

Dynamic Mechanical Properties of Poly(vinyl Alkyl Ethers)*

JOGINDER LAL, JAMES E. McGRATH, and KENNETH W. SCOTT,
The Goodyear Tire and Rubber Company, Research Division, Akron, Ohio

Synopsis

The temperature dependence of the dynamic mechanical properties of dicumyl peroxide/sulfur vulcanizates of seven members of the poly(vinyl alkyl ether) series of elastomers has been determined. The relative position of the curves, relating the dynamic resilience to the dynamic modulus of these polymers, was generally in the order of their glass transformation temperatures (T_g). The dynamic mechanical property data on poly(vinyl *n*-pentyl ether) and poly(vinyl 2-ethylhexyl ether), which have the same T_g , fall on a common curve characteristic of the temperature of measurement. The dynamic resilience versus dynamic modulus curves are displaced towards higher dynamic resilience and usually lower dynamic modulus values as the temperature of measurement is increased. Poly(vinyl isobutyl ether) and poly(vinyl ethyl ether) show a larger temperature coefficient of resilience than do the other poly(vinyl alkyl ethers), which also include the *n*-butyl, *n*-hexyl, and *n*-octyl members. Apparently, the T_g is a major factor in correlating the dynamic mechanical behavior of this homologous series of elastomers. The size and shape of the alkyl group appear to be reflected primarily in their effect on the T_g . Poly(vinyl isobutyl ether) was the only member of the series showing any anomalies in dynamic mechanical properties that might be ascribed to structure. Because the dynamic resilience of various poly(vinyl alkyl ether) vulcanizates, possessing the same concentration of chemical crosslinks, correlate better with their degree of polymerization than with their molecular weight it appears that the dynamic resilience depends more on the length of the free chain ends than it does on their mass or volume.

INTRODUCTION

Ferry and co-workers¹ have studied the dynamic properties of five poly(*n*-alkyl methacrylates) and have emphasized the influence of increasing the length of the ester alkyl group on the relaxation spectra of these polymers. Schmieder and Wolf² have determined the glass transformation temperatures of poly(vinyl alkyl ethers) in which the pendant alkyl groups were methyl, ethyl, *n*-propyl, *n*-butyl, isobutyl, and *tert*-butyl by measuring the dynamic shear modulus and logarithmic decrement of unvulcanized polymers at different temperatures. Dynamic properties of vulcanized poly(vinyl alkyl ethers), which are of considerable practical interest, have not been reported in the literature.

We have systematically varied the side chain alkyl group in poly(vinyl alkyl ethers) and evaluated quantitatively the influence of these variations

* Presented at the 11th Canadian High Polymer Forum, Windsor, Ontario, Sept. 7, 1962.

on the dynamic properties of vulcanizates of these polymers. Such an investigation became feasible due to the availability of convenient catalysts for preparing high molecular weight poly(vinyl alkyl ethers)^{3,4} and the development of a suitable curing system for the vulcanization of these saturated polymers.⁵

EXPERIMENTAL

Materials

The poly(vinyl ethyl and isobutyl ethers) were purchased. The remaining polymers were synthesized with the aid of the catalysts listed in Table I. The inherent viscosities of 0.1% solution in benzene at 30°C. and dilatometrically determined glass transformation temperatures, T_g ,⁶ of these polymers are also given in this table. All these polymers were reasonably high molecular weight materials. As the length of the normal alkyl group is increased from ethyl to *n*-butyl, *n*-pentyl, *n*-hexyl, and *n*-octyl, the T_g values of these polymers decrease. Due to the bulky isobutyl group, the T_g of poly(vinyl isobutyl ether) is highest among those listed in this table. It is noteworthy that poly(vinyl *n*-pentyl ether) and poly(vinyl 2-ethylhexyl ether) have identical T_g values.

TABLE I
Polymer Characterization

Polymer	Source or polymerization conditions	Inherent viscosity, dl./g.	Dilatometric T_g , °C. ^a
Poly(vinyl ethyl ether)	Union Carbide Chemical Co.	4.0	-42
Poly(vinyl <i>n</i> -butyl ether)	AHS; 50°C. ^b	4.3	-54
Poly(vinyl isobutyl ether)	Putnam Chemical Co.	4.0	-19
Poly(vinyl <i>n</i> -pentyl ether)	AHS; 30°C. ^b	2.1, 5.2	-66
Poly(vinyl <i>n</i> -hexyl ether)	" "	5.5	-77
Poly(vinyl <i>n</i> -octyl ether)	" "	4.2	-80
Poly(vinyl 2-ethylhexyl ether)	BF ₃ etherate; -78°C.	2.1, 3.2	-66

^a Data of Lal and Trick.⁶

^b AHS = aluminum hexahydrosulfate heptahydrate catalyst.³

Vulcanization

A typical gum vulcanization recipe for curing vinyl alkyl ether polymers is shown in Table II. Different degrees of cure were attained by varying the

TABLE II
Vulcanization Recipe

	Wt. parts, phr
Poly(vinyl alkyl ether)	100
Dicumyl Peroxide, 95% ^a	4
Sulfur	0.5
Cure: 10-80 min./143°C.	

Di-Cup (Hercules Powder Company).

cure time. In compounding the poly(vinyl *n*-pentyl and 2-ethylhexyl ethers) materials of two different inherent viscosities were used in each case. The lower inherent viscosity polymers were milled with 2 phr dicumyl peroxide, 95%, and 0.2 phr sulfur and cured for 20–80 min. at 143°C. The higher inherent viscosity polymers were mixed according to the recipe in Table II.

Measurement of Dynamic Properties

Vulcanized cylindrical samples ($1/2$ in. long, $1/2$ in. diameter) were used for measuring dynamic mechanical properties with the Goodyear forced resonance Vibrotester.⁷ The frequency of the tester was 60 cycles/sec. The samples were subjected to 8% static compression and 2% dynamic longitudinal strain. Measurements were made principally at three different temperatures: 31, 60, and 93°C.

RESULTS AND DISCUSSION

In Figure 1 the dynamic resilience and the dynamic modulus have been plotted as a function of cure time for vulcanizates of the high molecular weight poly(vinyl *n*-pentyl ether). The dynamic resilience has been defined as the ratio of the energy in two successive cycles of free vibration, but is commonly expressed as a percentage. The per cent dynamic resilience is equal to $100 \exp \{-2 \pi \tan \delta\}$, where $\tan \delta$ is the mechanical loss factor. In the range of cure times used, the upper limit of which represents about 2.5 half-lives for the decomposition of dicumyl peroxide,⁸ the dynamic modulus and the dynamic resilience increase with cure time. The data of Figure 1 are consistent with the expectation that the rate-controlling step in the crosslinking of poly(vinyl alkyl ethers) is the rate of decomposition of dicumyl peroxide.

While Figure 1 indicates that the dynamic modulus and resilience of this rubber depend on its degree of crosslinking it also suggests that, at this frequency and temperature of measurement, only a limited range of dynamic modulus and resilience values is permissible, i.e., the dynamic modulus and resilience values may not vary independently of each other as there may be a functional relation between the two. This functional relation may be seen by eliminating the independent variable of cure time from Figure 1 by plotting the dynamic resilience versus the dynamic modulus of samples each at a different degree of cure as in Figure 2. The least crosslinked sample is represented by the point with the lowest dynamic modulus and resilience values. Samples with increasing degrees of crosslinking are located further along the curve at higher dynamic modulus and resilience values. While Figure 2 again indicates that no single dynamic modulus value and no single dynamic resilience value can be considered as characteristic of a rubber crosslinked to an unspecified degree it does indicate that for vulcanizates of a given rubber the dynamic modulus and resilience values are limited to a rather narrow range of permissible values as indicated by the curve of Figure 2. The principal utility of dynamic modulus versus dynamic resilience plots is the graphical convenience they offer in comparing

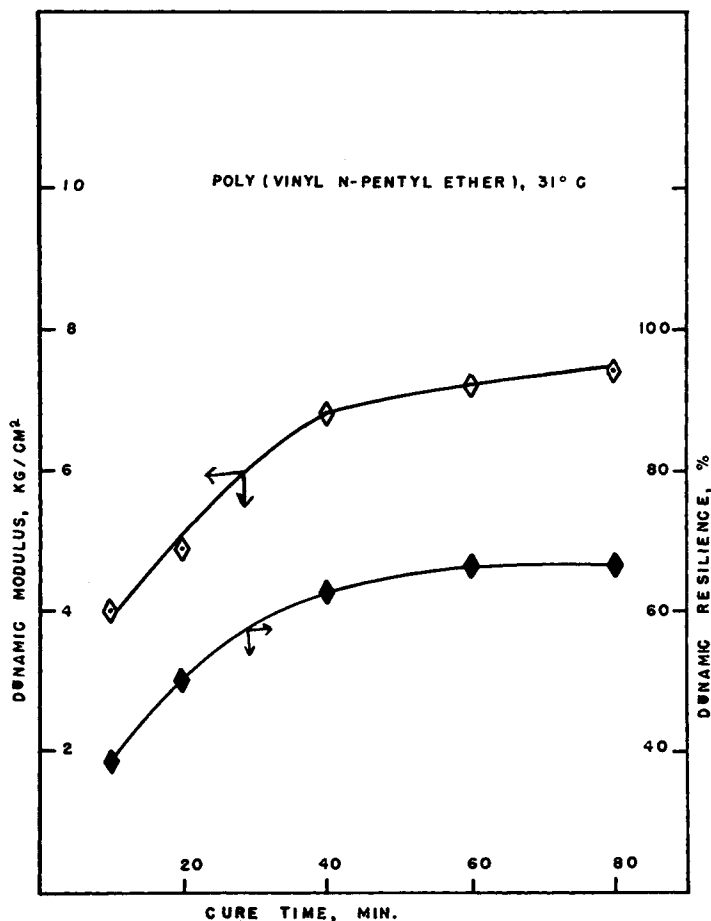


Fig. 1. Dependence of (◆) dynamic resilience and (◇) dynamic modulus of poly(vinyl *n*-pentyl ether) vulcanizates at 31°C. on cure time (at 143°C.).

and categorizing the dynamic mechanical properties of crosslinked rubbers and in suggesting the contribution of molecular weight and crosslinking to dynamic mechanical properties. In this regard these plots may be considered as a modification of the mechanical analog⁹ of Cole-Cole plots which have proved useful in studies of dielectric properties.

In Figure 3 dynamic resilience values at 31°C. are plotted against dynamic moduli for samples of six poly(vinyl alkyl ethers), each at a different degree of cure. Each polymer has its own characteristic locus of points in such a plot and in each case an increase in cure time, i.e., degree of crosslinking, has the effect of moving the data points upward along this characteristic curve. In addition, in the case of poly(vinyl *n*-pentyl ether) and poly(vinyl 2-ethylhexyl ether) the data points fall on a common curve even though for each of these polymers two materials with different molecular weights were used and two different levels of dicumyl peroxide were used in crosslinking the samples. The upward progression of the data points along

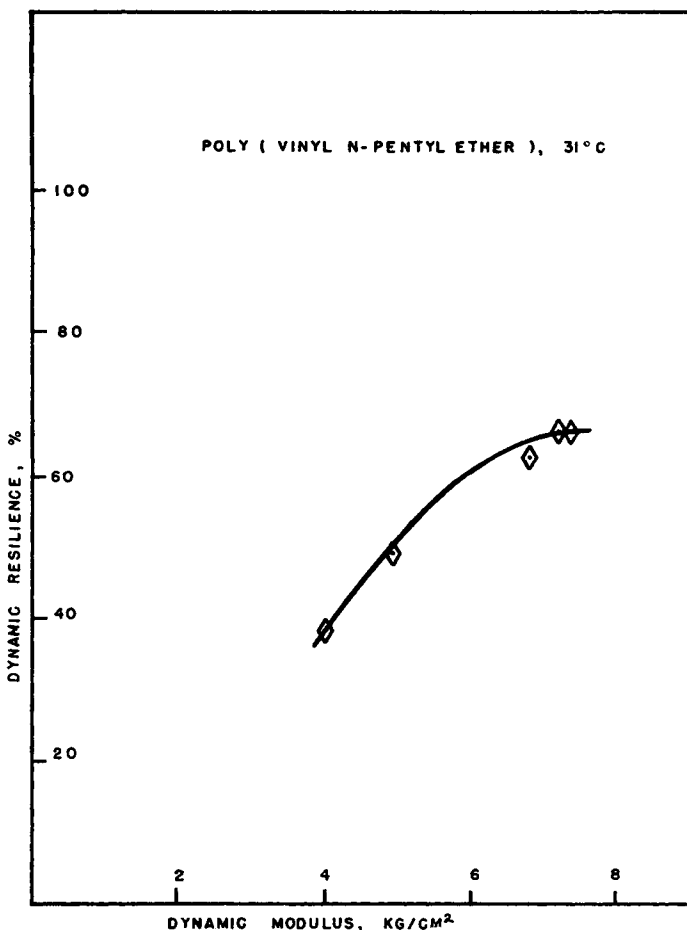


Fig. 2. Relationship between dynamic resilience and dynamic modulus of poly(vinyl *n*-pentyl ether) vulcanizates at 31°C.

the characteristic curve for a polymer with either increasing molecular weight or increasing degree of crosslinking agrees with similar observations made on four diene rubbers.¹⁰

The relative position from left to right of the various curves in Figure 3 is in increasing order of their glass transformation temperatures. As was pointed out earlier, T_g values decrease with increasing length of the *n*-alkyl group from ethyl to *n*-octyl. The data for poly(vinyl *n*-pentyl and 2-ethylhexyl ethers), which have the same T_g , fall practically on a common curve.

In Figures 4 and 5 are shown similar data at 60 and 93°C. and it is important to stress the following features. The curves in Figure 3 at the test temperature of 31°C. maintain their positions relative to each other at these higher test temperatures. However, poly(vinyl isobutyl ether) which would be represented by a point in the lower right corner of Figure 3 shifts to the left of the curve for poly(vinyl ethyl ether) as the test temperature rises.

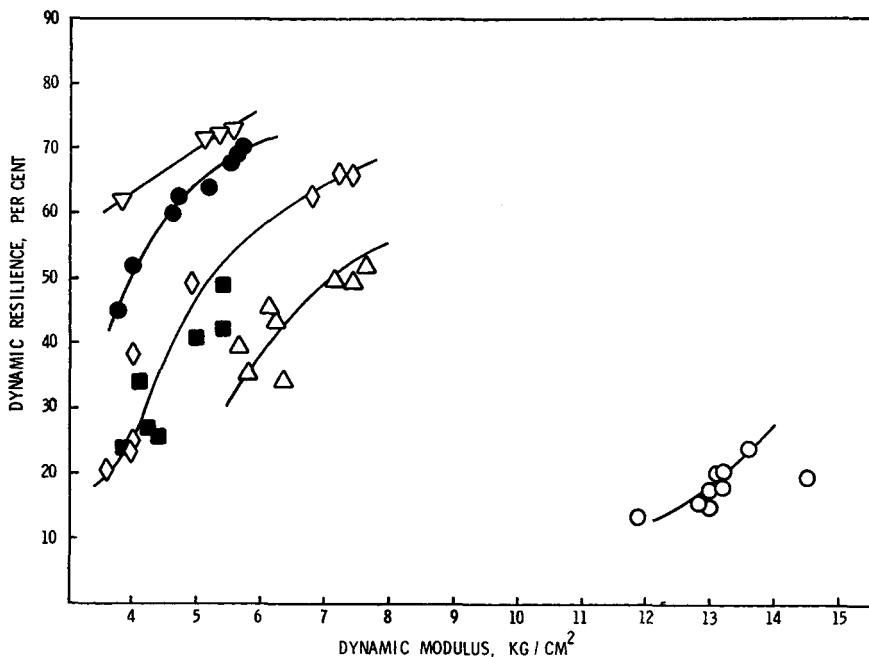


Fig. 3. Relationship between dynamic resilience and dynamic modulus of poly(vinyl alkyl ether) vulcanizates at 31°C., with alkyl groups; (O) ethyl; (Δ) *n*-butyl; (\diamond) *n*-pentyl; (\bullet) *n*-hexyl; (∇) *n*-octyl; (\blacksquare) 2-ethylhexyl.

With the exception of poly(vinyl isobutyl ether) the remaining polymers are still arranged from left to right in increasing order of their T_g values.

In Figures 3-5, it is observed that at a given temperature of measurement the dynamic modulus for each rubber is limited to a relatively small range of values. It is preferable to consider only the 93°C. data in Figure 5 since this temperature is sufficiently above the T_g of each of these rubbers to minimize any of several difficulties that one might expect at temperatures closer to the T_g of a rubber. On the basis of rubber elasticity theory, one expects the dynamic modulus to reflect the contributions of both chemical and physical crosslinks in these rubbery networks. Because the chemistry of crosslinking these poly(vinyl alkyl ethers) should be similar, about the same order of chemical crosslinking should be present in all these rubbers for equal cure times for a given amount of dicumyl peroxide used. Hence, the different dynamic modulus values exhibited by these rubbers primarily represent differences in degrees of physical crosslinking for the rubbers. These differences in physical crosslinking most likely are due to differences in the amount of chain entanglements occurring in these polymers. The generalization that the concentration of chain entanglements, and hence dynamic modulus, decreases as the T_g decreases may be accounted for by at least two approaches. Both approaches are probably dependent on free volume considerations.

The first approach is a strictly experimental one and might be called the

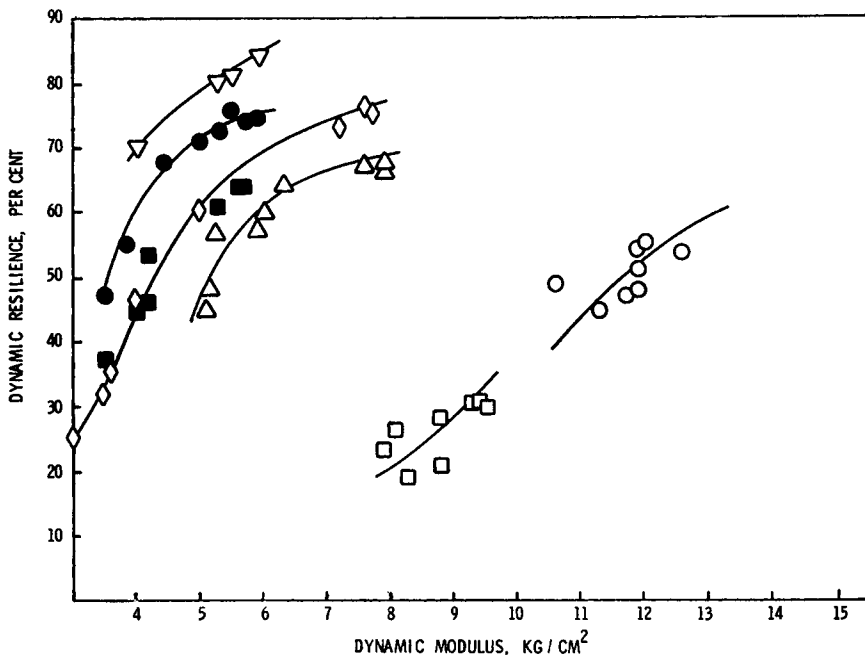


Fig. 4. Relationship between dynamic resilience and dynamic modulus of poly(vinyl alkyl ether) vulcanizates at 60°C.: (O) ethyl; (Δ) *n*-butyl; (\square) isobutyl; (\diamond) *n*-pentyl; (\bullet) *n*-hexyl; (∇) *n*-octyl; (\blacksquare) 2-ethylhexyl.

diluent effect; i.e., the various side groups may be considered simply as various diluents added to a hypothetical polymer made up only of the backbone or main chain atoms. The larger side groups correspond to more diluent being present. Several experimental techniques have shown that the concentration of chain entanglements decreases in proportion to the amount of diluent present.¹¹ Likewise, it is well established that diluents lower the T_g of a polymer.¹² Hence, it should be expected that as the side group increases in length, both the T_g and the concentration of chain entanglements (or dynamic modulus) decrease.

The other approach is a theoretical one based on what might be termed the chain stiffness effect. Bueche¹³ has presented a theoretical model that predicts that the stiffer the polymer chain, the greater will be the number of chain entanglements associated with it. The Gibbs and DiMarzio theory¹⁴ of the T_g predicts that the T_g will increase as the polymer chain becomes stiffer. Theories of the glass transformation temperature based completely on a critical free volume concept will lead to this same prediction if we include the additional assumption that stiffer chains, which will necessitate a higher degree of coordination of segmental motion, will require a greater critical free volume in order to achieve a detectable degree of mobility at the T_g .¹¹ On the basis of these theoretical models, one expects both the T_g and the concentration of chain entanglements (and hence the dynamic modulus) to increase as the stiffness of the polymer chains increases. Slichter and

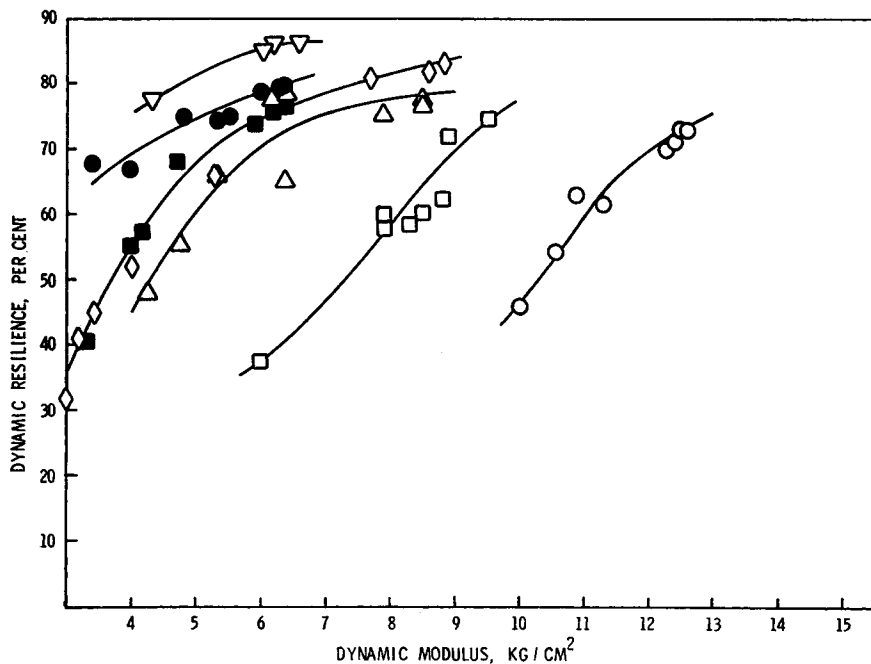


Fig. 5. Relationship between dynamic resilience and dynamic modulus of poly(vinyl alkyl ether) vulcanizates at 93°C.: (O) ethyl; (Δ) *n*-butyl; (\square) isobutyl; (\diamond) *n*-pentyl; (\bullet) *n*-hexyl; (∇) *n*-octyl; (\blacksquare) 2-ethylhexyl.

Davis¹⁵ have shown by NMR relaxation studies of polymers of normal α -olefins that an increase in the length of the *n*-alkyl side chain contributes to an increased segmental mobility in the polymer. Hence, an increase in the length of a *n*-alkyl side chain should again lead to a decrease in both the T_g and the concentration of chain entanglements (or dynamic modulus).

Since there are exceptions to these generalizations, e.g., poly(vinyl isobutyl ether), one must conclude that neither of these simple approaches alone gives a complete accounting of the facts and that a combination of these approaches and other further speculations are required to account for all the facts.

In Figure 6, the data for poly(vinyl *n*-pentyl ether) and poly(vinyl 2-ethylhexyl ether) from Figures 3-5 at 31, 60, and 93°C. are shown together. It has already been pointed out that the data for these two polymers, which have identical T_g values, fall practically on a common curve characteristic of the temperature of measurement. This demonstrates even more vividly that the T_g apparently is a major factor in correlating the dynamic mechanical behavior of this homologous series of elastomers. The influence of the size and shape of the alkyl group is to be seen primarily in the T_g value. There is very little direct dependence of the dynamic mechanical properties on the structure of the alkyl side group.

In Figure 7, data for poly(vinyl ethyl, *n*-butyl, and isobutyl ethers) at the three temperatures of measurements are shown together. Poly(vinyl iso-

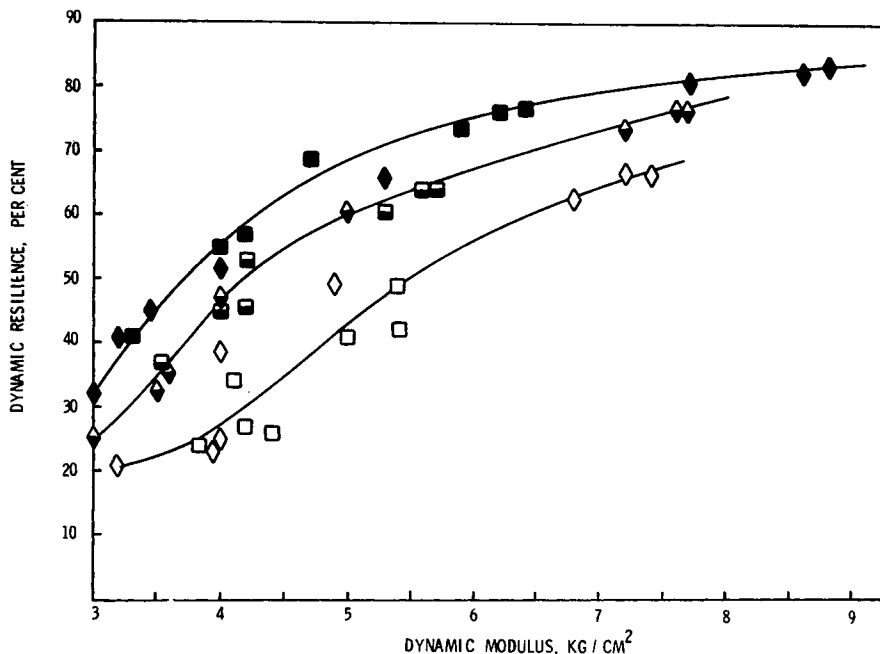


Fig. 6. Relationship between dynamic resilience and dynamic modulus of poly(vinyl alkyl ether) vulcanizates at three test temperatures: (\diamond) *n*-pentyl, 31°C.; (\square) 2-ethylhexyl, 31°C. (\diamond) *n*-pentyl, 60°C.; (\square) 2-ethylhexyl, 60°C.; (\blacklozenge) *n*-pentyl, 93°C., (\blacksquare), 2-ethylhexyl, 93°C.

butyl and ethyl ethers) show a larger temperature coefficient of resilience than do the other polymers of vinyl alkyl ethers. The relative position of the curves for poly(vinyl isobutyl ether) and poly(vinyl ethyl ether) is reversed when the temperature of measurement is increased from 31 to 93°C. Poly(vinyl isobutyl ether) has a high internal friction or dynamic viscosity at 31°C. Its modulus is about 15 kg./cm.² and the resilience value is less than 1% for various degrees of cure. At 60°C., its curve shifts considerably more to the left in relation to the curves for the other poly(vinyl alkyl ethers). This large shift should be expected since poly(vinyl isobutyl ether) has the highest T_g . At 93°C., the curve for poly(vinyl isobutyl ether) lies to the left of the curve for the poly(vinyl ethyl ether). This position is anomalous with respect to the order of the T_g values of the polymers. It is evident that the curve for poly(vinyl ethyl ether) also shifts considerably to the left with increase in temperature, much more than the curves for the polymers with higher *n*-alkyl side chains. In general, the amount of displacement or shift with temperature of the various curves for the polymers increases as their glass transformation temperatures increase and approach the test temperature. This agrees with the general temperature dependence observed for other viscoelastic materials.¹

In Figure 8, it is apparent that the vulcanizates of vinyl alkyl ether polymers have a low dynamic modulus as compared to accelerated sulfur gum

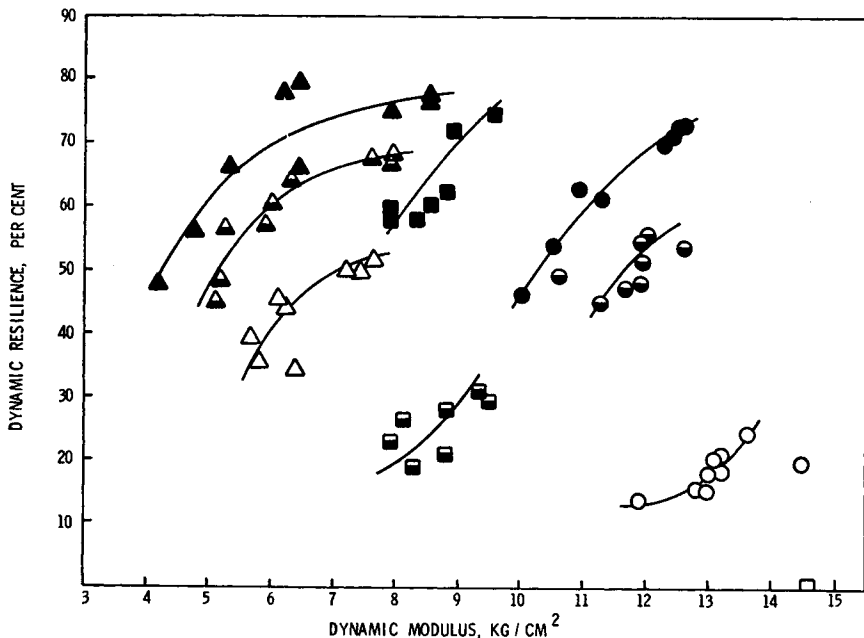


Fig. 7. Relationship between dynamic resilience and dynamic modulus of poly(vinyl alkyl ether) vulcanizates at three test temperatures: (O) ethyl, 31°C.; (Δ) *n*-butyl, 31°C.; (\square) isobutyl, 31°C.; (\ominus) ethyl, 60°C.; (\blacktriangle) *n*-butyl, 60°C.; (\blacksquare) isobutyl, 60°C.; (\bullet) ethyl, 93°C.; (\blacktriangle) *n*-butyl, 93°C.; (\blacksquare) isobutyl, 93°C.

vulcanizates of either SBR¹⁶ or natural rubber. By suitably choosing the length of the alkyl group in these vinyl ether polymers a series of elastomers can be obtained having desirable combinations of dynamic modulus and dynamic resilience values. Figure 8 indicates that the glass transformation temperature is not the only factor controlling dynamic mechanical properties when chemical structural differences larger than those between polymers of a homologous series are involved; observe the marked displacement to the right for the curves of natural rubber ($T_g = -72^\circ\text{C}.$) and SBR ($T_g = -56^\circ\text{C}.$) in comparison to the curves for poly(vinyl alkyl ethers) having similar T_g values. Apparently, structural changes in the main chain of a polymer have a marked influence on dynamic behavior.

Figure 9 shows in finer detail the effect of temperature on the dynamic modulus of three poly(vinyl alkyl ethers). These data were obtained on samples cured for 80 min. at $143^\circ\text{C}.$, and it is assumed that the various samples have about the same degree of chemical crosslinking. Poly(vinyl isobutyl ether) begins to stiffen below $30^\circ\text{C}.$, and poly(vinyl ethyl ether) begins to stiffen starting at about $0^\circ\text{C}.$ In the limited temperature range of 0 – $93^\circ\text{C}.$, the dynamic modulus of poly(vinyl *n*-hexyl ether) increases with temperature at about two-thirds the rate predicted by the kinetic theory of rubberlike elasticity.

The effect of temperature on the dynamic resilience of these same vulcanizates is presented in Figure 10. Over the entire temperature range the

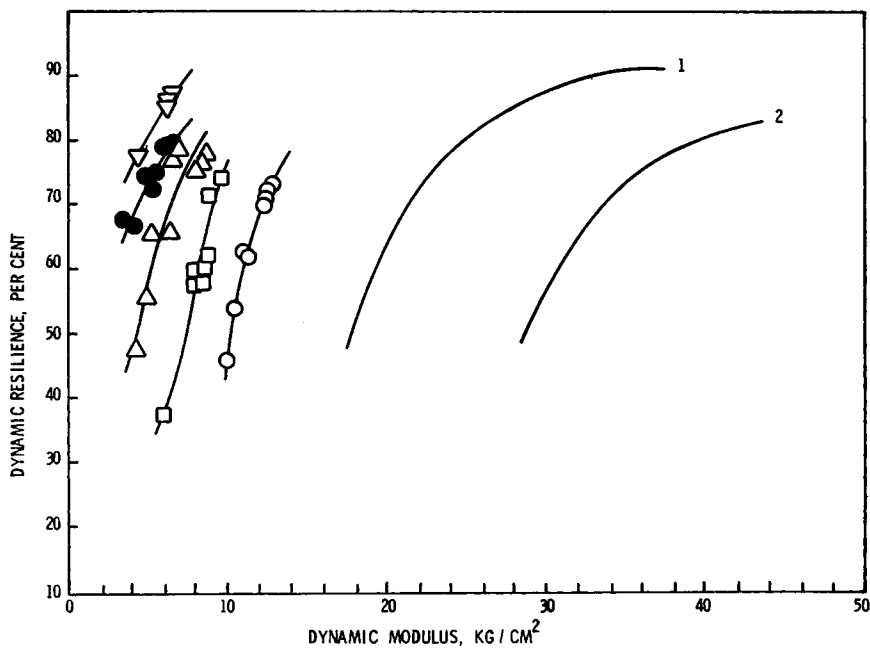


Fig. 8. Dynamic properties of rubber vulcanizates at 93°C. for various poly(vinyl alkyl ethers): (O) ethyl; (Δ) *n*-butyl; (\square) isobutyl; (\bullet) *n*-hexyl; (∇) *n*-octyl; (1) natural rubber; (2) SBR.¹⁶

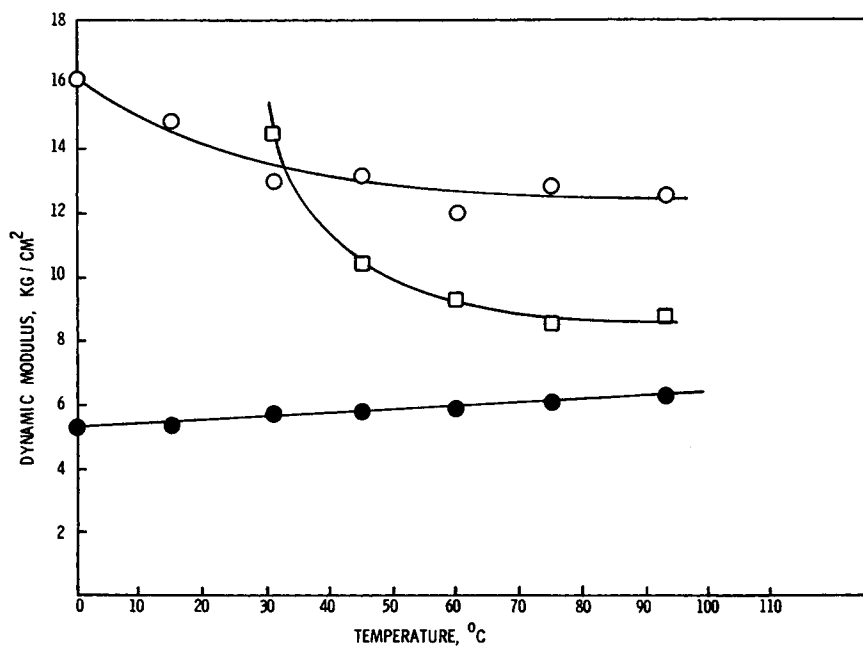


Fig. 9. Effect of temperature on the dynamic modulus of poly(vinyl alkyl ether) vulcanizates: (O) ethyl; (\square) isobutyl; (\bullet) *n*-hexyl.

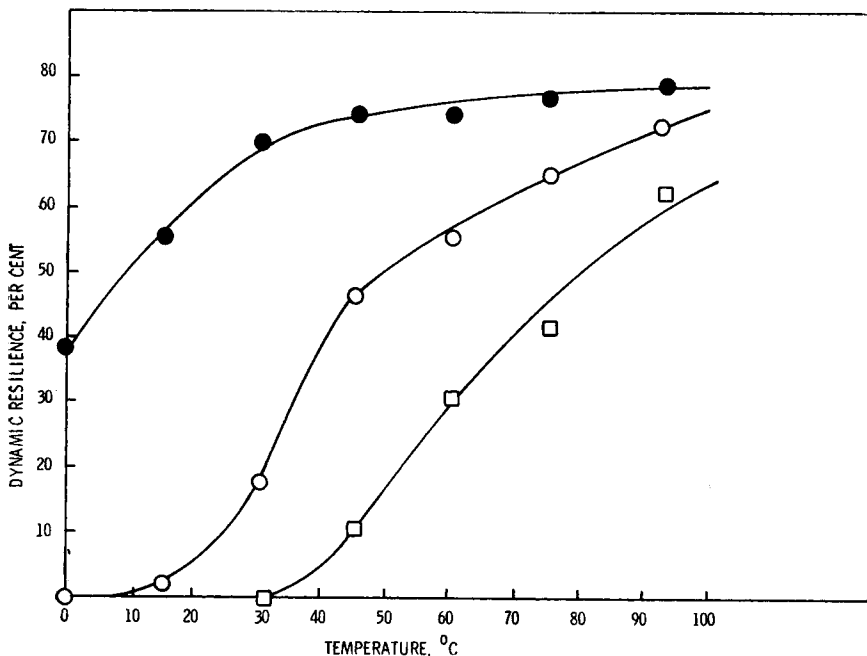


Fig. 10. Effect of temperature on the dynamic resilience of poly(vinyl alkyl ether) vulcanizates: (O) ethyl; (□) isobutyl; (●) *n*-hexyl.

curves are lined up in the order of the T_g of the polymers. The curves are all rather similar in shape, the dynamic resilience being only 5% at temperatures about 60°C. higher than the dilatometric T_g of the polymer and then increasing with temperature to a limiting value (for this degree of vulcanization) of 70–80% at temperatures which are 100–140°C. above the T_g . The curves appear to be superposable by translation parallel to the temperature axis.

In Figure 11 the dynamic resilience values for the polymers shown in Figure 10 and also for all of the other vinyl alkyl ether polymers are plotted against $T - T_g$ values, where T is the test temperature (Centigrade). Only vulcanizates cured for 80 min. at 143°C. by the recipe shown in Table II were used. It is assumed that the dynamic resilience values of these vulcanizates have not been greatly affected by the differences in chemical crosslink density and degree of polymerization that exists between these samples. Apparently, the T_g dominates the dynamic resilience behavior of these elastomers from a homologous series. This is in accord with what one would expect from the WLF equation¹ and other observations on viscoelastic-dependent properties.¹⁷

In Figure 11, poly(vinyl isobutyl ether) exhibits a normal dependence of resilience on T_g ; hence, the anomalous position of the poly(vinyl isobutyl ether) curves in Figures 4 and 5 is to be attributed to the anomalous dependence of its dynamic modulus (and hence low degree of chain entanglements) on T_g . This is the only polymer of the homologous series investi-

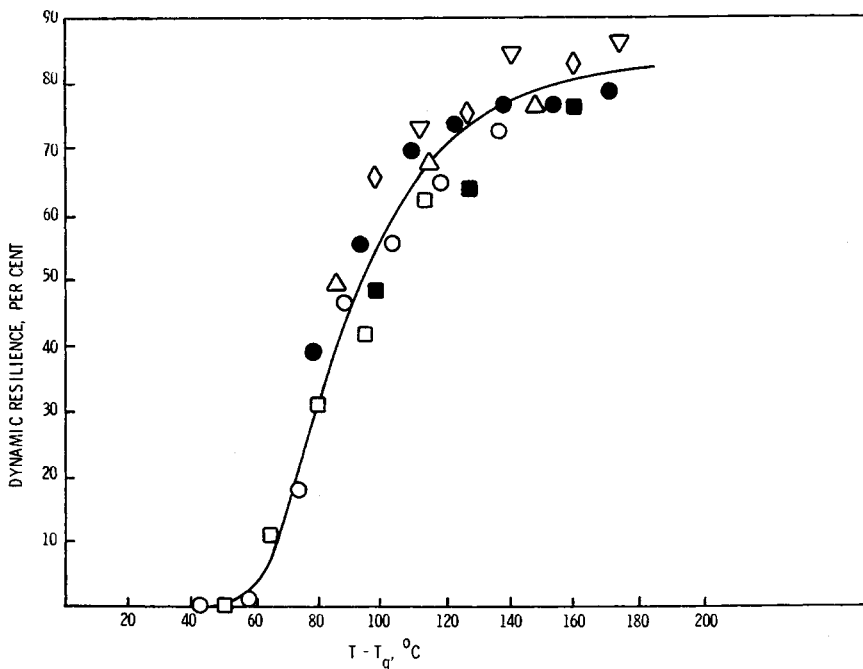


Fig. 11. Relationship between dynamic resilience and $(T - T_g)$ for poly(vinyl alkyl ether) vulcanizates: (O) ethyl; (Δ) *n*-butyl; (\square) isobutyl; (\diamond) *n*-pentyl; (\bullet) *n*-hexyl; (∇) *n*-octyl; (\blacksquare) 2-ethylhexyl. T = test temp., $^{\circ}\text{C}$.

gated here that has shown any unusual dependence of dynamic mechanical properties on structure, as the other polymers all had dynamic mechanical properties that could be correlated with their T_g . (A plot of dynamic modulus at 93°C . of the 80 min. cure samples versus T_g suggests that the anomaly in Figures 4 and 5 is due somewhat more to the fact that the dynamic modulus of poly(vinyl isobutyl ether) is low with respect to its T_g rather than that the dynamic modulus of poly(vinyl ethyl ether) is high with respect to its T_g .)

We present now some evidence to support our assumption that the data of Figure 11 are not seriously affected by the differences in chemical crosslink density or degree of polymerization that exist between these particular samples. We propose to do this by redetermining Figure 11 for the four poly(vinyl alkyl ethers) for which sufficient quantitative information is available to select cured samples with similar degrees of chemical crosslinking and polymerization.

The per cent efficiency of chemical crosslinking Z is defined as 100 times the ratio of the moles of chemical crosslinks formed to the moles of dicumyl peroxide decomposed. Knowing Z and the density of these polymers,⁶ one may calculate how much dicumyl peroxide must decompose to yield the arbitrarily chosen value of $21.9 \mu\text{moles}$ of chemical crosslinks per cubic centimeter of rubber. Table III lists values¹⁸ of Z determined by a previously described method⁵ based on the Charlesby and Pinner¹⁹ modification of the

TABLE III
 Characteristics of Poly(Vinyl Alkyl Ether)-Dicumyl Peroxide-Sulfur Vulcanizates

Alkyl group in poly(vinyl alkyl ether)	Z, %	p/q	$p \times 10^2$	$q \times 10^2$	Dicumyl peroxide decomposed phr ^a	Cure time, min. ^b	\overline{DP}_n^c	$\overline{DP}_n'^d$	$\overline{M}_n' \times 10^{-3}$ ^e
Ethyl	28.7	0.188	0.0287	0.153	2.16	38	5140	1230	88
<i>n</i> -Butyl	32.6	0.15	0.0353	0.235	1.96	33	4200	1080	108
Isobutyl	20.5	0.11	0.0167	0.152	3.16	80	3700	1250	125
<i>n</i> -Octyl	57.4	0.046	0.0304	0.66	1.15	16.5	2560	1350	211

^a Dicumyl peroxide decomposed to give 21.9 μ mole crosslinks/cc. of rubber.

^b Cure time at 143°C. (290°F.) to produce 21.9 μ mole crosslinks/cc. of rubber.

^c \overline{DP}_n = number-average (osmotic) degree of polymerization of rubber in the compounded and milled stock before curing in the press.

^d \overline{DP}_n' = number-average degree of polymerization of rubber after an amount of scission equal to that occurring during the time of cure; calculated from eq. (1).

^e \overline{M}_n' = number-average molecular weight corrected for scission during curing.

theory of gel network formation. Table III also gives p and q values which are defined as the fraction of repeat units in the polymer that have undergone molecular chain scission due to the decomposition of 1 phr dicumyl

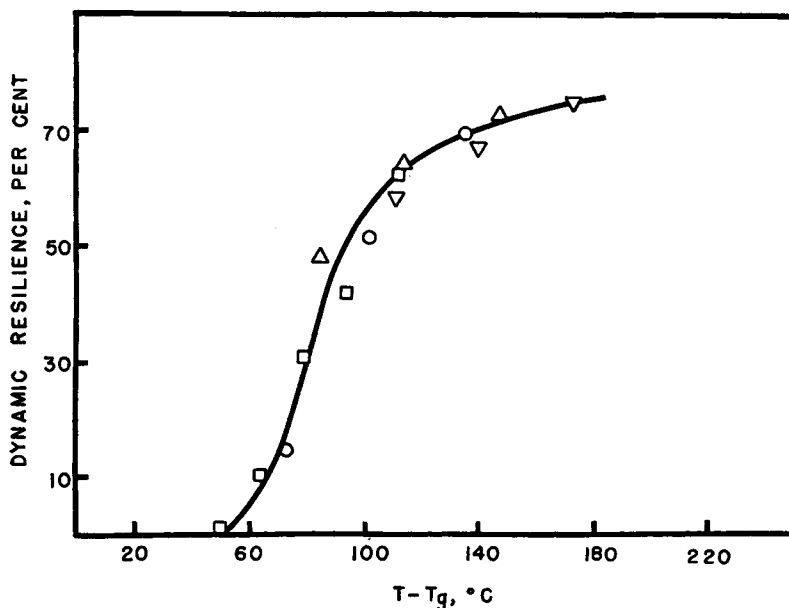


Fig. 12. Relationship between dynamic resilience and $(T - T_g)$ for four poly(vinyl alkyl ether) vulcanizates having the same concentration of chemical crosslinks and essentially the same degree of polymerization: (O) ethyl; (Δ) *n*-butyl; (\square) isobutyl; (∇) *n*-octyl. T = test temp., °C.

peroxide and the fraction of repeat units crosslinked due to the decomposition of 1 phr dicumyl peroxide, respectively. Z , p , and q values were determined only for 80 min. cure time conditions on a recipe containing a 10:1 weight ratio of peroxide to sulfur, and it was necessary to assume that the same values applied at shorter cure times in the 7.6:1 weight ratio of peroxide to sulfur recipe used here. From the kinetics of decomposition of dicumyl peroxide⁸ it is possible to calculate for the recipe of Table II the cure times required to decompose an amount of dicumyl peroxide which will result in the same concentration of chemical crosslinks in each rubber sample. From plots, similar to Figure 1, of dynamic resilience versus time it is possible to estimate, by interpolation, values of dynamic resilience corresponding to the cure times of Table III and hence for samples of equal concentrations of chemical crosslinks. Figure 12 is a plot of such dynamic resilience values against $T - T_g$, and it is not very different from Figure 11 except for perhaps a somewhat reduced scatter of the data.

Finally, we shall show that the data points of Figure 12 correspond to samples with reasonably similar degrees of polymerization. The dynamic resilience undoubtedly depends on the number of free chain ends in the vulcanizate network which in principle may be calculated from the number-average degree of polymerization, \overline{DP}_n , of the rubber. If permanent molecular chain scission occurs during vulcanization, then \overline{DP}_n must be suitably modified to reflect that each chain scission yields two new free chain ends or one more molecule. The number-average degree of polymerization corrected for permanent molecular chain scission is given by the well-known expression

$$\overline{DP}_n' = \overline{DP}_n / (1 + Cp\overline{DP}_n) \quad (1)$$

where C is the parts (per hundred parts rubber) of dicumyl peroxide decomposed, and p is the fraction of the polymer repeat units that have undergone permanent molecular chain scission due to the decomposition of 1 phr of dicumyl peroxide. Table III lists values for \overline{DP}_n and \overline{DP}_n' , and it is seen that \overline{DP}_n' varies by only $\pm 11\%$ about the mid-point of its range. We estimate that this variation in \overline{DP}_n' would produce a variation of only ± 4 resilience percentage units at about the 50% dynamic resilience level. This estimate is based on the observation (Table IV) that a $\pm 34\%$ variation in \overline{DP}_n' for poly(vinyl n -pentyl ether) produces a variation of ± 13 resilience percentage units. In Table IV the dynamic resilience values for samples

TABLE IV
Effect of Degree of Polymerization on Dynamic Resilience of
Poly(vinyl n -Pentyl Ether) Crosslinked with 1.35 phr of Dicumyl Peroxide

\overline{DP}_n	\overline{DP}_n'	Dynamic resilience at 60°C., %
5050	1480	60.5
1100	720	35

crosslinked by the decomposition of 1.35 phr of dicumyl peroxide were determined by the interpolation procedure described above, and \overline{DP}_n' was estimated assuming that p had the same value as that determined for poly(vinyl *n*-butyl ether).

Figure 12 representing the dynamic resilience behavior of four poly(vinyl alkyl ether) vulcanizates having the same concentration of chemical crosslinks and essentially the same degree of polymerization thus indicates that the T_g dominates the dynamic resilience behavior of a homologous series of elastomers having the same network structure. The close similarity between Figures 11 and 12 suggests that the assumption of sufficiently similar network structures used with Figure 11 was valid; although, in the particular case of poly(vinyl octyl ether) Table III suggests that the higher efficiency of crosslinking was partly compensated by considerable molecular scission. The close agreement shown in Figure 12 for vulcanizates of about the same \overline{DP}_n' would not have been obtained had we used vulcanizates of the same number-average molecular weight. This is readily seen from a comparison of the range of number-average molecular weights of these samples (Table III) and the observed dependence of dynamic resilience on molecular weight (Table IV). This suggests that the dynamic resilience depends more on the length of the free chain ends than it does on the mass or volume of the free chain ends.

References

1. Ferry, J. D., *Viscoelastic Properties of Polymers*, Wiley, New York, 1961.
2. Schmieder, K., and K. Wolf, *Kolloid-Z.*, **134**, 149 (1953).
3. Mosley, S. A., U. S. Pat. 2,549,921 (1951).
4. Lal, J., and J. E. McGrath, *J. Polymer Sci.*, **A2**, 3369 (1964).
5. Lal, J., and J. E. McGrath, *Rubber Chem. Technol.*, **36**, 1159 (1963).
6. Lal, J., and G. S. Trick, *J. Polymer Sci.*, **A2**, 4559 (1964).
7. Gehman, S. D., D. E. Woodford, and R. B. Stambaugh, *Ind. Eng. Chem.*, **33**, 1032 (1941).
8. Thomas, D. K., *J. Appl. Polymer Sci.*, **6**, 613 (1962).
9. Payne, A. R., *Rubber Chem. Technol.*, **37**, 1190 (1964).
10. Gui, K. E., Figure 26 in S. D. Gehman, *Rubber Chem. Technol.*, **30**, 1202 (1957).
11. Bueche, F., *Physical Properties of Polymers*, Interscience, New York, 1962.
12. Kelley, F. N., and F. Bueche, *J. Polymer Sci.*, **50**, 549 (1961).
13. Bueche, F., *J. Polymer Sci.*, **25**, 243 (1957).
14. Gibbs, J. H., and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373 (1958).
15. Slichter, W. P., and D. D. Davis, *J. Appl. Phys.*, **35**, 10 (1964).
16. Costanza, A. J., Goodyear Research Laboratories, unpublished work.
17. Smith, T. L., and A. B. Magnusson, *J. Appl. Polymer Sci.*, **5**, 218 (1961).
18. Lal, J., and J. E. McGrath, *Preprint, Intern. Symp. Macromol. Chem. Prague, 1965*, P616.
19. Charlesby, A., and S. H. Pinner, *Proc. Roy. Soc. (London)*, **A249**, 367 (1959).

Résumé

On a déterminé la dépendance de la température des propriétés mécaniques dynamiques de sept poly(vinyl alcoyl éther) élastomères vulcanisés par le soufre et le peroxyde de dicumyle. On a trouvé que la position relative des courbes reliant la résilience dynamique et le module dynamique de ces polymères se plaçait dans le même

ordre, que leur point de transition vitreuse (T_g). Les résultats expérimentaux se rapportant aux propriétés mécaniques de l'éther de poly(vinyl *n*-pentyle), de poly(vinyl 2-éthylhexyle), polymères possédant la même température de transition, se situent sur une courbe commune caractéristique de la température de mesure. L'éther de poly(vinyl isobutyle) et de poly(vinyl éthyle) possède un coefficient de température pour la résilience plus large que les autres éthers polyvinyl alcoyles, ce qui comprend également les radicaux *n*-butyle, *n*-hexyle, et *n*-octyle. Il semble donc que le point de transition vitreuse est le paramètre le plus important lorsqu'on veut mettre en relation les propriétés dynamiques de cette série homologue d'élastomères. Il semble que le volume et la forme du groupe alcoyle influence d'abord la température de transition vitreuse. On connaît seulement une exception dans ces séries, il s'agit de l'éther de poly(vinyl isobutyle), polymère qui présente des propriétés dynamiques anormales en raison de sa structure. Comme la résilience dynamique de nombreux vulcanisats de plusieurs éthers de poly(vinyl alcoyle), possédant la même densité de pontage, se justifie mieux lorsqu'on met en relation leur degré de polymérisation plutôt que leur poids moléculaire, il semble donc que la résilience dynamique dépend plutôt de la longueur des fins de chaînes libres que de la masse ou du volume.

Zusammenfassung

Die Temperaturabhängigkeit der dynamisch-mechanischen Eigenschaften von Dicumylperoxyd/Schwefelvulkanisaten von sieben Gliedern der Poly(vinylalkyläther)-elastomerenreihe wurde bestimmt. Die relative Lage der Kurven für die Abhängigkeit der dynamischen Resilience vom dynamischen Modul dieser Polymeren entsprach ungefähr der Reihenfolge ihrer Glasumwandlungstemperatur T_g . Die dynamisch-mechanischen Eigenschaftsdaten für Poly(vinyl-*n*-pentyläther) und Poly(vinyl-2-äthylhexyläther), welche dasselbe T_g besitzen, fallen auf eine gemeinsame, für die Messtemperatur charakteristische Kurve. Die Kurven dynamische Resilience gegen dynamischen Modul werden bei Erhöhung der Messtemperatur gegen höhere dynamische Resilience- und gewöhnlich niedrigere Modulwerte verschoben. Poly(vinylisobutyläther) und Poly(vinyläthyläther) zeigen einen grösseren Temperaturkoeffizienten der Resilience als die anderen Poly(vinylalkyläther), wozu auch die *n*-Butyl-, *n*-Hexyl- und *n*-Octylglieder gehören. Offenbar bildet T_g einen Hauptfaktor für die Korrelation des dynamischmechanischen Verhaltens dieser homologen Elastomerenreihe. Grösse und Gestalt der Alkylgruppe scheinen sich primär in ihrem Einfluss auf T_g widerzuspiegeln. Poly(vinylisobutyläther) war das einzige Glied der Reihe, welches auf die Struktur zurückführbare Anomalien bei den dynamisch-mechanischen Eigenschaften zeigte. Dass die dynamische Resilience verschiedener Poly(vinylalkyläther)vulkanisate mit der gleichen Konzentration an chemischen Vernetzungsstellen in besserer Korrelation zu ihrem Polymerisationsgrad als zu ihrem Molekulargewicht steht, scheint die dynamische Resilience eher von der Länge der freien Kettenenden als von ihrer Masse oder ihrem Volumen abzuhängen.

Received June 25, 1965