From the Natural Rubber Producers Research Association, Welwyn Garden City, Herts. (England)

Dynamic properties of materials*)

Part II. Dynamic properties of clay-natural rubber vulcanizates

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With 7 figures and 1 table

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1. Introduction

Earlier papers (1) have demonstrated how the modulus of a rubber vulcanizate containing carbon black or clay decreases with increasing amplitude of dynamic oscillation. Recently, similar dynamic properties have been reported in clay-water compositions (2). This paper extends these studies by considering the changes in modulus and phase angle that occur in clay-rubber vulcanizates and demonstrates that these changes are similar in magnitude to the modulus and energy changes occurring in the clay-water and rubber-carbon black systems.

2. Experimental

A conventional sulphur santocure NR gum mix was prepared and filled with increasing amounts up to 280 parts per hundred rubber of bentonite and stockalite clays. The mix details and cure times are given in the Appendix. The cylindrical test specimens, 1.80 cm in diameter and 2.54 cm in height were cured in a multicavity mould and were handled with the minimum deformation when removed from the mould.

The samples were tested on the sinusoidal-strain dynamic tester described in earlier publications in the same way as the rubber-carbon black and clay-water systems. Two test pieces were bonded to either side of a central metal plate which applied the oscillating movement and the other sides of the specimens on to restraining static plates (3).

After setting up and resting overnight, the specimens were firstly tested at displacements of 10^{-4} to 10^{-2} cm where it was experimentally convenient to apply a chosen stress and record the strain. They were then tested at successively higher strains by selecting the strain and observing the stress up to displacements of 1.25 cm or before if the rubber-metal bond had broken.

The experimental measurements were of the maximum straining force, the resulting amplitude of strain and the phase angle between the sinusoidal stress and strain oscillation at each individual setting of the dynamic tester. The variation of the complex shear modulus (G^*) and phase angle (δ) with increasing amplitude of dynamic oscillation could then be determined.

The relationship between the moduli are shown by eqs. [1] and [2]

$$G^* = G' + i\,G' \qquad [1]$$

$$\tan\delta = \frac{G''}{G'}, \qquad [2]$$

where G' is the in-phase modulus with the strain and G'', the out-of-phase modulus (3).

3. Dynamic results

Fig. 1 shows the variation of dynamic shear modulus with double amplitude of strain oscillation for the NR-bentonite clay vulcanizates. Similar results are shown in fig. 2 for the NR-stockalite clay vulcanizates.

The familiar decrease in modulus with amplitude of oscillation is noticed for

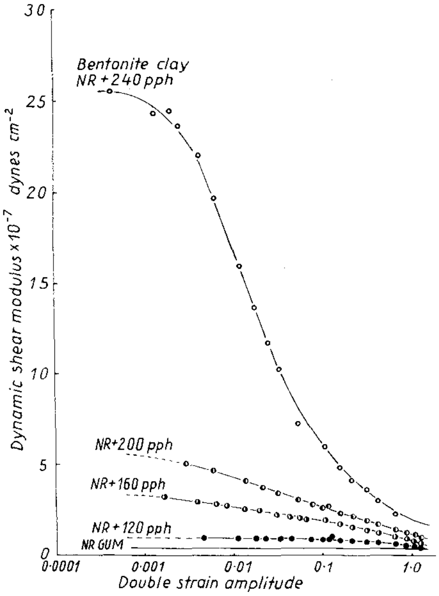

Fig. 1. Variation of dynamic shear modulus with double strain amplitude for the NR-bentonite clay vulcanizates

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loadings of clay above about 120 parts per hundred of rubber. Similar results to the gum mix were found for loadings of clay below 120 parts per hundred rubber.

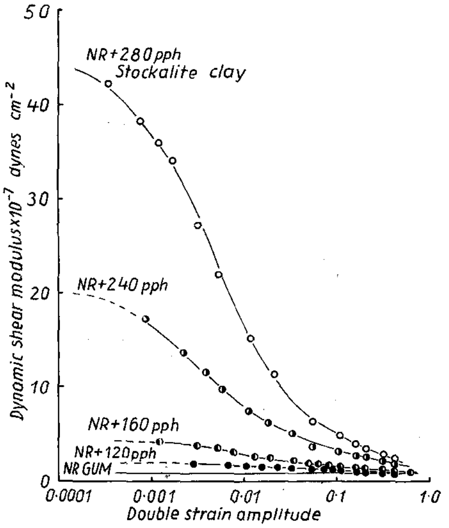

Fig. 2. Variation of dynamic shear modulus with double strain amplitude for the NR-stockalite clay vulcanizates

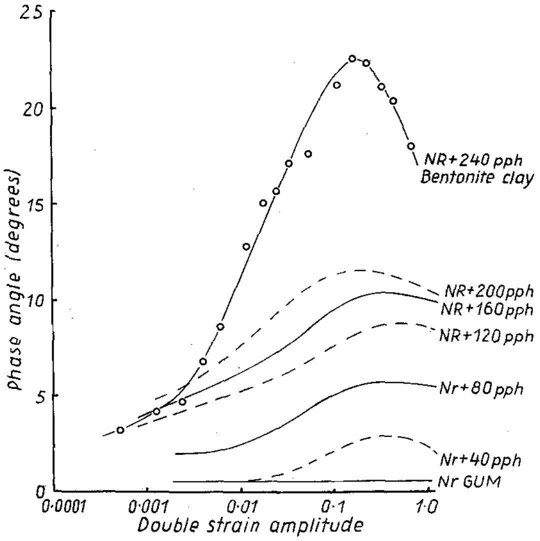

Fig. 3. Variation of phase angle with double strain amplitude for the NR-bentonite clay vulcanizates

The variation of phase angle with double strain amplitude is shown in fig. 3 and 4 for the two NR-clay mixes. The higher loadings of clay show the characteristic peak values of phase angle occurring at the same strain amplitude as the inflection point in the modulus-strain graphs.

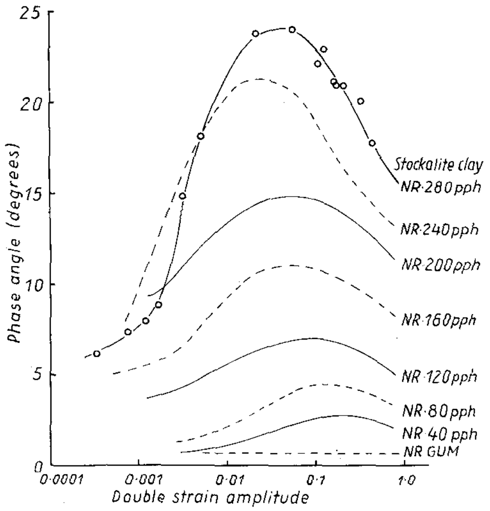

Fig. 4. Variation of phase angle with double strain amplitude for the NR-stockalite clay-vulcanizates

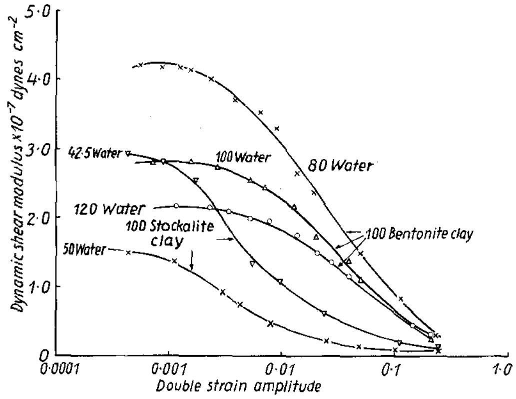

Fig. 5. Variation of dynamic shear modulus with double strain amplitude for bentonite clay-water and stockalite clay-water systems

The dynamic shear modulus-strain amplitude graphs for the clay-water systems are shown for comparison in fig. 5. The moduli at very low strains, less than 0.001, are constant and similar in magnitude to the clay-rubber systems. The shape of the curves is also very similar, and this suggests that the modulus breakdown is due to the same mechanism in each system. It should be pointed out however, that the complex dynamic modulus for the clay-water system can only be separated into its components G' and G'' for results at low amplitudes of strain when the hysteresis loop was clearly an ellipse. At higher amplitudes, the hysteresis loop departs markedly from an ellipse so that the dynamic modulus is taken as the total stress amplitude divided by the total strain amplitude. The hysteresis behaviour of the clay-water system is discussed in more detail in the earlier publication (2). It should also be noticed that the effect of increasing the clay content in water is to increase the modulus at very low strains. This behaviour is similar to increasing clay or carbon black content in rubber.

Macey (4) and *Astbury* and *Moore* (5) have examined the behaviour of clay under sinusoidal cyclic deformation, and have shown that normal clays containing 20 to 30 per cent of moisture produce well defined hysteresis loops bearing a marked resemblance to the familiar loops of ferromagnetism. These observations were also noted by *Payne* and *Whittaker* (2) for the dynamic behaviour of clay-water systems subjected to strain amplitudes of one per cent or more. At much lower strains the clay-water systems produce simple stress-strain ellipses. Examination of the ellipses of clay-rubber systems show that under sinusoidal stresses or strains they produce simple responses which are sinusoidal with no evidence of any harmonics.

Normalisation of moduli

In order to compare dynamic results, it has been found convenient in earlier work to normalise the data between the highest and lowest strains. This has been done by considering the shear modulus G' to reach a limit G_0' at low strains and a second limit G'_∞ at very high strains when there is no further change in G' with increase in strain amplitude. The normalized modulus Z can then be defined at any strain (1).

$$Z = \frac{G' - G'_\infty}{G_0' - G'_\infty} \,. \qquad [3]$$

It has also been shown in previous papers on rubber-carbon black systems, that neither stress nor strain is the independent parameter which governs the variation of the dynamic modulus with strain, but the product of double stress amplitude and double strain amplitude which is referred to as "strainwork". Fig. 6 shows a plot of the normalised modulus against logarithmic strainwork on probability paper for the two highest loadings of each clay. The linear graph obtained demonstrates that the modulus decreases sigmoidally with the strainwork of oscillation and implies a relationship of the type (1).

$$Z = \frac{G' - G'_\infty}{G_0' - G'_\infty} = 1 - \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{x} \exp - \frac{(x-\mu)^2}{2\sigma^2}\, dx \,, \qquad [4]$$

where

$x = \log_{10} X$, X being the strainwork.

$\mu = \log_{10} X_{0.50}$, $X_{0.50}$ being the value of strainwork at $Z = 0.50$

$$\sigma = \frac{(x_{0.10} - x_{0.90})}{2.56} \,.$$

$(x_{0.10} - x_{0.90})$ being referred to as the "width" of the distribution. It is the difference between the values of the logarithms of strainwork corresponding to $Z = 0.10$ and $Z = 0.90$ respectively.

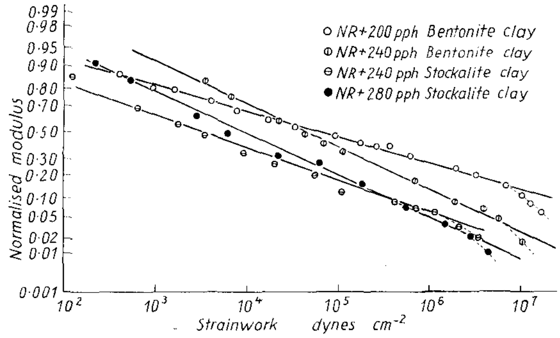

Fig. 6. Variation of normalised modulus with strainwork for two highest loadings of bentonite and stockalite clays in rubber. Strainwork equal to double stress amplitude × double strain amplitude

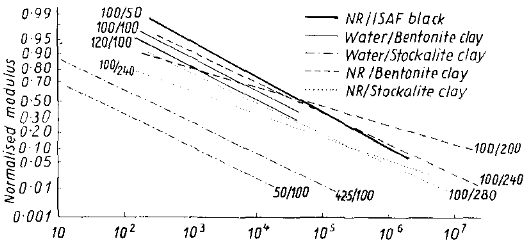

Fig. 7. Variation of normalised modulus with strainwork for clay-water, clay-rubber and rubber-carbon black systems. Strainwork equal to double stress amplitude × double strain amplitude

A linear graph when plotted in this manner was also obtained for the clay-water and rubber-carbon black systems. The rubber clay results in fig. 6 are compared with the other two systems in fig. 7. The individual points on the graphs have been left off for clarity. The G'_∞ value for the clay-water system was taken as zero so that $Z = G'/G_0'$. The modulus-strainwork changes for the three systems are shown to be very similar although the concentrations of clay in rubber and water are quite different. Values of G_0', strainwork at $Z = 0.50$ and width of the distribution are listed in table 1. Values

Table 1. Comparison of data from normalised modulus-strainwork

Material	G_0' dyne cm^{-2} $\times 10^{-7}$	Strainwork at $Z = 0.50$ dyne cm^{-2}	"Width" log units
100/240 NR/Stockalite clay	1.80	3.0×10^3	3.80
100/280 NR/Stockalite clay	2.00	9.5×10^3	3.15
100/200 NR/Bentonite clay	0.80	5.4×10^4	4.95
100/240 NR/Bentonite clay	1.50	3.7×10^4	3.10
100/80 Bentonite clay/water	4.20	1.3×10^4	2.65
100/100 Bentonite clay/water	2.80	2.1×10^4	2.80
100/120 Bentonite clay/water	2.15	1.1×10^4	2.95
100/42.5 Stockalite clay/water	3.00	2.3×10^2	3.05
100/50 Stockalite clay/water	1.55	4.2×10	3.00
100/50 NR/ISAF carbon black*)	5.50	5.5×10^4	2.70

*) Values vary depending on mixing technique (1).

of strainwork at $Z = 0.50$ for ISAF black in rubber and bentonite clay in either water or rubber are very similar. The results for stockalite clay in either rubber or water are very much lower than for the other systems.

4. Discussion

Bentonite clays are well known in rheology as materials which when suspended in liquids give rise to three dimensional or pack-of-cards structures and these effects are often associated with thixotropy when these systems are subjected to shearing. For instance when a fluid suspension of bentonite clay in water is poured into a test tube and allowed to stand for some time, it changes into a rigid gel, and does not flow out if the test tube is turned over. However tapping of the test tube is sufficient to liquify the gel. This process is not accompanied by a heat effect and can be repeated indefinitely. It indicates that the structural features which are responsible for the rigidity of the gel can be disturbed by slight vibrations (6).

Weyl and *Ormsby* (6) have identified three schools of thought regarding the mechanism of thixotropy of clay-water systems. One group, in particular *Freundlich* (7), *von Engelhardt* (8) and *Hauser* (9) assume long range electrical forces which permit the individual particles to interact over distances of the order of 1000 Å. Another group, *Usher* (10), *Kuhn* (11) and *Hofmann* (12) prefer a mechanical picture according to which the particles touch one another, adhere on contact and build up a spacious network resembling a "house-of-cards". A third group explains the rheology of clay-water mixtures by assuming that the water which surrounds the clay particles becomes rigid. This view is shared by *Macey* (13), *McBain* (14), *Grim* and *Cuthbert* (15).

Thixotropy has been observed in many systems involving a great variety of solids, e. g. clay, iron oxide, carbon and organic substances such as indanthrene dyes. The phenomenon is not restricted to water as the dispersing medium but may also occur in benzene for example. *Payne* (1) has shown that carbon-black-nujol systems behave in a similar way to the clay water sytems discussed above.

It also seems to be an established fact that the sol-gel transformation in clay-water systems does not lead to a definite geometrical alignment of the particles. The strength of these thixotropic gels increases with decreasing particle size. This appears to show up in the present results by comparing the stockalite with the bentonite clay strainworks at $Z = 0.5$ which shows that the smaller particle bentonites are stronger than the larger sized stockalites, the size and shape of the bentonite plate crystals are between 2 to 15 × 700 × 700 mμ whereas the stockalites are 50 × 2000 × 2000 mμ in size.

Hauser and his associates (6, 9, 11) have contributed to the elucidation of the mechanism of the sol-gel transformation by observing the process in the ultra-microscope. The Brownian molecular motion comes to a stand-still and in truly thixotropic systems of highly dispersed bentonite fractions, the particles which have ceased to move seem to be clearly separated from each other by the water. The findings of *Hauser* (6, 11) according to *Weyl* and *Ormsby* (6) are in no way contradictory to the findings of *Hofmann* (12) who studied suspensions which contained higher concentrations of clay, a condition which is conductive to the formation of a house-of-cards.

The high activity of the surface of clay and its influence on water is well appreciated but discussion of this is beyond the scope of this paper but the basic phenomena are reasonably well documented and reference should be made to suitable reviews. However one similarity of the behaviour of water and rubber near the surface of the clay could be found in the increased rigidity of the absorbed layer. For instance *Macey* (13) attributes the plasticity of clay to an oriented overgrowth of "ice" on the clay surface, and his epitaxis theory "ice on clay" was a convenient explanation of the rigidity of the water film. It is suggested that water can be immobilised by electric fields by a mechanism that bears no relation to crystallisation but does lead to rigidity of the water near the surface thus giving properties referred to in the ice theories. Similarly it is believed that in filled rubbers the network of the rubber near the surface of the black has been restricted preferentially in the vicinity of the rubber black interface (16). For instance *Grosch* (17) in swelling measurements on filler loaded vulcanisates, found it necessary to assume that the increase in cohesion between rubber chains due to the presence of the carbon black is not uniform throughout the network but is more pronounced in the vicinity of the carbon black particles. The boundary condition of the stiffening effect of the black requires that no dewetting should occur between black and rubber and an almost inevitable consequence of such a condition must be that there will be some modification to the rubber network, most likely in the form of a higher concentration of network chains or of molecular alignment in the vicinity of the boundary between rubber and filler. Such 'shells' of rubber around the black particles have been postulated by *Westlinning* et al. (18), for natural rubber where the cohesive forces are large enough for the natural rubber chains near the black surface to show crystallisation at room temperature in the unstrained conditions.

An analogy can therefore be drawn between the alignment of water near a clay surface to produce 'ice', and the alignment of rubber near the black surface which can in the case of natural rubber exhibit a crystallisation effect.

Payne has attempted to show in an earlier paper (19) describing the dynamic properties of carbon black-nujol systems that Van der Waal-London dispersion forces could well account for the stiffness of the three-dimensional aggregated networks of the carbon black. A subsequent paper (20) has demonstrated similar behaviour in PBNA (phenyl β naphthylamine) crystals in natural rubber vulcanizates where the three-dimensional structures of the PBNA are clearly formed by dendritic crystals, which are easily studied optically. In the case of PBNA-NR vulcanizates the modulus decrease on increasing oscillation is due to fracture of this dendritic network.

The nature of the forces which are responsible for the high modulus of the clay or carbon black structures is still however unresolved and especially in clay-water systems is still the subject of considerable controversy and of many publications. This paper however has demonstrated clearly that the non-linear behaviour of clay-rubber composites is similar to that of clay-water composite systems which are well known for their thixotropic characteristics.

Acknowledgements

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Summary

The dynamic properties of bentonite and stockalite clay-natural rubber vulcanizates have been studied with respect to the changes in modulus and phase angle that occur with amplitude of oscillation. These changes are shown to be similar in magnitude to the modulus and energy changes that occur on deformation in clay-water and carbon black-rubber systems which have been reported earlier.

Zusammenfassung

Es werden die dynamischen Eigenschaften von Bentonit- und Stockalit-Ton–Naturgummi-Vulkanisaten unter Berücksichtigung der mit der Variation der Schwingungsamplitude auftretenden Änderungen des Moduls und Phasenwinkels untersucht. Es zeigt sich, daß diese Änderungen in ihrer Größe den Modul- und Energieänderungen ähnlich sind, die bei den bereits früher veröffentlichten Meßergebnissen von Deformationen an Ton–Wasser- und Ruß–Gummi-Systemen auftreten.

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Appendix

Compounding details

RSS (SMR 5)	100
Zinc Oxide	5
Stearic Acid	2
Sulphur	2.5
CBS	0.6

The above gum mix with:
40, 80, 120, 160, 200, 240 pph Bentonite clay
and also with:
40, 80, 120, 160, 200, 240, 280 pph Stockalite clay.
All cured for 40 minutes at 140 °C.

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The dynamic shear modulus of bitumens as a function of frequency and temperature

By R. Jongepier and B. Kuilman

With 7 figures in 12 details and 2 tables

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1. Introduction

Bitumens are viscoelastic liquids prepared from crude oil distillation residues. They include members with widely varying properties, satisfying the requirements of a multitude of applications. Among these the rheological properties are usually considered of paramount importance.

The bitumen rheologist has to deal with the linear as well as the non-linear behaviour of his materials.

In the present paper we shall confine our attention to the linear visoelastic properties as a function of frequency and temperature. These properties have their bearing not only on the design of road constructions as far as road bitumens are concerned, but they also enable many other bitumens to be characterized.

By a very useful graphical representation *Van der Poel* (1) demonstrated the regular pattern of the thermorheological properties of bitumens using routine test data for the characterization of type and hardness.

Brodnyan (2) gives a comparable survey of a wide range of types of bitumen and discusses the influence of frequency and temperature separately. He applied a "free volume" equation to account for the effects of temperature.

The free volume concept has been further explored for bitumens by other investigators (3, 4), who combined dilatometric glass-transition temperature with thermorheological measurements.

The regular patterns for the frequency dependence in ref. (1) and (2) suggest that bitumens can be described by a common formula and the observations in ref. (3) and (4) lead to the same conclusion for the influence of temperature. The information in the literature is, however, not sufficient to establish both formulas as well as their mutual relation and the significance of glass-transition temperatures in this respect. Hence we investigated the thermorheological properties and glass-transition temperatures of a series of bitumens of varying types.