A Note on the Existence of a Yield Point in the Dynamic Modulus of Loaded Vulcanizates

Previous workers[1-4] have reported on the increase of the dynamic Young's modulus of rubber vulcanizates loaded with carbon black as the amplitude of straining is decreased. The range of experimental strains has now been extended by over a decade to include strains as small as 0.002% and has shown some interesting new features. A yield point exists at these low strains, the strain at which the latter occurs being dependent on the loading of the carbon black. At lower strains the vulcanizates behave almost elastically (tan δ being approximately that of the pure gum) with the Young's modulus independent of the strain.

Figure 1 shows the absolute Young's modulus $|E(w)| = (E'^2 + E''^2)^{1/2}$, where the complex Young's modulus $E^* = E' + iE''$, plotted against the logarithm of the dynamic strain amplitude, for a range of natural rubber compounds containing varying amounts of carbon black. (Compound formulations are given at the end of this note.) From this plot it can be seen that $|E(w)|$ increased with a decrease in the amplitude of the dynamic strain for vulcanizates containing appreciable amounts of carbon black. At very low strains, $|E(w)|$ becomes constant, and the position of the yield point is dependent on the filler concentration. The results clearly show the existence of a yield point typical of nonlinear thixotropic systems. The yield occurs at very much lower strains than those at which breakdown of the structure has been demonstrated,[5] and the modulus changes are very much greater in magnitude.

The measurements were made on a nonresonant dynamic tester which imparts a sinusoidal strain on cylinders or rubber,[6] 3 in. long and 0.5 in. diameter, with the planar ends being bonded to metal. The test pieces were strained in tension by extending 0.25 in. and the dynamic modulus was measured at a frequency of 0.5 cycles/sec., and imposed strain being varied sinusoidally about the prestrained position with a range of strain amplitudes from 0.002 to 10%.
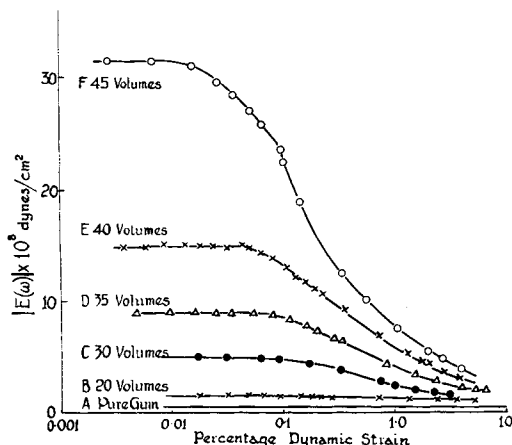
A deformation is thixotropic if the resistance to it changes its course and if the original rheological properties return at rest, the recovery being accelerated by raising the temperature. The rubbers tested behave in this manner. If the higher loaded rubbers are first deformed at high amplitude, subsequent tests at a lower amplitude show that the modulus increases with time until it reaches the level expected for the smaller amplitude. Higher temperatures accelerate this process.

According to Houwink and Jannsen,[7] the mechanical properties of compounded vulcanized rubbers are due to three types of molecular linkage; rubber-rubber, rubber-filler, and filler-filler. The thixotropy discussed above suggests that the mechanical properties observed are due mainly to the breakage and subsequent reformation of the filler-filler structure.

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Appendix

Compounds used (composition in part per 100 parts by weight of rubber).

	A	B	C	D	E	F
Smoked sheet	100	100	100	100	100	100
Philblack A	0	50	85	100	110	150
Cure time at 401 lb. pressure	40	40	40	40	50	60

All compounds contained zinc oxide 3, stearic acid 2, PBN 1, CBS 0.6, and Dutrdx R 5 parts by weight in addition to the above.

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Fig. 1. $|E(w)| \times 10^8$ dynes/cm.² versus percentage dynamic strain amplitude. Letters indicate the rubber compound.