

Viscoelastic Properties of Plasticized Polymers

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In the literature there is a paucity of comparative data concerning the viscoelastic properties of plasticized polymers. Why, in particular, are certain polymers used more often in plasticized form than in others?

To obtain some data we selected the polymers polystyrene, polymethyl methacrylate, and polyvinyl chloride, whose T_g values are listed as 100, 105, and 75°C. respectively. In all cases the polymers were plasticized with dioctylphthalate in the proportion, by weight, of 100 parts polymer and 20 parts dioctylphthalate.

From a combination of torsional creep for the high modulus data and stress relaxation in tension for lower modulus data, stress relaxation master curves for these three plasticized polymers were obtained. The primary data for plasticized polyvinyl chloride, reduced to stress relaxation modulus, is shown in Figure 1. The master curves $E_r t/K(T)$, are shown for the three polymers in Figures 2-4. $K(T)$, the characteristic relaxation time at temperature T , is defined as the time required for $E_r(t)$ to attain a value of 10^9 dynes/cm.². T_i is the temperature at which $K(T)$ equals 10 sec. The values of T_i for plasticized polystyrene, polymethyl methacrylate, and polyvinyl chloride are, respectively, 39, 70, and 36°C.

Table I gives the experimental values of $K(T)$ for these polymers at several temperatures. In the immediate vicinity of T_i the data for $K(T)$ fit the following equations:

Polystyrene/DOP:

$$\log K(T)/K(T_i) = -0.178(T - T_i) \quad (1)$$

Polymethyl methacrylate/DOP:

$$\log K(T)/K(T_i) = -0.115(T - T_i) \quad (2)$$

Polyvinyl chloride/DOP:

$$\log K(T)/K(T_i) = -0.135(T - T_i) \quad (3)$$

TABLE I
Characteristic Relaxation Times for Plasticized Polymers

Temp., °C.	$K(T)$
Polyvinyl Chloride	
-62	4.71×10^{14}
-46.5	2.69×10^{12}
-22	4.75×10^9
-13	1.71×10^9
0	2.07×10^7
+10	2.07×10^6
24	1.79×10^4
31.4	2.89×10^3
36	2.19×10^1
43.6	1
55.4	9.56×10^{-3}
70.2	5.20×10^{-4}
82.6	1.64×10^{-5}
93	3.26×10^{-6}
107	2.61×10^{-7}
122.5	3.92×10^{-11}
Polystyrene	
0	6.76×10^6
+7	1.20×10^6
25.5	5.12×10^3
30	1.34×10^1
38.2	1
41	2.51×10^{-1}
44	5.01×10^{-2}
50.2	1.77×10^{-2}
56.3	2.51×10^{-3}
61.0	1.41×10^{-4}
77	3.54×10^{-6}
Polymethyl Methacrylate	
0	7.94×10^9
27	7.94×10^6
45	1.13×10^3
55	1.34×10^2
65	2.81×10^0
69.6	1
72	9.33×10^{-2}
74	5.88×10^{-3}
78	3.31×10^{-3}
87	1.17×10^{-3}
100	6.16×10^{-4}
115	2.34×10^{-6}
125.5	4.89×10^{-7}

By comparison, the value of $K(T)$ in the vicinity of T_i predicted by the WLF equation is:

$$\log K(T)/K(T_i) = -0.338(T - T_i) \quad (4)$$

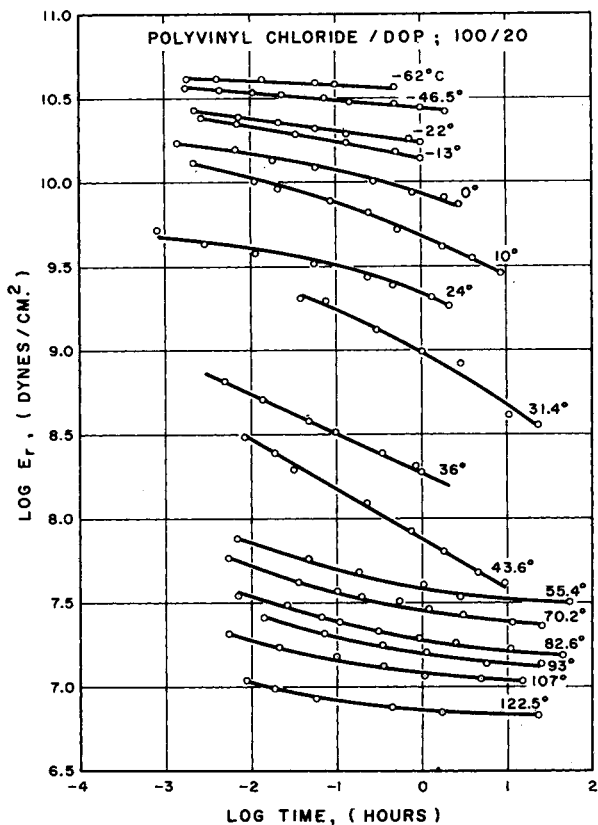


Fig. 1. Primary data reduced to stress relaxation modulus for plasticized polyvinyl chloride.

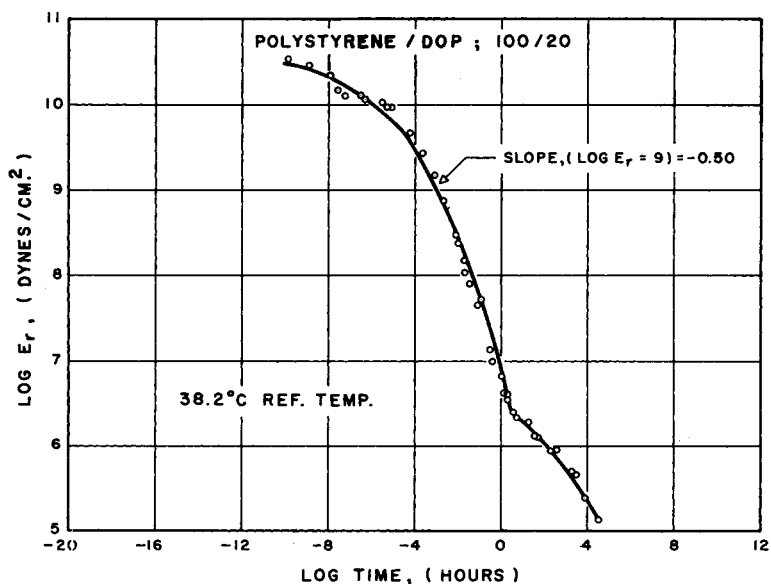


Fig. 2. Master curve of $E_r, t/K(T)$, for plasticized polystyrene.

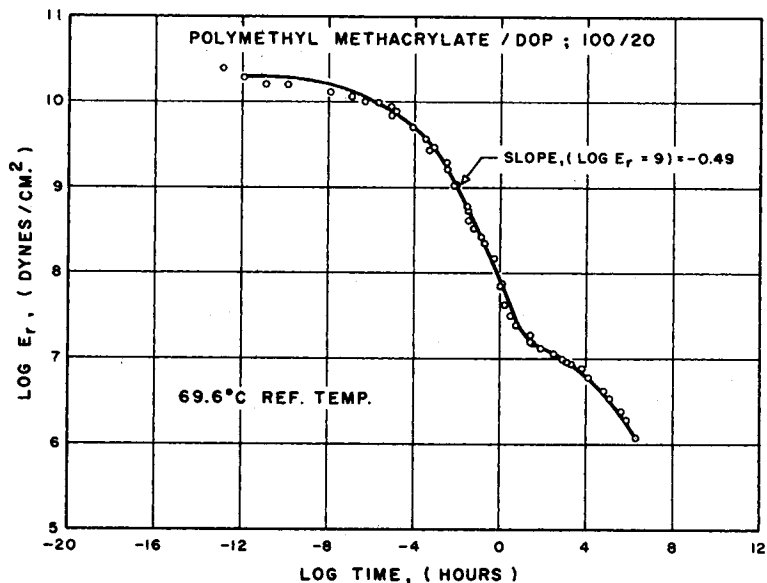


Fig. 3. Master curve of $E_r, t/K(T)$, for plasticized polymethyl methacrylate.

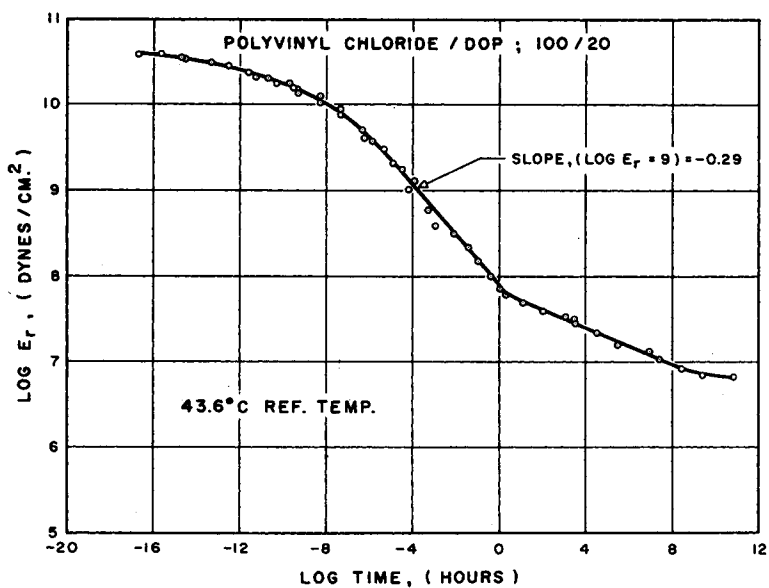


Fig. 4. Master curve of $E_r, t/K(T)$, for plasticized polyvinyl chloride.

Finally, the slope $\log E_r (t/K)$ versus $\log t$ at the point where $E_r (t/K)$ is 10^9 dynes/cm.² is particularly noteworthy. For the plasticized polystyrene and the plasticized polymethyl methacrylate these slopes were essentially equal to the theoretical value of Rouse³ and Bueche,⁴ namely -0.50 . For

the plasticized polyvinyl chloride, the value of the slope is -0.29 (Fig. 4). There is no point in the entire transition region where the slope is any steeper.

An x-ray diagram of this particular plasticized polyvinyl chloride sample (Fig. 4) failed to reveal any evidence of crystallinity, nor is dioctylphthalate regarded as an incompatible plasticizer for polyvinyl chloride. We have, therefore, no certain explanation of the unusually broad master curve shown by plasticized polyvinyl chloride. In previous studies on plasticized polyvinyl chloride we had concluded^{1,2} that it was very slightly (and imperfectly) crystalline, but at that time we had positive x-ray evidence for this and also some evidence from birefringence, in addition to our inferences from mechanical behavior. Perhaps some very borderline crystallinity not revealed by x-ray diagrams is responsible for the unusual viscoelastic behavior of the sample studied here.

Whatever the cause for it may be, we believe that this type of viscoelastic behavior probably is one of the reasons why plasticized polyvinyl chloride compositions are so much more widely used than plasticized compositions of polystyrene or polymethyl methacrylate.

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Synopsis

Stress relaxation master curves were obtained for polystyrene, polymethyl methacrylate, and polyvinyl chloride, all plasticized with dioctylphthalate. The plasticized polyvinyl chloride results were quite different from the others, and this was tentatively ascribed to borderline crystallinity.

Résumé

Des courbes maitresses pour la relaxation de tension ont été obtenues pour trois polymères plastifiés parmi lesquelles le polystyrène, le polyméthacrylate de méthyle et le chlorure de polyvinyle; le plastifiant était le phthalate de dioctyle. Le chlorure de polyvinyle plastifié donnait des résultats légèrement différents des autres. On devait attribuer cela à la cristallinité des arêtes.

Zusammenfassung

Spannungsrelaxations-Einheitskurven wurden für Polystyrol, Polymethylmethacrylat und Polyvinylchlorid, alle mit Dioctylphthalat weichgemacht, erhalten. Die Ergebnisse am weichgemachten Polyvinylchlorid waren von den anderen Ergebnissen recht verschieden, was versuchsweise auf Grenzlinienkristallinität zurückgeführt wird.

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