

Dynamic Mechanical Properties of Some Polymeric Acid Zinc Salts

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Synopsis

Mechanical properties, shear modulus, and damping of a series of polyacid divalent metal salts have been correlated with the degree of salt formation. The salts were prepared *in situ* by molding mixed powders of 94/6 acrylic acid-2-ethylhexyl acrylate and zinc oxide at temperatures of 200-300°C. and pressures of 5,000-10,000 psi. Zinc oxide consumption was followed by x-ray techniques. Compositions contained 25-200% of theory metal oxide as charged. Excesses, over theory, of metal oxide were shown to lead to the formation of substantial amounts of pendent half-salts which are high damping and have temperature-sensitive shear moduli. Only complete reaction as the di-salt, at 300°C. and 10,000 psi, leads to low damping products with temperature-insensitive high modulus. The modulus increase due to ionic bonding as the di-salt, over that expected from classical filler action alone, ranged from 40 to 80%, depending upon the theory chosen to calculate filler action. The pendent half-salt gives much smaller moduli increases and unreacted metal oxide appears to act as classical filler in an intertangled complex polyelectrolyte salt matrix. The modulus of the di-salt was found to be 6-7 times higher than moduli for normal organic rigid polymers.

Introduction

Mechanical properties of a range of rigid polyelectrolyte polymers have been reported.¹ Polyelectrolytes such as the metallic salts of polymeric acids were shown to have moduli values several times greater than those of the common thermoplastic materials. Since preformed salts of such polyacids do not measurably soften below their decomposition temperatures, specimens were fabricated by *in situ* reaction of mixed polyacid and metal oxide powders in a mold at high temperatures (over 200°C.) and high pressure (5,000-10,000 psi). Such techniques may easily lead to variable property results, partly due to nonuniform degree of reaction as molding conditions may vary.

In this work, the degree of reaction was followed by x-ray techniques so that the composition of the molded specimens could be estimated. With such information answers were obtained to such questions as the following: (a) How dependent is modulus upon degree of reaction? (b) How much increase, over classical filler action, is obtained by ionic bonding through salt formation? (c) What is the effect of excess (over theory) metal oxide when charged as additional filler?

TABLE I
Sample Molding Conditions^a

Mold cycle	Temp., °C./pressure, kpsi/time, min.						
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
1	200/0/1	200/0/1	200/5/11	200/5/8	200/5/11	200/5/30	250/10/10
2	200/5/1	200/5/1	250/5/11	200/10/60	250/5/10	200/10/60	250/10/60
3			250/5/5		250/5/5		
4			275/10/8		275/5/7		
5			300/10/8		300/10/8		
6			300/10/10		300/10/5		

^a Pressure relieved for venting between each cycle. Mold cooled to room temperature under final pressure used. Sample 2a molded under same conditions as first four steps of sample 3.

Materials and Techniques

The polyelectrolyte system used was a 94/6 (by weight) copolymer of acrylic acid and 2-ethylhexyl acrylate, a product of Monsanto Company, designated PDR-14. The polyacid had a glass transition temperature T_g of 130°C. with the onset of decomposition at 300°C. as determined by a Perkin-Elmer differential scanning calorimeter. The density of molded specimens of PDR-14 (by buoyancy) was determined as 1.3589. Predried PDR-14 (110°C., 48 hr., vacuum) with a loss on drying at 110°C., of 0.3% was used throughout.

Various zinc PDR-14 salts were prepared *in situ* from intimately mixed dry powders of PDR-14 and ZnO by positive pressure-molding techniques.¹ The powders were mixed in a Spex Wiggle-L-Bug for 10 min. in a metal mixing jar. Molding conditions (200–300°C. and 5,000–10,000 psi) for the various materials are given in Table I. Strip specimens, 0.377 × 4.00 in. with thicknesses varying from 0.020 to 0.035 in. were prepared for dynamic mechanical testing.

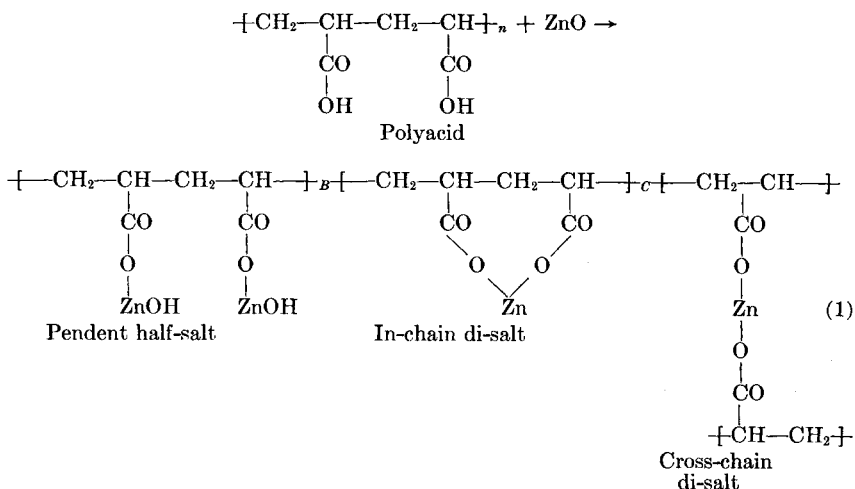
Dynamic mechanical properties; shear modulus, damping, and glass transition T_g were measured on a recording torsion pendulum.² The T_g was measured as the maximum in the mechanical damping peak at about 1 cps. The theory and discussion of dynamic mechanical testing is presented by Nielsen.³

The extent of reaction of molded specimens was determined by measuring the intensity of unreacted zinc oxide crystal peaks in x-ray goniometer tracings which were standardized by mixed but unreacted powders of known composition. In all cases the proportionality between the (100) (002) (101) lines for ZnO remained constant and the estimated error was plus or minus 2%.

Infrared analyses of KBr pellets containing samples identical with those used for x-ray analysis were made in order to correlate metal oxide disappearance with carboxyl carbonyl disappearance.

Results and Discussion

In any reacted system a possibility exists that five species may be present in varying amounts depending upon the course of reaction, as shown in eq. (1). These are (a) pendent half-salt, (b) in-chain di-salt from either adjacent or nonadjacent carboxyls, (c) cross-chain di-salt, (d) unreacted polyacid, and (e) unreacted ZnO. A system containing the first four of these species exists as an intertangled network of the species present and not as a mixture of the various species. However, each species will have its own influence upon the total property, either modulus, damping, or T_g . Thus, di-salt forms (b) and (c) will contribute more to stiffening than the half-salt (a) due to greater restrictions on rotation. However, the half-salt (a) will contribute more, per unit, than (b) or (c) from a simple filler standpoint because of its higher metal content. From the standpoint of bond strength, the [—O—Zn—O—] ionic type bonds of the



di-salt (b) or (c) are considered stronger than the $[-\text{O}-\text{Zn}-\text{OH}]$ bonds of the half-salt and, again, would contribute more to stiffness due to a smaller tendency for interchange between reaction sites. The greater interchange tendency for the half-salt (a) would result in lower modulus increases, higher damping, and lower T_g levels. In a partially reacted system there is no way of knowing which species may act as the continuous or discontinuous phase. However, one can assume that any unreacted ZnO will act as filler to all other species in relation to the volume fraction of that phase present.

A series of zinc polyacrylate (PDR-14) salts were prepared with the use of from 25 to 200% of the stoichiometric amount of zinc oxide as shown in Table II together with the determined extent of reaction and the properties of the molded products. Typical dynamic mechanical results are illustrated in Figure 1 and Figure 2.

TABLE II
Composition and Dynamic Properties

Sample no.	Composition, % of theory			Shear modulus G_2 (25°C.), dyne/cm. ² $\times 10^{-10}$	Relative modulus G_2/G_1	Glass temp. T_g , °C.
	ZnO added	ZnO reacted	ZnO as filler			
1	0 (PDR-14)			2.97 (G_1)		127
2	100	24	76	4.40	1.48	200
2a	25	100	0	4.17	1.41	210
3	50	100	0	5.58	1.88	>300
4	100	94	6	6.07	2.04	240
5	100	100	0	6.55	2.21	>300
6	150	86	64	7.58	2.55	230
7	200	146	54	8.02	2.70	>250

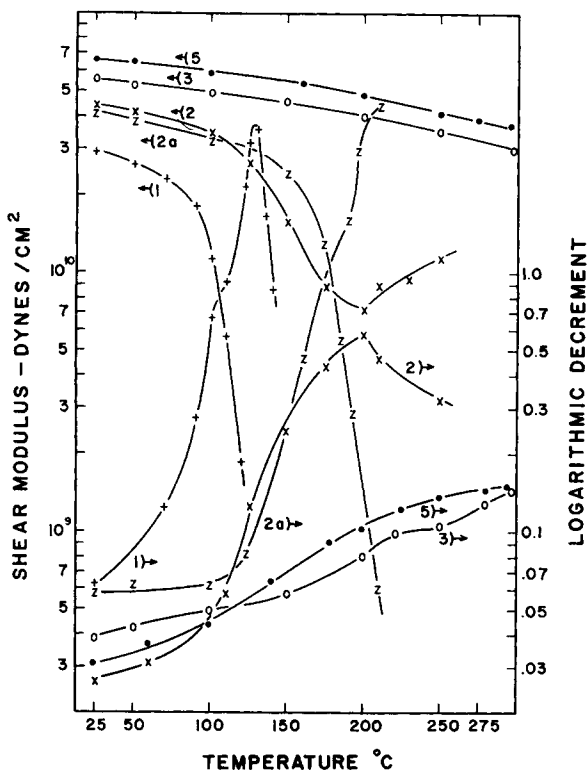


Fig. 1. Dynamic mechanical properties: (1) PDR-14 polyacid; (2) 100% theory ZnO, 24% reacted; (2a) 25% theory ZnO, 100% reacted; (3) 50% theory ZnO, 100% reacted; (5) 100% theory ZnO, 100% reacted. Numbers refer to sample numbers (Tables I and II).

Infrared analyses of KBr pellets containing samples identical with those used for x-ray analysis were made for samples 1–5 in order to correlate metal oxide disappearance with carboxyl carbonyl disappearance. As metal reacted approached 100% of the stoichiometric, complete disappearance of the carboxyl carbonyl also was noted. No other interpretation of the complex spectra was attempted.

Whereas most common rigid organic polymers have a shear modulus of about 1×10^{10} dyne/cm.², the free polyacid modulus was found to be 2.97×10^{10} , probably due to its highly hydrogen-bonded structure. As more and more metal salt was incorporated through reaction with ZnO, a steady increase in the modulus was noted, as expected, due to formation of strong ionic-type bonds. Further, the T_g increased with greater amounts of salt formation until 100% of theoretical salt formation was reached, where no glass transition was noted, at least up to 300°C. At this point (sample 5), both ZnO and carboxyl were absent by analysis, and the modulus of 6.55 can be considered as the modulus of the di-salt forms. Whereas ZnO additions greater than theoretical further increased the 25°C.

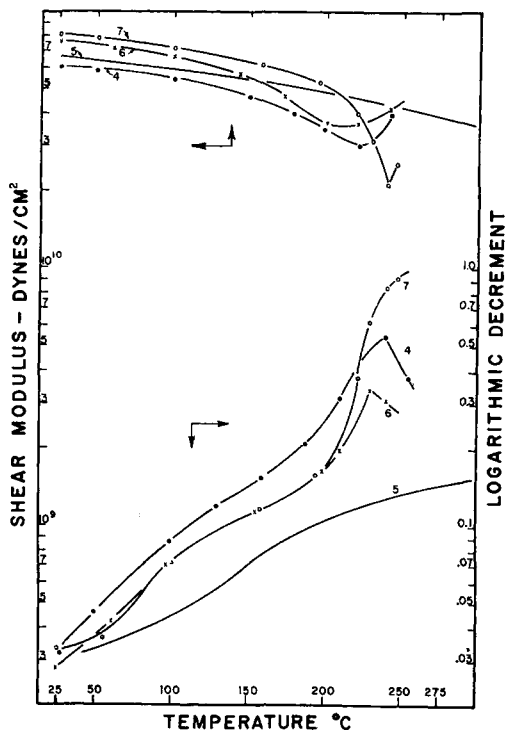


Fig. 2. Dynamic mechanical properties: (4) 100% theory ZnO, 94% reacted; (5) 100% theory ZnO, 100% reacted; (6) 150% theory ZnO, 86% reacted; (7) 200% theory ZnO, 146% reacted. Numbers refer to sample numbers (Tables I and II).

modulus, the T_g appeared to drop below that attained by adding (and reacting) only the theoretical amount. This effect on T_g will be discussed later.

For products containing up to 100% theory ZnO, incomplete reaction (Fig. 1, curve 2; Fig. 2, curve 4) leads to complex product mixtures, containing reacted zinc salts, unreacted portions of polyacid, and unreacted ZnO acting as filler. Such compositional heterogeneity, evident from the specimen opacity, results in high and broad mechanical damping areas and lower moduli at high temperatures. The sharp discontinuities observed over 200°C. are not characteristic of the polymer but are probably due to continuation of incomplete reactions of half-salt forms, polyacid, and unreacted ZnO as suggested by Fitzgerald and Nielsen.¹ Such further reaction cannot occur until the T_g of the system is reached. For example, with sample 2, further reaction became evident at over 200°C. This point corresponds to the T_g (about 210°C.) for sample 2a, wherein only 25% theory ZnO was added. In this case complete reaction of ZnO precluded further reaction, and the product contained only di-salt and polyacid species. The complete modulus and damping curves for 2a resembled those of the unreacted polyacid (curve 1) except for a much higher 25°C. modulus and a

TABLE III
Relative Shear Modulus Found vs. Calculated Values for ZnO Acting Only as Filler
(PDR-14 as Reference)

No.	Composition as charged		G_2/G_1 found (Table II)	Kerner ^b		Mooney ^c	
	ZnO added, %	Volume fraction ^a PDR-14 ZnO		$\frac{G_{oK}}{G_1}$	IR ^d	$\frac{G_{oM}}{G_1}$	IR ^d
1	0 ^e						
2	100	0.883	1.48	1.29	1.15	1.42	1.05
2a	25	0.968	1.41	1.07	1.32	1.08	1.31
3	50	0.938	1.88	1.14	1.64	1.19	1.59
4	100	0.883	2.04	1.29	1.59	1.42	1.44
5	100	0.883	2.21	1.29	1.71	1.42	1.56
6	150	0.835	2.55	1.43	1.78	1.71	1.49
7	200	0.791	2.70	1.57	1.72	2.09	1.29

^a Density ZnO = 5.47, PDR-14 = 1.359.

^b Using Poisson's ratio of 0.35 for PDR-14.

^c Using crowding factor (S) of 1.4.

^d IR = improvement ratio; increase in modulus found over that calculated only as filler.

^e PDR-14, $G_1 = 2.97 \times 10^{10}$ dyne/cm.².

displacement of the curves, to higher temperatures by about 70–80°C. Complete reaction of the ZnO (Fig. 1, curve 3, 5), whether at the 50 or 100% theory level, leads to more tightly crosslinked systems through cross-chain di-salt formation. These products yield modulus curves which are relatively insensitive to high temperatures and shows low damping.

The modulus improvement due to ionic-type bonding through salt formation relative to the classic filler effect was calculated assuming no reaction of the ZnO. Results are given in Table III and illustrated in Figure 3. For comparison, the reinforcing action of spherical filler particles was calculated by three theories, those of Kerner,⁴ Guth-Smallwood,^{5,6} and

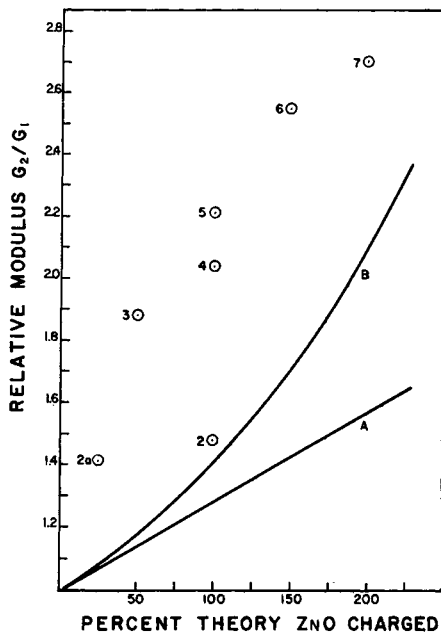


Fig. 3. Relative shear modulus at 25°C., found vs. calculated as filler: (A) theoretical (Kerner); (B) theoretical (Mooney). The numbers 2–7 refer to experimental points from Table II.

Mooney.⁷ These relationships are given in the Appendix. A comprehensive comparison of the merits of these and other theories of filler action is given by Nielsen.⁸ Only the Kerner and Mooney comparisons are shown, since at the ZnO levels employed, below 0.2 volume fraction, the Guth-Smallwood and Mooney relations give substantially equivalent results.

A substantial improvement ratio (increase in modulus found over that calculated only as filler) is noted in all cases (for 25–200% theory ZnO added). This increase in modulus, due to ionic bonding versus filler effect, was found to be 60–80% greater as calculated by the Kerner relation and 40–60% greater as calculated by either the Guth-Smallwood or Mooney relations.

The modulus curves (Fig. 2, curves 6, 7) for added excesses over theory of ZnO relate quite well with the found degree of reaction (Table II). Although the 25°C. modulus continues to increase, the results at higher temperatures are more revealing. With 150% theory charged (curve 6) the product analyzed as 86% of a theory reacted with a remainder of 64% of a theory ZnO acting as filler. Thus, curve 6 is similar in shape to curve 4, Figure 2 obtained from 94% of theory reacted but with a lower level of unreacted filler. At the level of 200% theory ZnO charged, a lowering of the improvement ratio is noted (Table III). Analysis of the product indicated 146% theory ZnO consumed with 54% theory remaining as filler. To obtain over-theory reacted zinc one must introduce a new salt species, the pendent half-salt form. As mentioned previously this salt-form may be expected to increase the modulus at 25°C. somewhat, but to have a definite T_g at elevated temperatures barring further reaction. Curve 7, Figure 2, illustrates this prediction with precipitous lowering of the modulus over 150°C. and a very high damping effect. Since 46% reacted excess, over theory, implies the splitting of an identical portion of a theoretical disalt, then the salt portion of sample 7 must contain 92% of a theory as pendent half-salt and only 54% of a theory as disalt. The corresponding unit volume fractions are 0.63 pendent and 0.37 disalts. Thus the dominating effect on any mechanical property is due to pendent half-salt which would not be expected to exhibit high temperature modulus stability.

One can estimate a modulus (G_x) for the pendent half-salt form as 7.08×10^{10} dyne/cm.². This was done by distributing unreacted ZnO, on a volume basis, between the half-salt and di-salt species and, by using the Mooney relation with 6.55 for the modulus of the di-salt species, calculating a modulus for the filled di-salt species. Then, using the rule of mixtures and the found modulus of sample 7, one can obtain a modulus for the filled half-salt species. From this, G_x is obtained, again from the Mooney relation. G_x , 7.08, for the half-salt species is higher than G_2 found (6.55) for the disalt because of its higher metal content. However, the improvement ratio for the pure half-salt-form (over theoretical filler action) is lower than that for the corresponding disalt because of weaker and more mobile salt linkages. At a volume fraction of 0.209 ZnO, equivalent to pure half-salt, the improvement ratio was only 1.14 contrasted with the higher improvement ratio of 1.56 found for the disalt by using the Mooney relation. This smaller improvement ratio accounts for the lower trend noted for relative moduli found for sample 7, where major amounts of pendent half-salt are present.

The almost identical broad and high damping curves for samples 6 and 7 (Fig. 2) below 200°C., again indicating compositional heterogeneity, suggests the presence of pendent half-salts in the 150% theory ZnO sample. The same suggestion also applies to samples 2 and 4, where less than complete reaction was observed. The short stress relaxation times reported¹ for monovalent sodium salts of similar polyacids, compared with much longer stress relaxation times for divalent barium salts, may likewise be

evident in the case of pendent half-salt forms compared with more heat-stable di-salt forms.

Summary

In the *in situ* formation of polyacid metal salts by compression molding of mixtures of polyacid and metal oxide powder, it has been shown that only complete reaction of oxide will lead to temperature-insensitive high-modulus low-damping products. Incomplete reaction, whatever its cause (low temperature, low pressure, poor mold venting, or excess metal oxide), results in products which are high-damping and have poor modulus-temperature characteristics. This effect may be due to pendent half-salts of the form, $R-C(O)-O-Zn-OH$. Such a salt form must be assumed to be present where excesses of over the theoretical ZnO were used and where more than theoretical amounts of zinc were found to be reacted.

The increase in modulus due to ionic bonding, from whatever salt form may be present, over that expected from classical filler action alone ranges from 40 to 80% depending upon the theory chosen to calculate filler action. Any unreacted metal oxide appears to act as classical filler in the poly-electrolyte salt matrix. For the theoretical di-salt form, modulus values of 6-7 times those for normal organic rigid polymers were obtained.

APPENDIX

The Kerner relation⁴ is:

$$G_0 = G_1 \left[\frac{\frac{\phi_F G_F}{(7 - 5\nu_1)G_1 + (8 - 10\nu_1)G_F} + \frac{\phi_P}{15(1 - \nu_1)}}{\frac{\phi_F G_1}{(7 - 5\nu_1)G_1 + (8 - 10\nu_1)G_F} + \frac{\phi_P}{15(1 - \nu_1)}} \right]$$

where G_0 is the shear modulus of the two-phase system and G_1 and G_F are the shear moduli of the polymer or continuous phase and of the filler or discontinuous phase, respectively. The volume fraction of the polymer is ϕ_P and that of the filler is ϕ_F . Poisson's ratio of the material in the continuous phase is ν_1 .

For rigid fillers which have moduli much greater than that of the polymer, Kerner's equation may be simplified at low volume fractions of filler to:

$$G_0 = G_1 \left\{ 1 + \frac{\phi_F}{\phi_P} \left[\frac{15(1 - \nu_1)}{8 - 10\nu_1} \right] \right\}$$

For calculations, ν_1 of the polyacid was used as 0.35 and that for any salt form as 0.30.

The Guth-Smallwood relation^{5,6} is:

$$G_0 = G_1 (1 + 2.5\phi_F + 14.1\phi_F^2)$$

The Mooney equation⁷ is:

$$\ln (G_0/G_1) = [2.5\phi_F/(1 - S\phi_F)]$$

For calculations, the packing factor S was taken as 1.4.⁸

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