteristic for the
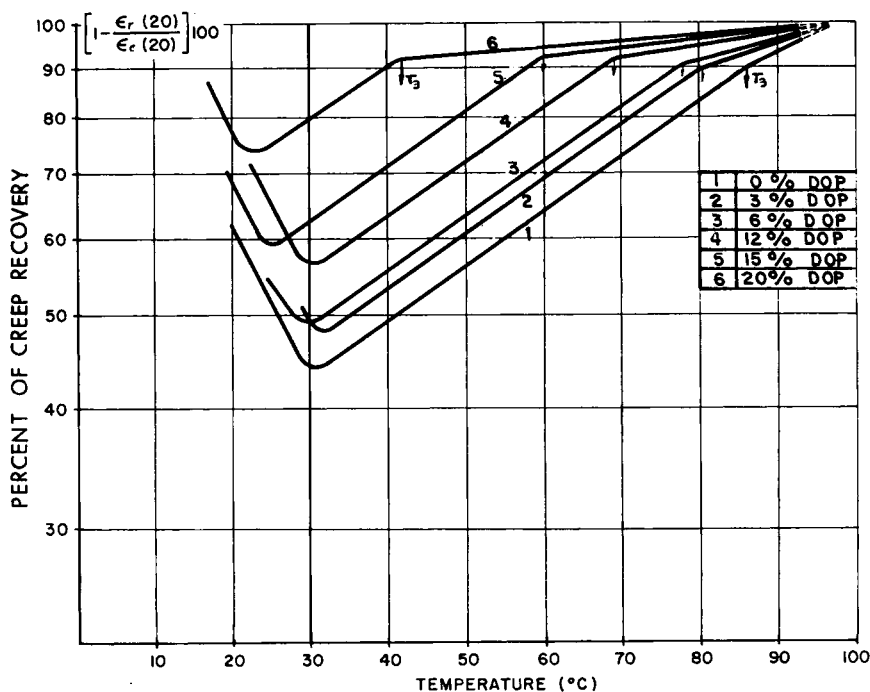
Fig. 6. Logarithms of creep recovery % vs. temperature curves for Laminac 4116–DOP systems.

glassy and transition regions in thermorheograms shown in Figure 7, temperatures T_g' close to the glass transition temperature of the polymers are obtained; they are listed in Table I together with the temperatures of the inflection points T_i on the part of the curve representing the transition region. Values of T_g' when plotted versus weight percentage of plasticizer show, with the exception of the last one (for 20% DOP), a linear relation (Fig. 8).

TABLE I

Glass Transition and Inflection Temperatures
(T_g', T_i) Determined from Thermorheograms Obtained in 10-Sec
Compression Experiments for Laminac 4116–DOP Systems

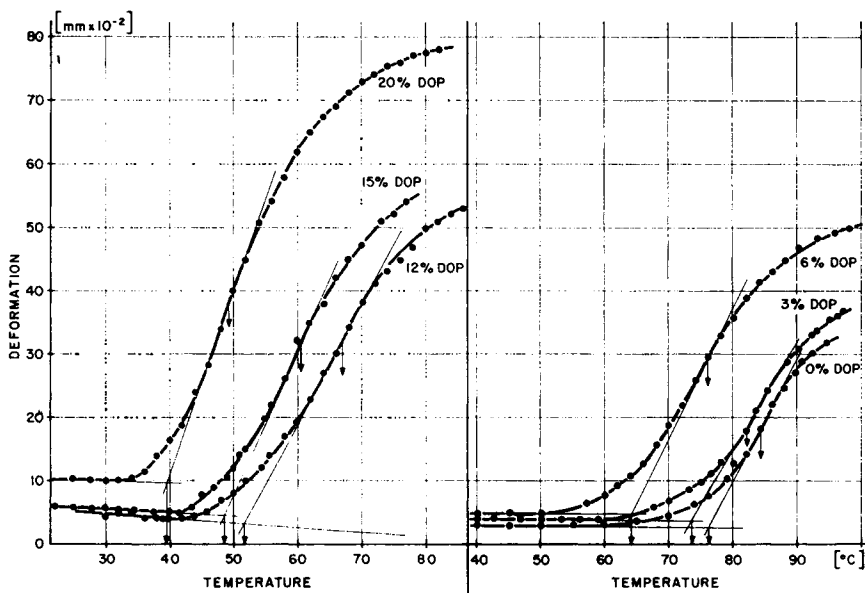| % Plasticizer	T_g', °C	T_i, °C	T_3,[a] °C
0	77	85	86
3	71	82	81
6	64	76	77
12	52	67	69
15	47	60	59
20	40	49	42

[a] From Figure 6.

Fig. 7.   10-Sec compression deformation vs. temperature curves for Laminac 4116–DOP systems.

According to experimental results, the investigated polymers have two quasiequilibrium zones: one in the low glassy and the second in the rubbery plateau region. In the first region, small elastic deformations (tenths of per cent) and in the second one, deformations of a few per cents of highly elastic nature were almost completely recoverable.

DISCUSSION

In order to correlate the structure of the investigated polymers with their behavior in the described 20-min compression creep and 20-min creep recovery experiment, an explanation assuming the presence of supermolecular structures in the investigated networks is suggested. Due to polar carboxylic and hydroxylic groups in the polymer networks built by chemical crosslinking, the chains are also held together by secondary forces of different strength and form randomly distributed supermolecular structures of thixotropic nature. Application of compression forces induces two effects: (a) orientation of the supermolecular structures; and (b) destruction of existing secondary bonds that resist orientation and creation of new secondary bonds and structures. Both effects were found in the polyester system before polymerization[10] and are assumed to be present also in the cured state.

At low temperatures in the glassy state, small deformations are created by the applied stress, the amount of orientation and changes in the basic structure is negligible, and almost complete recovery occurs at the end of
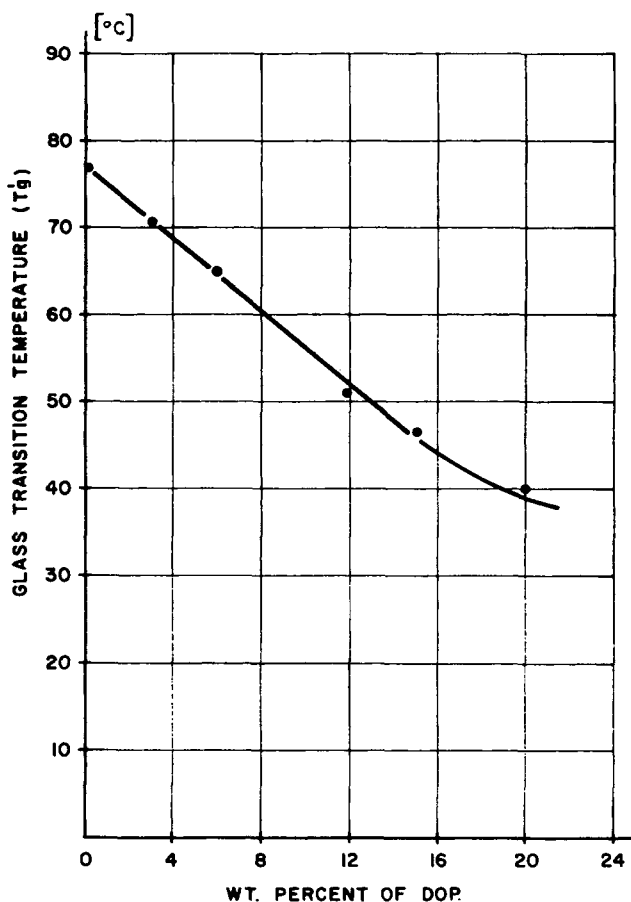
Fig. 8. Glass transition temperature T'_g vs. wt-% curves of plasticizer in Laminac 4116–DOP systems.

the recovery period (20 min after stress removal). With increasing temperatures, due to change of location of small chain segments caused by stress redistribution inside the sample, orientation and changes in supermolecular structures take place. The amount of chain segments involved in stress redistribution grows with temperature and the process of creep recovery becomes more time consuming until a minimum in the creep recovery percentage is reached for equal periods of recovery at the same loading conditions. Up to this temperature, the deformations due to creep and recovery were very small and our results in this region are of qualitative character only. But the general trend in the behavior of the investigated systems is clear: full recovery was not obtained even after a rest time of two weeks. At higher temperatures than the one characteristic for the lowest percentage of creep recovery, but still in the glassy state, the compressed material undergoes growing deformations; the rate of creep re-

covery increases, but no equilibrium was reached during the time of stress application (20 min). It is important to mention that this type of deformation, highly thermocoverable due to the fact that the polymer is cross-linked, is different in its nature from the true plastic deformation. The increasing rate of creep recovery is probably caused by the weakening of secondary bonds involved in formation of supermolecular structures. Close to the glass transition temperatures, larger segments of the network defreeze and introduce their highly elastic contribution. The identical temperature coefficient of creep recovery in both plasticized and non-plasticized polymers, as seen in the second part of curves in Figure 6, below and close to the glass transition, can be explained by assuming the occurrence of identical physical processes in the investigated systems. Secondary structures are formed and broken down and the influence of the plasticizer is similar to that of temperature. The per cent of creep recovery characteristic for our experiment in this region can be defined by

$$R = [36.7 + P] \cdot 2.1 \times 10^{-4} \cdot e^{1.33 \times 10^{-2} T} \tag{1}$$

where T is the temperature in °K and P is the wt-% of DOP in the polymer. By application of eq. (1), the behavior of additional polymeric systems with the same basic ingredients and in the same conditions of loading can be predicted on the base of even one experiment with the plasticized or unplasticized polymer. Equation (1) can also be expressed in a slightly different form when P is replaced by its value calculated from the T_g vs. P relation (Fig. 8):

$$R = \left[36.7 + \frac{350 - T_g}{2.08}\right] \cdot 2.1 \times 10^{-4} \cdot e^{1.33 \times 10^{-2} T} \tag{2}$$

Parallel shifting of the curves shown in Figure 6 by values of $[36.7 + P] \cdot 2.1 \times 10^{-4}$ along the temperature coordinate gave satisfactory results for DOP percentages lower than 20.

The growing, highly elastic contribution of the network chains with temperature increase, very evident in the last part of the curves in Figure 6, enables the systems to reach a creep equilibrium and an almost complete recovery in the conditions of the experiment. The decrease of the temperature coefficient of creep recovery expressed in percentages with increasing plasticizer amounts in the systems can be attributed to differences in network structures formed during polymerization processes in the presence of different amounts of plasticizer inside the network. The last factor is probably enhancing the creation of secondary rheopectic structures up to a certain limit and causes the decrease in the rate of creep recovery. The prevailing influence of rheopectic-type structures in this temperature region can be explained in the following way: up to the temperature T_3, which is identical with the transition temperature T_i, most of the molecular structures are of the globular type, thixotropic in their nature. With increasing temperatures, the dimensions of those structural units decrease until most of them reach in the vicinity of T_i the size of M_c. Application of
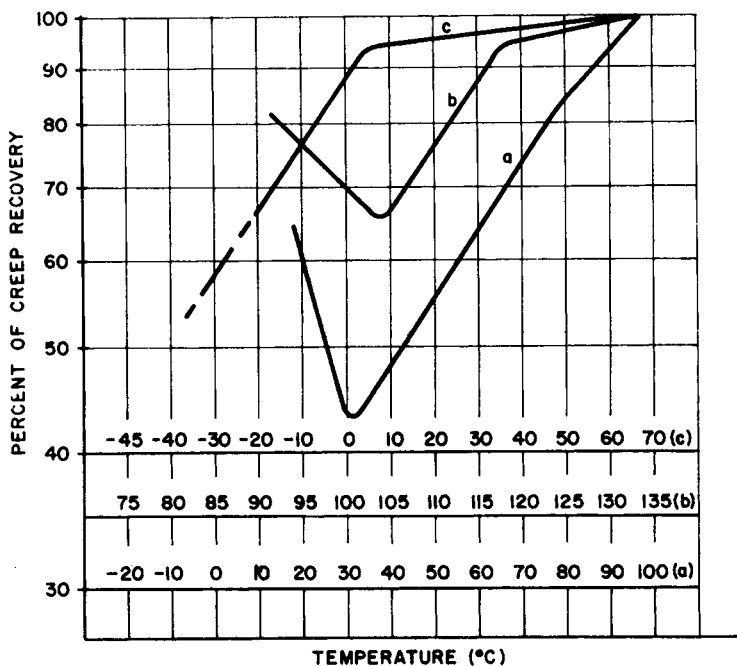
Fig. 9. Logarithms of % creep recovery vs. temperature curves: (a) unplasticized Laminac 4116; Epon 828–DETA; (c) a flexible styrenated polyester.

load to such a system creates, in the field of stress, oriented structures of fibrillar type. These new structures, which are rheopectic in nature, are stronger than the former ones and are responsible for the lowering of the temperature coefficient of creep recovery. The same explanation of super-molecular structure changes from globular to fibrillar type under the influence of temperature and stress was used by Gull and co-workers in a different case.[11] The presence of fibrillar structures fulfills the condition mentioned by Weltmann[12]—anizodiametricity—to obtain rheopectic structures. The values of $[1 - (\epsilon_{r(20)}/\epsilon_{c(20)})] \times 100$ at the temperature T_3 are very close for all investigated polymers: 0.90–0.92. It should be mentioned that swelling of the sample before and after the creep experiment showed no difference in the crosslink density of the polymer. It was shown in an earlier work on a plasticized epoxy system that even when deformations up to 5–7% were imposed on the polymers in their glassy and transition regions, no destruction of chemical networks occurred.[13]

This creep recovery behavior of the Laminac 4116–DOP system is also typical for some other highly crosslinked polymers, like Epon 828 cross-linked with 8% diethylene triamine (DETA) or a flexible-type styrenated polyester prepared and tested for comparative reasons (Fig. 9).

References

1. J. Mellan, *The Behavior of Plasticizers*, Pergamon Press, Ditchling, Sussex England 1961.

2. W. Aiken, T. Alfrey, Jr., A. Jansen, and H. Mark, *J. Polym. Sci.*, **2**, 178 (1947).

3. T. Alfrey, Jr., N. Wiederhorn, R. Stein, and A. V. Tobolsky, *I.E.C.*, **41**, 701 (1949).

4. M. Shen and A. V. Tobolsky, *J. Poly. Sci.*, **A-2**, 2513 (1964).

5. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw Hill, New York, 1967, Chapters 15–16.

6. J. C. Rosso and B. Perzos, *C. R. Acad. Sci.* (Paris), **260**, 5550 (1965).

7. D. Katz and A. V. Tobolsky, *J. Polym. Sci.*, **A-2**, 1587 (1964).

8. P. S. Theocaris, *Rheol. Act B*, **6**, 246 (1967).

9. E. F. Cluff, E. K. Gladding, and R. Pariser, *J. Polym. Sci.*, **45**, 341 (1960).

10. I. Steg and D. Katz, *J. Appl. Polym. Sci.*, **9**, 3177 (1965).

11. N. E. Gull, V. A. Kargin, M. R. Riabova, W. G. Kalashnikova, and A. J. Beresteneva, *Vysokomol. Soedin.* **9**, 312 (1967).

12. R. N. Weltmann, *Rheology*, Vol. III, R. F. Eirich, Ed., Academic Press, New York, 1956, p. 216.

13. J. Steg and O. Ishay, *J. Appl. Polym. Sci.*, **11**, 2303 (1967).