CHAPTER 18

PHYSICAL AND TECHNOLOGICAL PROPERTIES OF NATURAL RUBBER

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Natural rubber (NR) is a high molecular weight polymer, *whose* chemical structure is cis-1,4-polyisoprene. The crude rubber as obtained from the tree contains, in addition to the pure rubber hydrocarbon, various other substances like proteins, fats and fatty acids, carbohydrates, mineral matter etc. The hydrocarbon content is reported to be about 94% (Allen and Bloomfield, 1963). The non-rubber substances, although only present in low concentrations, influence the chemical and physical properties of the hydrocarbon polymer. The cis content of the polymer was reported to be almost 100%. But a recent work (Tanaka, 1985) indicated the presence of about three trans units per chain. The properties of NR depend very much upon the state of crosslinking. Therefore, the important properties of the raw unvulcanized rubber and those of the vulcanized rubber are discussed separately.

UNVULCANIZED RUBBER

Molecular weight

As natural rubber is a linear long chain polymer, it is composed of molecules of different size. Therefore, the numerical value of its molecular weight depends on how the heterogeneity is averaged. Thus it can be expressed either as number average molecular weight, $\bar{M}n$ or as weight average molecular weight, $\bar{M}w$. The relation between $\bar{M}n$ and $\bar{M}w$ depends on the molecular weight distribution. The two averages are equal only when the polymer is homogeneous. In other cases, it is found that $\bar{M}w > \bar{M}n$. The weight average molecular weight of natural rubber ranges from 30000 to about 10 million. A random blend would have a weight average molecular weight of about 2×10^6 and a number average molecular weight of about 5×10^5. Determination of $\bar{M}n$ of natural rubber involves measurement of colligative properties, like osmotic pressure (Bristow and Place, 1962). Measurement of $\bar{M}w$ is possible by the light-scattering method which is particularly useful for polymers with molecular weights in the region of 10^6 (Schulz et al. 1956).

Intrinsic viscosity measurements have been widely used for the determination of molecular weight of natural rubber using toluene as solvent (Onyon, 1959).

Molecular weight distribution

In addition to the measurements of $\bar{M}n$ and $\bar{M}w$, a full characterization of a polymer like natural rubber requires determination of its molecular weight distribution (MWD). Using direct visual measurement of sizes of natural rubber molecules, Schulz and Mula (1960) determined its molecular weight distribution. This method is restricted to molecular weights in excess of approximately 5×10^5. Later, using more advanced techniques like gel permeation chromatography (GPC), Subramaniam (1972) demonstrated that the molecular weight distribution of unmasticated natural rubber is distinctly bimodal. The MWD curve shows that the peak at lower molecular weight is less pronounced than that of the higher molecular weight. The districtuion is wide, the ratio $\bar{M}/\bar{M}n$ being in the range of 2.5 to 10. The various commercial grades of NR show differences in molecular weight and its distribution. Storage hardening of NR tends to change the shape of its MWD curve from bimodal to unimodal and to raise $\bar{M}w$ slightly.

It has long been known that properties of raw NR are characteristic of the clones from which the rubber is obtained. Subramaniam (1975) studied clonal variation in molecular weight and its distribution using GPC. Though the range of molecular weight is nearly the same for all the clones, the mean values and the shapes of the MWD curves are different. While the low and average molecular weight clonal rubbers show distinct bimodal distribution, the high molecular weight clonal rubbers usually show a unimodal distribution with a shoulder of shallow plateau in the low molecular weight region. The effect of the yield stimulant 'ethrel' on the molecular weight and its distribution was studied by Subramaniam (1971) and it was shown that the average molecular weight decreases quite sharply a few days after stimulation. As the effect of the stimulant wears off, the molecular weight recovers to reach normal values. MWD studies indicated that the additional latex obtained from the stimulated trees contains a greater proportion of lower molecular weight material.

Macro and micro gel

When NR is immersed in a solvent, the rubber first swells. On prolonged standing some soluble rubber is extracted from the swollen gel.This phenomenon gives rise to a two-phase theory of rubber, comprising 'sol' and 'gel' phases and various factors are responsible for increasing the proportion of either of these phases at the expense of the other. The gel phase consists of the more highly branched and lightly crosslinked components of the rubber closely intertwined with insoluble high-molecular non-rubber substances like proteins. The gel phase thus observed in solid or latex rubber which underwent prolonged storage is known as macrogel. The increase in the macrogel content during storage is responsible for the hardening of rubber stored in bulk (Wood, 1953). Factors such as mechanical shear or oxidative degradation etc. are known to disaggregate the macro gel and to make it soluble.

Fresh NR latex contains crosslinked particles of colloidal dimensions. Bloomfield (1951) coined the name microgel for this crosslinked fraction in Hevea latex considering their similarity with the microgel in SBR latex. The usual concentration of microgel in normal Hevea latex is of the order of 7-30%, but in long rested, and particularly newly opened trees, it may be as high as 60-80%. Both microgel and macrogel in rubber have technological implications. While macrogel is responsible for storage hardening, formation of microgel in latex affects only the original level melt viscosity of the resulting rubber. Unlike macrogel, which is formed in dry rubber on storage, microgel is formed in the latex present within the vessels of the tree. Sekhar (1962) reported that microgel formation in latex is initiated by aldehyde condensing groups, numbering between 100 and 420 per polyisoprene molecule.

Chain branching

The presence of abnormal chemical groups on the rubber chain is believed to cause formation of branched chains. Bristow (1962) showed the existence of branched chains in natural rubber through dilute solution viscometry. Chain branching is responsible for the lower values of molecular weight determined by GPC techniques. The rheological properties of NR are strongly influenced by long chain branching. The slow rate of stress relaxation of Hevea rubber compared to guayule and synthetic polyisoprene rubber has also been attributed to chain branching (Montes and White,1982).

Storage hardening

Natural rubber, either in the form of latex or solid rubber, when stored for long periods, develops higher hardness, as measured by Mooney viscosity or Wallace plasticity. It is also known that the change in viscosity is greater if the initial viscosity is lower. The hardening process is accelerated by low relative humidity and higher temperature of storage.

The increase in hardness occurring when ammoniated latex is stored is believed to be the result of intra-particle crosslinking and microgel formation. However, with solid rubber the crosslinking process is not confined to the original latex particle.

The mechanism of storage hardening is known to involve carbonyl groups in rubber, since hardening is almost fully suppressed by the addition to latex of reagents that could block carbonyl groups (Sekhar, 1958). It is possible to estimate the number of such carbonyl groups per rubber molecule by measuring the concentration of hydroxylamine required to fully inhibit storage hardening, and values of 9-29 were found for a number of clonal rubbers. The amino acids present among the non-rubber constituents are also believed to be playing a role in the hardening reaction (Gregory and Tan, 1975). The change in hardness could be quite large. Nair (1970) compared melt viscosity of rubbers prepared from ordinary and viscosity-stabilised latices of different clones. For the former, Wallace plasticity values were found to be 10-45% higher, depending upon the clonal source.

Low temperature crystallization

In the raw form, natural rubber freezes even at 0°C if the exposure time is sufficiently long (say, one week). This also causes stiffening of raw rubber during storage (Bristow and Sears, 1982). The maximum rate of crystallization occurs at about -24°C when crystallization is virtually complete in about eight hours. Such frozen rubber can be thawed to its original amorphous condition in several hours at 70-100°C. Any significant stiffening due to crystallization can be avoided by ensuring storage above 15°C. It may be noted that laboratory measurements at room temperature can be influenced by very small amounts of pre-existing crystallization.

Melting temperature, Tm

The temperature at which the last traces of crystallinity disappear is usually described as melting temperature, Tm. The experimental procedures used for the determination of Tm present difficulties and the observed values are influenced by factors like chemical modification, presence of diluents, degree of deformation of the amorphous material etc. The observed melting temperature also depends markedly on the temperature at which crystallization occurs. It is probable that in the case of NR, the low melting temperatures observed when the crystallization takes place at a relatively low temperature, reflect the improbability of forming large crystals under these conditions. Although a value of 28°C has been assigned for the Tm of NR, a value of 30°C and higher have been occasionally reported. However, they have been attributed to the presence of some degree of orientation in the amorphous rubber prior to crystallization (Andrews and Gent, 1963).

Transition temperatures

One of the most fundamental measurements on any polymer is the measurement of the temperature(s) at which solid state transitions occur, since specific properties and the manner of usage depend to a large extent on the relation of these transition temperatures to the temperature at which the material is to be used. All polymeric materials will, at some temperature, undergo a glass transition (Tg) change from a plastic to a rubbery state. In addition, many polymeric materials exhibit a first order transition at a temperature (Tm), resulting from the melting of the polymer crystals to form an amorphous rubber. In general, a useful rubber should have a Tg considerably below the temperature of application and have such a structure that crystallization with its associated increase in hardness does not take place on long term standing of the finished product.

Specific volume measurements on NR have established a Tg of -72°C. Boyer (1963) reported many of the complexities associated with solid state transitions. Since such transitions are associated with the allowance of some hitherto restricted chain segmental motion, it has been found to change with degree of crosslinking in NR stocks (Wood et al. 1972). Presence of carbon black has relatively little effect on Tg. If low operating temperatures are desired, plasticisers may be incorporated and this is found to depress the Tg of NR, the degree of depression being dependent on the viscosity of the plasticiser. Of all the elastomeric materials showing first order transition, none has been studied as extensively as NR. This situation arises from a number of factors, particularly the fact that NR was found to undergo crystallization at a readily measurable rate at convenient temperatures and hence served as a model for the development of experimental and theoretical treatments of crystallization of polymers in general. A detailed summary of a variety of experimental work on the crystallization of NR was made by Andrews and Gent (1963).

Rubber solvent interactions

Information on the interactions of a polymer with a given solvent can be obtained from measurements of properties of dilute solutions such as viscosity, osmotic pressure, light scattering etc. However, measurements made over a much broader concentration range provide data on solvent resistance of polymers and on the characteristics of vulcanizates prepared therefrom. The most generally applied technique for measuring such interactions involves combining equilibrium swelling measurements on vulcanized rubber with some parameters characterising the vulcanizate network by means of the following equation (Flory and Rehner, 1943).

$$-\ln(1-V_r) - V_r - \chi V_r^2 = \frac{2VoC_1}{RT} V_r^{1/3} \qquad (1)$$

where V_r is the volume fraction of rubber at equilibrium swelling, Vo is the molar volume of the swelling liquid, C_1 is a network parameter from elasticity measurements and χ is the solvent-polymer interaction parameter. A modification of this equation includes the term involving the functionality (f) of the crosslink points (Flory, 1950).

$$-\ln(1-V_r) - V_r - \chi V_r^2 = \frac{2VoC_1}{RT} \left(V_r^{1/3} - \frac{2V_r}{f}\right) \qquad (2)$$

The application of gas liquid chromatography to solvent-polymer interactions resulted in the rapid generation of data on many solvents and into high polymer concentration ranges (Summers et al. 1972).

Among all the measurements that have been made combining stress-strain and swelling measurements on NR, the most extensive appear to be those of Bristow (1965) with the following results for NR.

χ = 0.411 (decane, 25°C, equation [1])

χ = 0.40 + 0.20 V_r (decane, 25°C, equation [2])

Much less extensive data give the following results.

χ = 0.42 (benzene, 25°C, equation [1])

χ = 0.41 + 0.20 V_r (benzene, 25°C, equation [2])

χ = 0.425 + 0.20 V_r (heptane, 25°C, equation [1])

χ = 0.415 + 0.35 V_r (heptane, 25°C, equation [2])

Cohesive energy density

The polymer-solvent interactions, as described in the previous section cover specific polymer-solvent systems. However, it is highly desirable to be able to consider a more general case where it is possible to predict the solvent-polymer behaviour of a particular combination from a knowledge of two parameters each representing a given polymer and a given solvent. Such parameters can be derived from measurements of heat of mixing. The parameter usually employed is the cohesive energy density (CED) or more commonly its square root δ, the solubility parameter. The values reported for natural rubber are 8.08 and 8.10 (Trick, 1977).

Flow properties

Studies on flow properties of rubbers started with the advent of the parallel-plate plastimeters like the Wallace rapid plastimeter, and the rotating disc viscometers like the Mooney viscometer. The former provides a measure of the flow produced during a simple compression at 100°C, while the latter a measure of the shear viscosity at a particular strain rate also at 100°C. Both instruments provide a measure of the flow behaviour at low strain rates and there is a broad correlation between the results of the two tests (Anon, 1981; Subramaniam, 1975). Freshly prepared natural rubber is variable in plasticity and viscosity. Normal modifications of the method of preparation have only minor effects. It is now clear that variations in plasticity and viscosity of raw NR are due to the differences in the molecular size and structural arrangements of the rubber hydrocarbon, and these characteristics are specific to the clone. Rubber with a low Mooney viscosity normally has a low intrinsic viscosity in solution and vice versa, but this correlation is not as good as might be expected, due to the presence of microgel, as discussed earlier in this chapter. The presence of microgel causes increase in Mooney viscosity without contributing much to solution viscosity. Subramaniam (1975) studied clonal variation in Mooney viscosity and reported that the value normally ranges from 63 to 94, seasonal variation being apparent in a few cases. The Wallace rapid plasticity values for the same set of clones ranges from 42 to 68.

Ong and Subramaniam (1975) derived a linear correlation between the *initial maximum torque* $V_{i\ max}$ *and the Mooney viscosity* V_r *of raw NR.* Mastication, storage hardening and method of coagulation did not alter the linear relationship. A hypothesis involving the mechanism of disentanglement orientation of polymer chains with chain slippage was proposed to explain the variation of torque with time of shearing. It was also suggested that the initial maximum increase in torque in Mooney viscosity determination and the subsequent thixotropic phenomenon are of the same origin.

The inherent disadvantages of flow measurements at low shear rates as in Wallace rapid plastimeter and Mooney viscometer, led to the development of capillary rheometers which are being extensively used to extend measurements to high shear rates (10^3 s^{-1}). Investigations on the capillary flow behaviour of raw and filled NR stocks have been reported (Ong and Lim, 1983; Bristow, 1985; Gupta, 1989). The relation between viscosity and shear stress depended upon the natural rubber grade and samples of different grades with similar Mooney viscosities exhibited significantly different flow behaviour at high shear rates (Bristow and Sears, 1988; 1989). This again suggests that useful additional information could be gained by high shear rate tests.

Viscoelastic behaviour

Natural rubber shows viscoelastic behaviour indicating that its physical properties are partly liquid-like (viscous) and partly solid-like (elastic). This in fact, is the case for all rubbers. Rubbers behave in many ways like highly viscous liquids before they are crosslinked. The vulcanization process which introduces crosslinks reduces the flow properties and makes a rubber more elastic. Nevertheless, there is still evidence of flow behaviour even in a crosslinked rubber. This is demonstrated in the creep and stress-relaxation behaviour of rubbers.

Tack and green strength

The term processability refers to the way in which a rubber behaves through a series of processing operations or to the reproducibility of that behaviour. Easy processability of NR has been regarded as one of its main attributes. The most important aspects of processability of NR are its high inherent tack and good green strength. These two characteristics are of utmost importance in the manufacture of products like tyres. Tack is important so that the components of a green tyre will hold together until moulding. Green strength is needed so that the uncured tyres will not creep and hence distort excessively before moulding, or tear during the expansion that occurs upon moulding. A practical definition of tack is the ability for two similar materials to resist separation after they are brought into contact for a short time under a light pressure. The tack of NR and NR/SBR blends have been compared with that of SBR by Hamed (1981). The higher tack of NR compared to the SBR stock has been attributed to its greater ability to flow under compressive load and its higher green strength. NR is an ideal material for developing high tack. It can be processed to a low viscosity and still maintain high green strength. Furthermore, the mechanism responsible for high green strength (strain crystallization) is not active in the bond formation step, and hence does not interfere with contact and inter-diffusion, but rather develops upon stressing. The high level of molecular inter-diffusion is also responsible for the high tack of NR (Skewis, 1966). Tack and stickiness, although inter-related, are not the same. Juve (1944) was one of the first to try to differentiate between tack and stickiness. According to him, if two pieces of a rubber compound are pressed firmly together and form a joint so strong that attempts to separate them cause a failure at another point, that is excellent tack. If only partial tearing at the former interfaces occurs, tack is fair. If separation occurs at the interface, it is stickiness, and the degree of stickiness is dependent on the force required to separate the interface. Tack is also denoted as autoadhesion or autohesion, green strength as cohesion and stickiness as adhesion. All measurements of tack involve green strength or cohesive strength of the rubber compound, and all rubber compounds with high tack values have good green strength and this applies well to NR.

VULCANIZED RUBBER

Strength properties

As in the case of other engineering materials, strength properties are of great importance in most of the practical applications of rubber. A number of strength properties can be defined and measured. The most important among these are tensile strength, tear strength and resistance to fatigue.

Tensile strength

Tensile strength, in which the material is subjected to a uniform uniaxial tensile stress, is the simplest strength property as far as measurement is concerned. Perhaps the most striking characteristic of natural rubber, compared with most synthetic elastomers is its very high tensile strength even without the help of reinforcing agents. This is undoubtedly due to its ability to crystallize considerably on extension at normal temperatures. Strain induced crystallization in rubbers has been directly investigated by X-ray, density and other methods. Tensile strength of NR vulcanizates frequently exceeds 30 MPa which is almost ten times the values reported for gum vulcanizates of noncrystallizing rubbers such as SBR, under similar test conditions (Thomas, 1960; Greensmith et al. 1963). The tensile strength of NR gum vulcanizates depends on various factors (Hofmann, 1967) including the type and extent of crosslinking; a peroxide-cured vulcanizate showing a maximum tensile strength of 15 Mpa, a TMTD-cured rubber, containing mostly monosulphidic crosslinks, having tensile strength values upto 25 MPa and accelerated sulphur vulcanizates giving values above 30 MPa. The effect of reinforcing fillers on the tensile strength of NR is not as significant as in the case of noncrystallizing rubbers. Temperature is found to influence significantly the tensile strength of gum NR vulcanizates and there is a critical temperature around 100°C, above which the strength falls abruptly, crystallization being suppressed at that temperature. However, tensile strength of reinforced NR vulcanizates is found to be less temperature dependent.

Tear resistance

The tear resistance of elastomers reflects their tensile strength characteristics. As the tip of the tear sustains high strains, crystallization occurs and high tear resistance is observed in NR. The energy parameter for tear fracture is termed tearing energy, T, and is defined mathematically as:

$$T = \frac{-(\delta U)}{(\delta A)_l} \qquad (3)$$

where U is the total strain energy stored in the specimen containing a crack, A the area of one fracture surface, and the partial derivative indicates that the specimen is considered to be held at constant length, l, so that the external forces do no work. From measurement of tearing forces the values of T at which tearing occurs can be calculated. For noncrystallizing rubbers tearing energy shows a strong dependence on rate of tearing. Tearing in such rubbers often proceeds in a 'steady' manner in the sense that the force, when a 'trousers' type test piece is tested at a constant rate of separation of legs, remains relatively constant. However, in the case of crystallizing rubbers like NR, tearing generally proceeds in a 'stick-slip' manner with the force increasing during the 'stick'periods until a catastrophic failure point is reached at which the tear jumps forward. Over wide ranges, the catastrophic tearing energy is insensitive to rate and temperature for a crystallizing rubber like NR (Greensmith et al. 1963). It appears that in such materials the effect of crystallization which can induce substantial hysteresis at high strains, overshadows viscoelastic effects. Another factor promoting high tear resistance is roughening or branching of the tear tip. In extreme cases roughening can lead to 'knotty' tearing in which the tear tip circles around on itself under increasing force until finally a new tear breaks ahead. Although knotty tearing is not exclusive to filled rubbers, the tendency for it to occur can be greatly increased by reinforcing fillers (Gent, 1978). It seems probable that a strength anisotropy arising from orientation effects is at least partly responsible for tear deviation (Gent and Kim, 1978). Another factor that may influence tear deviation is cavitation ahead of the crack tip due to the hydrostatic component of the tensile stresses.

Crack growth and fatigue

Fatigue failure of rubber under cyclic deformation has been shown to be a crack growth process initiating from small pre-existing flaws, usually of size 2 x 10^{-3} cm (Gent et al. 1964; Lake and Lindley, 1964a; Mathew and De, 1983a). Thus crack growth behaviour and fatigue are intimately related. The strain dependence of fatigue life of different elastomers vary widely. Natural rubber is very good at high strains, compared with noncrystallizing elastomers. The difference is more pronounced under nonrelaxing conditions, that is, when the deformation cycle is repeated, stress does not return to zero (Fielding, 1943; Lake and Lindley, 1964b). This effect could be utilized to advantage in certain engineering applications such as springs. In these applications, suitable designs ensuring incomplete relaxation could exploit this desirable feature. Even for noncrystallizing elastomers, fatigue life under nonrelaxing condition is found to be longer which is essentially attributable to the reduction in the strain energy of the cycle (Lindley, 1974). For a crystallizing rubber, the much larger enhancement is attributed to two additional factors: an effective increase in the threshold energy (To), required for the initiation of mechanical crack growth, and a reduction in the rate of growth once the new To is exceeded. The minimum tearing energy needs to be a small but definite fraction of the maximum for these effects to become apparent. It has been shown that To can be approximately calculated from the molecular structure of the vulcanizate and from the strength of the chemical bonds (Lake and Thomas, 1967). It has also been shown that To for NR increases substantially if atomospheric oxygen is excluded and/or if certain antioxidants are incorporated in the vulcanizate. This behaviour is reflected in enhanced life, particularly in the region of the 'fatigue limit', that is a strain below which the fatigue life of elastomers is very long.

Frequency of deformation is found to have very little influence on the fatigue life of NR vulcanizates. The effect of temperature on crack growth and fatigue is also found to be much less for NR than for noncrystallizing rubbers. This difference is believed to be associated with the origin of mechanical hysteresis. In NR, hysteresis due to strain-induced crystallization, which does not vary greatly with temperature, far outweighs the viscoelastic contribution. Carbon black and other fillers provide an additional source of hysteresis and their inclusion can greatly modify the temperature dependence of crack growth and fatigue of noncrystallizing rubbers. For both crystallizing and noncrystallizing rubbers, resistance to crack growth could be increased by fine particle size fillers, the effect being attributable to blunting of the crack tip due to branching.

ELASTIC PROPERTIES

Modulus and hardness

According to the statistical theory of elasticity (Trelor, 1975), in simple shear the stress, τ, is proportional to the strain, γ, even for large deformations. Thus

$$\tau = G\gamma \qquad (4)$$

where G is the shear modulus. In simple tension or compression the nominal stress, σ, is related as

$$\sigma = G(\lambda - 1/\lambda^2) \qquad (5)$$

where λ is the extension ratio. At a low elongation, e, this becomes

$$\sigma = 3\ Ge = Eoe$$

where Eo is the Young's modulus. The two moduli at low strain obey the relationship Eo = 3G for an incompressible solid. The statistical theory explains reasonably well the stress-strain behaviour of unfilled rubber upto strains of a few hundred per cent when the stress rises much more steeply than the theory predicts. This is either due to the molecular chains between crosslinks approaching their limiting extension or, in the case of crystallizing elastomers like natural rubber, to the onset of strain-induced crystallization. However, the statistical theory of elasticity is not obeyed by filled rubbers. The values of G derived from both shear and tension/

compression tests decrease with increasing strain, though the values obtained are similar when e equals γ up to strains of about 50%. At higher strains the deformation within the rubber matrix becomes sufficient for strain-crystallization or limiting chain extensibility, to steepen the stress-strain curve.

Generally hardness measurements are used to characterize vulcanized rubbers approximately. In the case of rubbers, hardness is essentially a measurement of the reversible, elastic deformation produced by a specially shaped indentor under a specified load and is therefore related to the low strain modulus of the rubber. Readings are usually in International Rubber Hardness Degree (IRHD). Hardness is relatively simple and easy to measure, but is subject to some uncertainty in measurement and hence ±2 degrees tolerance is given. Shear modulus values are much more accurate, but are more difficult to measure. However, they are preferred as a basis for design calculations, particularly for filled rubbers as the modulus is dependent on strain.

The bulk modulus of rubber, β, is many times larger than its Young's modulus, Eo. For most purposes the Poisson's ratio can be taken as ½. The much larger bulk modulus indicates that rubber hardly changes in volume even under high loads, so that for most types of deformation, there must be space into which rubber can deform. The more restriction that is made on its freedom to deform, the stiffer it will become, a characteristic used in the design of compression springs.

Resilience, hysteresis and heat build-up

Resilience is a basic form of dynamic test on rubber in which the strain is applied by impacting the test piece with an indentor which is free to rebound after the impact. Rebound resilience is defined as the ratio of the energy given up on recovery from deformation to the energy required to produce the deformation and is usually expressed in percentage. Resilience is not an arbitrary parameter, but is approximately related to the loss tangent:

$$R = \frac{EA}{ER} = \pi \tan\delta \qquad (6)$$

where ER = reflected energy,
EA = absorbed energy = E_T - ER
where ET = incident energy

The relationship is not particularly accurate because tan δ is strain dependent and in an impact test, the form of applied strain is complex and its magnitude not controlled.

Hysteresis is the energy lost per cycle of deformation. It is the result of internal friction and is manifested by the conversion of mechanical energy into heat. Heat build-up is the temperature rise in a rubber body resulting from hysteresis. As the heat generated is not easily conducted away in a material of low thermal conductivity such as rubber, the rise in temperature may assume so much magnitude in products like heavy duty truck tyres as to cause failure through tread lift, blow-out and other delamination or crack growth processes. It is because of such risks that heat build-up influences the design, compounding and use of large tyres. Natural rubber has been the preferred polymer in such applications, considering its outstanding resilience, low hysteresis and heat build-up characteristics. Unlike in SBR, hysteresis in NR is contributed mostly by strain induced crystallization, which does not vary much with temperature and therefore the effect of temperature on crack growth and fatigue tends to be much less in the case of NR.

Creep, stress relaxation and set

When a vulcanized rubber is held under constant strain, the stress is found to decrease gradually with time as the crosslinked network approaches an equilibrium condition. This phenomenon is called stress relaxation. The same process leads to creep, which is defined as the additional strain occurring, after a lapse of time, beyond the immediate elastic deformation. Although all but a few per cent of the original deformation is recovered immediately on removal of the load, further recovery takes much longer and may never be complete. The extent of deformation not recovered is known as permanent set. If the time scale and the temperature are such that chemical effects are negligible, creep and stress relaxation are approximately proportional to the logarithm of the time after loading.

One of the most notable features of natural rubber, compared with most other elastomers, is its good elastic behaviour. This results in low creep and a lower stress relaxation rate. If the stress relaxation rate is expressed as per cent stress relaxation per decade of time, a typical NR gum vulcanizate may give a value of about two per cent per decade. If carbon black is present, the rate will be higher, about seven per cent per decade for a 70 IRHD rubber containing 50 phr of a nonreinforcing black. However, prestressing of such a filled rubber can reduce the stress relaxation rate to a little more than the gum value. This superior elastic behaviour of

NR is a consequence of the high mobility of the molecules, which is also reflected in the relatively low glass transition temperature.

Stress relaxation rates are substantially independent of the type or amount of deformation, but creep rates depend on both the rate of stress relaxation and the load-deflection characteristics. In tension the creep rate may reach double the rate of stress relaxation, in shear it is about the same and in compression, it is lower. For unfilled rubbers having the same type of vulcanizing system the relaxation rate decreases with increasing hardness. Over the usual range of hardness possible with gum vulcanizates this will not alter the rate by more than about a third. In filled rubbers the relaxation rates increase with the amount of filler. The amount of creep is the largest during the first few weeks under load but should not exceed 20% (for 70 IRHD) of the initial deflection in this period. Thereafter, only a further 5-10% increase in deflection should occur over a period of many years.

Measurement of set under compression provides a practical evaluation of either the creep or the stress relaxation of rubber and has been very useful for those purposes where a high degree of precision is not expected. To get quick results the test conditions are made much more severe than the anticipated conditions of service by either increasing the temperature or the deformation, or both.

Creep and stress relaxation are particularly important in load-bearing applications such as springs. Partly because of its good creep characteristics, NR is the most widely used rubber in this field.

Resistance to abrasion

The terms wear and abrasion are very often used synonymously. Wear is a general term covering the loss of material by virtually any means. As wear usually occurs by the rubbing together of two surfaces, abrasion is usually used to mean wear. Abrasion resistance is the reciprocal of abrasion loss. The mechanisms by which abrasion occurs when a rubber is in moving contact with any surface, are somewhat complex, involving principally cutting of the rubber and its fatigue. These mechanisms have been extensively reviewed (James, 1967; Zhang, 1984; Gent and Pulford, 1983; Grosch and Schallamach, 1969; Mathew and De, 1983b). It is possible to categorise wear mechanisms of rubber in various ways and one convenient system is to differentiate between four main factors:

(a) Abrasive wear, which is caused by hard asperities cutting the rubber.
(b) Fatigue wear, which is caused by particles of rubber being detached as a result of dynamic stress on a localized scale.

(c) Wear through roll formation, which occurs with a relatively high coefficient of friction between the rubber and the abrading surface.

(d) Smearing resulting from degradation of rubber from either thermal or mechanical stress.

One of the most important applications of rubber where resistance to abrasion is of great importance is tyre tread. It is generally accepted that some of the synthetic rubbers such as SBR and BR are superior to NR in abrasion resistance. However, it may be pointed out that the relative wear rating of compounds depends on the nature of the track as well as load. On very smooth surfaces SBR is superior to NR, but with increasing sharpness the difference between the two is reduced and reversals in ranking can in fact be observed. These effects could be seen in tyre tests on actual road surfaces and on vehicles of varying load. In going from passenger car tyres to truck tyres and to aircraft tyres, loading increases and the proportion of NR increases. Car tyre treads are in general based on synthetic rubber. However, truck tyre treads contain 50-100% NR and aircraft tyres, in general, are made entirely of NR.

Tyre surface temperature is another important factor influencing the relative wear rating of NR and SBR (Grosch, 1967). At low tyre surface temperatures, as encountered during winter, NR is superior; at high surface temperatures the reverse is true, the reversal occurring at about 35°C.

Resistance to degradation

Natural rubber being an unsaturated polymer, is highly susceptible to degradation by oxygen, ozone, radiation, heat, chemicals etc. Hevea rubber contains natural antioxidants, proteins and complex phenols, which protect it from deterioration during coagulation of the latex and the subsequent processing and drying of the coagulum. These natural antidegradants are lost or destroyed during further processing and hence additional protectants are needed to ensure adequate service life of end products.

The changes occurring during the degradation of rubbers could be described in three ways.

(a) Chain scission, resulting in a reduction in chain length and average molecular weight.

(b) Crosslinking resulting in a three-dimensional structure and higher molecular weight.

(c) Chemical alteration of the molecules by introduction of new chemical groups.

Natural and butyl rubbers degrade mostly by chain scission, resulting in a weak softened stock, often showing surface tackiness. Chemical analysis shows the presence of aldehyde, ketone, alcohol and other groups, resulting from oxidative attack at alpha hydrogens and double bonds. Synthetic rubbers such as SBR, polychloroprene and nitrile rubber degrade by crosslinking, resulting in brittle stocks.

Oxidative ageing

Oxygen is considered to be the most important degradant for NR. A small amount of one to two per cent of combined oxygen in rubber serves to render it useless for most applications. The oxidation of rubber is believed to take place through a free-radical chain reaction whose mechanism was first proposed by Bolland and Gee (1946). In order to prevent extensive deterioration of the rubber, it is necessary to interrupt the chain reaction and stop autocatalysis. This could be accomplished by either terminating the free radicals or by decomposing the peroxides into harmless products. Antioxidants, in fact, function this way. It is established that amine antioxidants act both by reacting with free radicals and by decomposing peroxides. Phenolic antioxidants, on the other hand, react primarily as free radical sinks or chain stoppers. Phosphites react readily with free peroxides such as ROOH to give ROH and a phosphate.

The attack by oxygen on raw rubber is different from that on vulcanized rubber. In the former case, an initial induction period is followed by rapid uptake of oxygen. With vulcanized rubber, there is no induction period and the oxygen uptake is essentially linear with time. The net result of oxygen attack on NR is an overall decrease in all properties. Tensile strength, elongation, flex life and abrasion resistance decrease progressively as oxidative ageing increases. Initially modulus and hardness increase slightly but then fall off. Antioxidants have great effect on the oxidation of rubber and as little as 0.001 per cent of a good amine antioxidant can protect rubber against oxidation for long periods.

Materials like heavy metal ions and peroxides catalyse oxidative ageing of rubbers and these are called pro-oxidants. Heavy metal ions such as copper, manganese and iron are pro-oxidants of NR. Some of the standard antioxidants, notably the aromatic diamines, are effective against metal catalysed oxidation of rubber, by forming stable coordination complexes with the ions.

The effect of heat and oxygen on rubber, in general practice, are never separated and the practical result of heat on rubber is a combination of crosslinking and an increase in the rate of oxidation.

Ozone

Ozone reacts readily with NR and the effect manifests itself in two ways.

(a) Cracks appear on the surface of rubber perpendicular to the direction of stress in rubber.

(b) A silvery film appears on the surface in unstressed rubber. This is usually called frosting.

The mechanism of ozone attack is thought to be the reaction of ozone with the double bonds in rubber to form ozonides. These are easily decomposed to break the double bond, and under strain, a crack appears. As the reaction proceeds the cracks become deeper.

Two factors which greatly influence ozone cracking are ozone concentration and the strain in the rubber. Initiation of crack is favoured by high strain and high ozone concentration.

Protection of NR stocks from ozone cracking can be accomplished by using antiozonants. Under static conditions physical antiozonants like wax which forms a bloom could be used. The bloom can act as a surface barrier against ozone. Under dynamic conditions, waxes are unsuitable and hence chemical antiozonants are employed. Blending of NR with more saturated rubber such as EPDM or EPM has also been found to be effective in protecting NR from ozone attack (Mathew, 1983; Mathew et al. 1988).

Light and weathering

Light promotes the action of oxygen at the surface of rubber, producing a film of oxidized rubber, having physical properties different from those of the original stock. The film then undergoes action by water vapour and heat to produce crazing. The oxidized layer expands and contracts on heating and drying. Finally, the oxidized layer washes away, leaving the filler exposed. The greatest amount of light damage is done by UV light. A familiar form of light ageing is the stiffening of the surface of rubber products. Products may be protected against light and weathering by the use of opaque pigments such as zinc oxide, titanium dioxide, carbon black etc. and also by certain chemicals.

Atomic radiation

The effect of radiation damage is very similar to that of heat ageing of vulcanizates. Loss of tensile strength and increase in modulus have been observed. Radiation degradation of NR has been found to be accelerated if the rubber is under strain (Alex et al. 1989). Antidegradants like p-phenylene diamine derivatives and fillers like carbon black have been found to improve radiation resistance of NR.

Permeability

Permeability of a rubber film is a measure of the ease with which a liquid or gas passes through it. The process of permeation involves absorption or solution on one side of the rubber film followed by diffusion through the film to the opposite side where evaporation takes place. In an ideal case, the quantity of gas or vapour being transmitted builds up to a constant steady level after a period of time and then

$$q = \frac{PtpA}{b} \qquad (7)$$

where q = volume of gas transmitted
P = permeability coefficient
t = time
p = partial pressure difference across the test piece
A = test piece area, and
b = test piece thickness

In many cases P is a constant for a given gas and polymer combination. The permeation of a gas through a polymer takes place in two steps, the gas dissolving in the polymer and then the dissolved gas diffusing through the polymer. The solubility constant is the amount of a substance which will dissolve in unit quantity of the polymers under specified conditions, and the diffusion constant is the amount of substance passing through unit area of a given plane in the polymer in unit time for a unit concentration gradient of the substance across the plane. It can be shown that:

$$P = SD \qquad (8)$$

where S = the solubility constant, and
D = the diffusion constant

Gases differ considerably in permeability rate since this is affected by the size of the gas molecule and its solubility in rubber. By far the lowest gas permeability among the common rubbers is shown by butyl rubber. Air permeability of NR is almost twenty times that of butyl rubber. Nitrile and chloroprene rubbers are in between. Epoxidised NR, a chemically modified form of natural rubber, has much lower air permeability than NR itself (Gelling and Porter, 1989).

Electrical properties

In general rubbers are electrically insulating and this property is widely taken advantage of in cables and in various components in electrical appliances. They can also be made anti-static and even conducting by suitable compounding. In all cases, it is the combination of the electrical properties and the inherent flexibility of rubbers which make them attractive for electrical applications. The electrical properties most commonly considered are:

Resistance or resistivity,
Power factor, and
Dielectric strength.

Maintenance of electrical properties on exposure to water is especially important when the product is to be used in wet environments.

Resistance and resistivity: As the surface of rubbers may conduct electricity more easily than the bulk, it is usual to distinguish between volume resistivity and surface resistivity. Volume resistivity is defined as the electrical resistance between opposite faces of a unit cube, whereas surface resistivity is defined as the resistance between opposite sides of a square on the surface. Insulation resistance is the resistance measured between any two particular electrodes on or in the rubber and hence is a function of both surface and volume resistivities and of the test piece geometry. Conductance and conductivity are *simply the reciprocals of* resistance and resistivity respectively.

It is not easy to make a clear distinction among insulating, anti-static and conducting rubbers. The definitions should be made with respect to *the resistance between two relevant points on a product* rather than to the resistivity of the rubber. Generally, resistances of up to 10^4 ohms are considered conductive, between 10^4 and 10^8 ohms anti-static and above 10^8 ohms insulating.

Dielectric strength: The dielectric strength of an elastomer is the voltage required to puncture a sample of known thickness and is expressed as volts per mil of thickness. The rate of voltage application, the geometry of the electrodes and of the test specimen have profound influence on the results obtained.

Dielectric constant and power factor: The dielectric constant or specific conductive capacity is a measure of an insulation's ability to store electrical energy. The dielectric constant is the ratio of the electrical capacity of a condenser using the elastomer under test as the dielectric, to the capacity of a similar condenser using air as the dielectric.

The power factor of an insulating material indicates its tendency to generate heat in service. If a capacitor using an elastomer as the dielectric is charged by a direct current and then immediately discharged, there is an energy loss in the form of heat. If this capacitor is repeatedly charged and discharged by an alternating current, the electrical loss results in heating of the dielectric. The ratio of this loss to the energy required to charge the capacitor is known as power factor.

The best electrical properties are obtained with hydrocarbon rubbers such as NR, butyl, EPDM etc. Natural rubber vulcanizates, in particular can be made to give very high electrical resistance. A comparative assessment of electrical properties of NR and chloroprene rubber has been reported (Anon. 1963) and the data are given in Table 1.

TABLE 1

	Chloroprene rubber	Natural rubber
Insulation resistance of 1.15 mm cover on No. 12 AWG wire, megohms per 300 meters.	4	4000
D.C. resistivity, ohm-cm	10^{12}	10^{15}
Dielectric strength, V per mil	400-600	400-600
Dielectric constant	6.7	2.3
Power factor, %	2.5	0.5

Thermal properties

Properties like specific heat, thermal conductivity, thermal expansion and Joule effect in rubbers are of great practical importance to the designer of rubber products, but have not been properly recognised.

Specific heat: Specific heat is the quantity of heat required to raise unit mass of the material through 1°C. It is usually determined by supplying heat to a calorimeter containing the test piece and measuring the resulting temperature rise. Except when the highest precision is required, when

TABLE 2

Physical constants of natural rubber

Property	Unvulcanized	Pure gum vulcanizate	Vulcanizate with 50 phr carbon black	Hard rubber (Ebonite)
Density, Mg m^{-3}	0.913 (0.906-0.916)	0.970 (0.920-1.000)	1.120 (1.120-1.180)	1.170 (1.130-1.180)
Thermal coefficient of volume expansion, $\beta = (1/V)\ (\delta V/\delta T)$, K^{-1}	$670 x 10^{-6}$	$660 x 10^{-6}$	$530 x 10^{-6}$ $(450-550 x 10^{-6})$	$190 x 10^{-6}$
Glass transition temperature, K	210 (199-204)	210 (201-212)	208	353
Specific heat, Cp, Cal g^{-1} $(°C)^{-1}$	0.449	0.437	0.357	0.331
Heat capacity, Cp, kJ kg^{-1}, K^{-1}	1.905	1.828	1.404	1.385
$\delta C_p/\delta T$, kJ kg^{-1} K^{-2}	$3.54 x 10^{-3}$			
Thermal conductivity, W m^{-1} K^{-1}	0.134	0.153 (0.14-0.15)	0.280	0.163 (0.160-0.180)
Heat of combustion, MJ kg^{-1}	-45.2	-44.4		-33.0
Equilibrium melting temperature, K	301 (303-312)			
Heat of fusion of crystal, kJ kg^{-1}	64.0			
Optical: Refractive index, nD	1.5191_5	1.5264_5		1.6
dn_D/dT, K^{-1}	$-37 x 10^{-5}$	$-37 x 10^{-5}$		
Electrical: Dielectric constant (1 kHz)	2.37-2.45	2.68 (2.5-3.0)		2.82 (2.8-2.9)
Dissipation factor (1 kHz)	0.001-0.003	0.002-0.04		0.0043-0.009
Conductivity (60s), fS m^{-1}	2-57	2-100		2-3000

Property	Unvulcanized	Pre-gum vulcanizate	Vulcanizate with 50 phr carbon black	Hard rubber (Ebonite)
Mechanical: Compressibility, $B = -(1/V_o)\ (\delta V/\delta P)$, MPa^{-1}	$515 x 10^{-6}$	$514 x 10^{-6}$	$410 x 10^{-6}$	$240 x 10^{-6}$
$\delta B/\delta P$, MPa^{-2}	$-2.1 x 10^{-6}$	$-2.4 x 10^{-6}$	$-1.8 x 10^{-6}$	$-0.41 x 10^{-6}$
$\delta B/\delta T$, MPa^{-1} K^{-1}	$+2.3 x 10^{-6}$	$+2.1 x 10^{-6}$		$+1.1 x 10^{-6}$
Thermal pressure coefficient, $\gamma = B/\beta$, MPa K^{-1}		1.22		
$\delta\gamma/\delta T$, MPa K^{-2}		-0.0052		
Bulk modulus (isothermal), GPa	1.94	1.95	2.44	4.17
Bulk modulus (adiabatic), GPa	2.27	2.26		
Bulk wave velocity, Vb (longitudinal wave) km s^{-1}	1.58	1.58 (1.5-1.58)	1.49	
$\delta vb/\delta T$, m s^{-1} K^{-1}	-3	-3		
Strip (longitudinal wave) velocity, V_1 (1 kHz), m s^{-1}		45 (35-51)	141	1540
Ultimate elongation, %		750-850	550-650	6 (3-8)
Tensile strength, MPa		17-25	25-35	60-80
Initiation slope of stress-strain curve,				
Young's modulus, E(60s), MPa		1.3 (1.0-2.0)	3.0-8.0	3000
Shear modulus, G(60s), MPa		0.43 (0.3-0.7)		
Shear compliance, J(60s), MPa^{-1}		2.3 (1.5-3.5)	0.5-0.7	0.0017
Creep rate (1/J) $(\delta J/\delta \log t)$, % / unit log t		2 (1-3)	8 (7-12)	
Dynamic properties				
Storage modulus, G', MPa	0.41(0.34-0.56)	0.41(0.31-0.60)	6.2(1.9-13)	1100
Loss modulus, G", MPa	0.029 (0.027-0.045)	0.0063 (0.0052-0.030)	0.68 (0.32-1.3)	45
Loss tangent, G"/G'	0.09(0.07-0.13)	0.016(0.01-0.05)	0.11(0.10-0.17)	0.040
Resilience (rebound) %	75-77	75-84	50 (45-55)	(63-67)

Values in parenthesis indicate the range.

an adiabatic calorimeter would be used, it is now usual to measure specific heat by a comparative method using differential scanning calorimetry (Richardson, 1976). It is also possible to determine the dry rubber content of raw rubber and rubber coagulum through specific heat measurements (Harris et al. 1985).

Thermal conductivity: Thermal conductivity is different for different rubber compounds, varying with the amount and conductivity of each constituent in the composition. Thermal conductivities of typical rubber compositions are (Btu/hr/Sq ft/in/°F): Chloroprene rubber 1.45, SBR 1.70, NBR 1.70 and NR 1.15. Conductivity is important to rubber technologists, because it affects the time required to heat the interior of a rubber product to the vulcanization temperature. It is also important to the designer of products in which heat is generated by vibration, flexing or friction. Care has to be taken to provide for heat dissipation in such products.

Coefficient of expansion: The coefficient of thermal expansion of rubber compositions vary with the kind and amount of filler used. Addition of fillers lowers the coefficient. The coefficient of volume expansion of rubbers is in the range of 4×10^{-4} to 7×10^{-4} per °C while that for steel is 0.3×10^{-4} per °C (Juve and Beatty, 1955). This results in shrinkage of moulded products, leading to difficulties in moulding rubber to close dimensional tolerance. In general, linear shrinkage figures fall within the range of 1.5-3.0%, depending on polymer type and filler loading.

Joule effect: When a rubber is heated under strain, it tries to contract. Its modulus of elasticity increases with rise in temperature. If the rubber is under constant load it will contract and if under constant strain it will exert a higher stress. This phenomenon is known as Joule effect and occurs only when the rubber is strained first and then heated.

Physical constants at a glance

The values of various physical properties of NR have been compiled by Wood (1966, 1976) and the same are reproduced in Table 2.

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