Kirk-Othmer Encyclopedia of Chemical Technology.

RUBBER, NATURAL

Virtually all the natural rubber [9006-04-6] EINECS 23 26890, used as of 1996, is obtained from the latex of the *Hevea brasiliensis* tree. The rubber tree grows best in a warm, damp, uniform climate, with temperatures remaining in the 24–28°C range year-round, humidity above 70%, and a well-distributed rainfall of 1800–2000 mm/yr falling on well-drained soils. It is usually limited to areas extending 15° on either side of the equator, where it can survive up to an altitude of 300 m. Rubber trees were originally found in South America, particularly in the Amazon valley, and in 1876 Sir Henry Wickham collected some 70,000 seeds at the request of the India office and brought them to Royal Botanic Gardens at Kew, in England. About 2000 of the seeds were successfully cultivated into plants, some of which were sent to Peradeniya in Sri Lanka and to Malaysia via the Singapore Botanical Gardens (1). Later shipments were sent to Indonesia, and by 1880 *Hevea* seedlings were widely distributed in Southeast Asia.

The rubber tree quickly flourished in Malaysia, where large areas of jungle were cut down and planted with rubber trees. Henry Ridley, who was appointed Director of the Singapore Botanical Gardens in 1888, did perhaps more than anyone else to encourage the planting of rubber, and in the 1890s devised modern methods of tapping that resulted in the economic harvesting of the rubber crop (2, 3). Further development, by John Parkins, of the coagulation process in which dilute acid was added to the latex also helped to develop the economic viability of the plantation industry.

By the end of the nineteenth century, there were 2500 ha of land under rubber cultivation in Southeast Asia. The start of the automotive era shortly afterward caused a rocketing demand for rubber, and by 1910 there were 500,000 ha of rubber planted and the countries of Southeast Asia had become the main suppliers of natural rubber worldwide.

It is thought that only 24 seedlings survived the original journey to Malaysia (4), and such a small number, coupled with selective breeding for high yield, has produced a narrow genetic base. In order to widen the base, the International Rubber Research and Development Board, in collaboration with Brazilian authorities, carried out a germplasm prospection in the Brazilian jungles in 1981.

1. Rubber Production

1.1. Dry Rubber

All commercial grades of dry rubber arise from the organization of tapping and tappers and from the methods of coagulation and processing. Rubber production is generally managed in three ways: (*1*) the tapper can be a smallholder with 2–20 ha who will sell the crop, either in latex or semiprocessed form; (*2*) the tapper can be an employee of a self-contained estate or plantation of several thousand hectares with the whole operation of dry rubber production managed by the estate; or (*3*) the tapper can be part of a government-sponsored cooperative and will deliver the crop to central manufacturing stations.

The first cultivated rubber trees produced 500 kg/ha of rubber and selective breeding over the years has resulted in yields during the mid-1990s as high as 3000 kg/ha. However, average yields in the principal producing countries can vary from 400–1200 kg/ha. In Malaysia the smallholder sector produces about 850 kg/ha, whereas the estate plantations can produce about 1200 kg/ha.

1.2. Latex and Its Collection

The latex from the *Hevea brasiliensis* tree is a colloidal dispersion consisting of nonrubber substances and rubber particles in an aqueous serum phase. The rubber hydrocarbon constitutes 30–45% of the whole latex; the nonrubber substances account for 3–5%. Rubber particles vary in size from 0.15–3 μ and contain 90–95% natural rubber, ie, *cis*-1,4-polyisoprene, with a molecular weight distribution of 10^5–10^7 g/mol. The shape of the molecular weight distribution curve, which varies from a skewed unimodal to a bimodal distribution, and the molecular weight of natural rubber is determined by clone (5, 6). In natural rubber, latex coagulation takes place under acid conditions at about pH 5. Coagulation can either be induced by the deliberate addition of acid or occurs naturally in the tapping cup by reaction with acids produced by bacterial action, ie, autocoagulation.

Rubber latex is formed and stored in rings of latex vessels found in the soft bark region of the tree, which lies between the inner cambium tissue and the outer hard bark layers. The physiological role of latex in the rubber tree is undetermined, as of 1996; however, the mechanism of production and methods of tapping are well understood (7, 8). Latex is collected from the rubber tree by tapping once every two or three days. A tree is tapped by carefully cutting into the trunk with a special knife that removes a thin slice of bark and severs the latex vessels without affecting the normal sap circulatory system. The cut is made at an angle of 25–30° halfway around the circumference of the trunk, and at the lowest point a short metal spout is inserted, from which the latex flows into cups and is collected four to five hours later. It is also possible to apply a stimulant such as Ethephon (9), the active ingredient of which is 2-chloroethanephosphonic acid; the latter releases ethylene gas to increase the time during which latex flows and thus increase yield with a reduced tapping frequency. Unless the latex is to be processed immediately, a small amount of preservative, eg, ammonia, is added to prevent premature coagulation before the latex is brought to a factory or smallholder processing center. Rubber collected in this manner is known as field latex.

Latex continues to drip after the initial collection and coagulates naturally in the cup to form cup lump. Coagulum which forms as a film of latex on the tapped cut, called tree lace, or from latex that has dripped onto the ground, called earth scrap, is collected the next day along with the cup lump. Some smallholders may not collect the latex at all, but allow it to coagulate in the cup and collect it as cup lump. All these methods produce rubber known as field coagulum.

1.3. Grade Production of Dry Natural Rubber

Field latex and field coagulum are the source materials for all varieties and grades of dry natural rubber that include the conventional International grades as well as the Technically Specified Rubbers (TSR).

1.3.1. Conventional Grades

Classification of traditional grades such as ribbed smoked sheet (RSS) is based on the source of raw materials and processing methods. Visual grading and comparison with international samples depend on factors such as color, cleanliness, and uniformity of appearance as described in the "Green Book," which lists all 35 grades (10). A schematic diagram of the routes by which conventional grades are produced is shown in Figure 1. Of all the 35 traditional grades, only ribbed smoked sheet and pale crepes are traded in any substantial quantity, because cup lump materials are used to make the lower grades of Technically Specified Rubbers.

1.3.1.1. Sheet Rubber. In large-scale operations, field latex is first preserved with either ammonia, sodium sulfite, or formalin and then diluted to ∼15% dry rubber content (DRC) and strained into

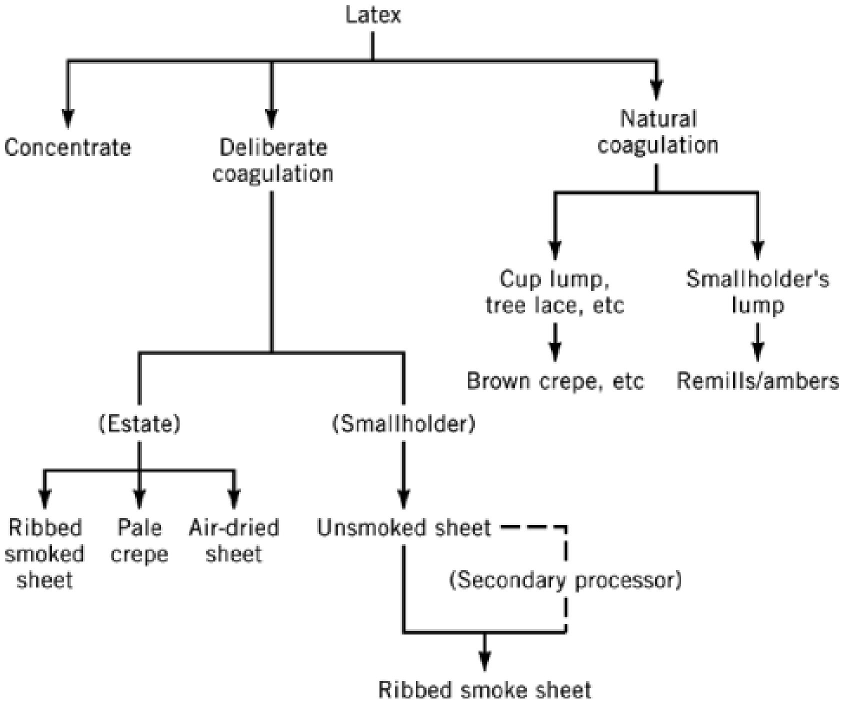

Fig. 1. Routes by which natural rubber latex is converted into traditional sheet and crepe.

coagulating tanks. Formic acid (5 wt %) is added and the acidified latex left to stand for several hours in tanks to coagulate. Separators are positioned in the tank so that after coagulation the spongy coagulum is in the form of a continuous sheet. Water is squeezed from the coagulum by passing it through as many as six pairs of rollers to produce a thin sheet. Grooves on the last pair of rollers introduce the characteristic criss-cross rib markings on the sheet to aid drying by increasing the rubber surface area. Wet sheets are dried on trolleys in a smokehouse at 60°C over a period of about a week, and the resulting ribbed smoked sheets (RSS) are pressed into 112-kg bales. The bales are coated with a talc slurry to prevent bales sticking to each other during transport.

1.3.1.2. Pale Crepes. Sri Lanka is the largest producer of crepe rubber, as either thin pale crepe or thick pale crepe, which accounts for 35% of rubber production. Pale crepes are divided into one of three classes, depending on the manufacturing process (11, 12): fractionated and bleached rubber (FB); unfractionated, but bleached rubber (UFB); or yellow fraction rubber (YF).

Light-colored pale crepes are made by selecting clonal species that give latices with low levels of naturally occurring yellow pigments (carotenoids) and so do not darken as much as other grades. However, sodium bisulfite is added to reduce this enzymatic darkening. Also, fractional coagulation to remove a pigment-rich fraction may be used in conjunction with a bleaching process to produce a light-colored latex. Latex is diluted to 20% DRC, followed by acid coagulation. The coagulum is milled and thoroughly washed by passing it through grooved rollers eight to nine times to produce thin crepes 1–2 mm thick. Thick pale crepe, or sole crepe, is made by plying thin crepes together to form a laminate about 1 cm thick, the surface of which is usually ribbed. The crepes are warm-air dried at 40°C over two weeks and packed as talc-coated 102-kg bales or polyethylene wrapped 33–35-kg bales.

Table 1. Standard Malaysian Rubber (SMR) Specifications Scheme[a]

	Latex			Sheet material	Blend	Field-grade material	
Parameter	SMR CV60	SMR CV50	SMR L	SMR 5[b]	SMR GP	SMR 10	SMR 20
dirt retained on 44 μ aperture, max, wt %	0.02	0.02	0.02	0.05	0.08	0.08	0.16
ash content, max, wt %	0.50	0.50	0.50	0.60	0.75	0.75	1.00
nitrogen, max, wt %	0.60	0.60	0.60	0.60	0.60	0.60	0.60
volatile matter, max, wt %	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Wallace rapid plasticity, P_0, min			35	30		30	30
plasticity retention index (PRI), min, %[c]	60	60	60	60	50	50	40
Mooney viscosity, ML (1 + 4), 100°C[c]	60 (±5)	50 (±5)			65 (±7)	[d]	[d]
color coding marker	black	black	light green	light green	blue	brown[e]	red[f]
plastic strip color[g]	orange	orange	transparent	opaque white	opaque white	opaque white	opaque white

[a] Mandatory from Oct. 1, 1991.

[b] Two subgrades of SMR 5 are SMR 5RSS and SMR 5ADS, which are prepared by direct baling of ribbed smoked sheet and air-dried sheet (ADS), respectively.

[c] Special producer limits and related controls are also imposed by the Rubber Research Institute of Malaysia (RRIM) to provide an additional safeguard.

[d] The Mooney viscosities of SMR 10CV and SMR 20CV (not listed) are not of specification status (ca 1996). They are, however, controlled at the producer end to 60 ($+7$, -5) for SMR 10CV and 65 ($+7$, -5) for SMR 20CV.

[e] Magenta for SMR 10CV.

[f] Yellow for SMR 20CV.

[g] Plastic wrap color is transparent for all grades.

1.3.1.3. Brown and Blanket Crepes. Several grades of these types of crepe are produced, and the source materials are field coagulum, unsmoked sheets, and smoked sheet cuttings. Such raw materials are thoroughly washed and blended through a series of crepers to produce long strips which are dried for two weeks in naturally ventilated buildings or by heating. When dry, the crepes are packed into talc-coated 102-kg bales.

1.3.2. Technically Specified Grades

The introduction of the Standard Malaysian Rubber (SMR) scheme in 1965 marked a turning point in the whole approach of production and marketing of natural rubber. The scheme was so successful that it led to the adoption of an international scheme for Technically Specified Rubber (TSR). These schemes led to fewer grades, all with guaranteed specifications relating to quality, packed in small, polyethylene-wrapped 33.3-kg bales for easy transport, storage, and factory handling. Faster drying processes for crumb rubber improved the efficiency of producing factories, and the technical specifications gave consumers a guarantee of quality that had not been previously available for the conventional grades.

A significant revision to the SMR scheme was introduced in 1991 in response to consumer desire for greater consistency in natural rubber (13). Other producing countries have similar specification schemes (14), as does the International Standards Organization (ISO) (15). An example of the specifications for TSR is given in Table 1 for the present Standard Malaysian scheme. Exceptfor SMR 5, rheograph and cure test data (delta torque, optimum cure time, and scorch) are provided.

Production of TSR is different from conventional rubber production, and Figure 2 shows the relationship between source materials and SMR grades; other producing countries have similar methods of production.

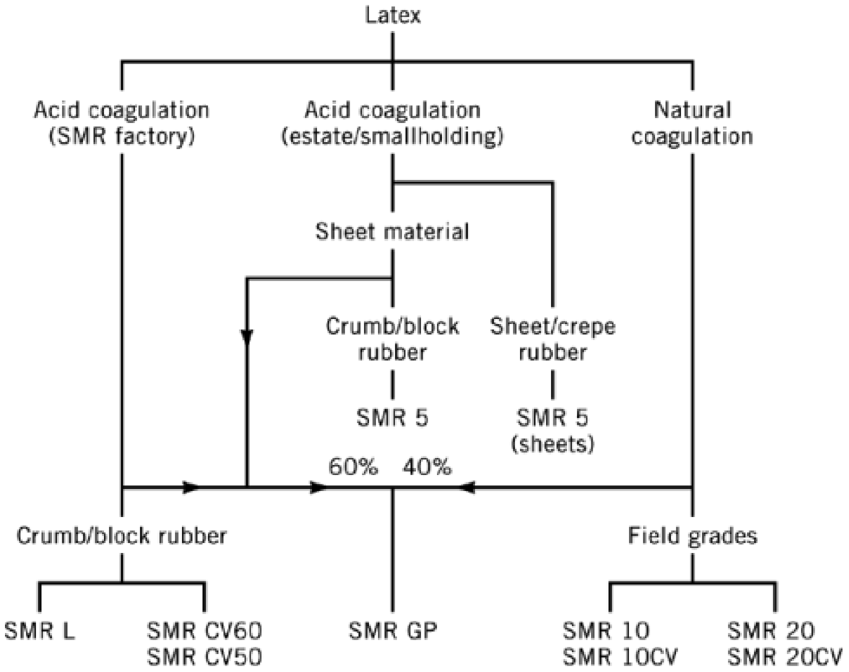

Fig. 2. Source materials and production processes used to make the various grades of Standard Malaysian Rubber (SMR).

The conversion of liquid latex to the SMR latex grades is a large-scale factory operation, involving the use of heavy-duty processing equipment. The incoming latex is bulked and blended and formic acid is added to reduce the pH to 5.0–5.2 and to produce rapid coagulation. The coagulum is covered with water and allowed to mature for about 16 h. Dewatering, cracking, and comminution of the coagulum is obtained by hammer mills, granulators, shredders, and pelletizers and produces small, uniformly sized crumbs. There are two processes for crumbing natural rubber, the Heveacrumb process where castor oil is used and the comminution process where no castor oil is used. In the Heveacrumb process, 0.3% castor oil is added before coagulation to facilitate the process of comminution to a crumb form, and any excess oil is removed in subsequent washing operations. In all operations the final wet crumbs are dried in deep bed or conveyor driers at 100–120°C for four to five hours, followed by cooling, baling, and wrapping.

Field coagulum is also converted to crumb form by similar size-reducing processes, but first it is important to wash the field coagulum thoroughly to remove bark and other contamination. The Heveacrumb process may also be used in the production of field-grade rubbers. Figure 3 shows two schematic diagrams illustrating typical processes involved in the production of latex and field-grade rubbers.

1.3.2.1. TSR L. TSR L is a color-specified rubber, and the light amber color is produced by selecting clones with a low carotenoid content. After collection, the field latex is preserved with a mixture of ammonia and boric acid and subsequently treated using 0.05% sodium metabisulfite to inhibit enzymic darkening. The latex is coagulated by addition of formic acid and allowed to mature for up to 12 h. The resulting coagulum is processed into crumb form, followed by hot air drying at 100°C for roughly five hours. The dried crumbs are cooled to 60°C and compressed into standard bales of 33.3 kg and wrapped in polyethylene.

The color of TSR L is measured with a Lovibond Comparator using methods outlined in the relevant International Standard (16). Raw rubber is molded into a disk 1.6 mm thick, and the color is compared and matched with that of standard glass disks. These glass disks provide a color index scale in which the

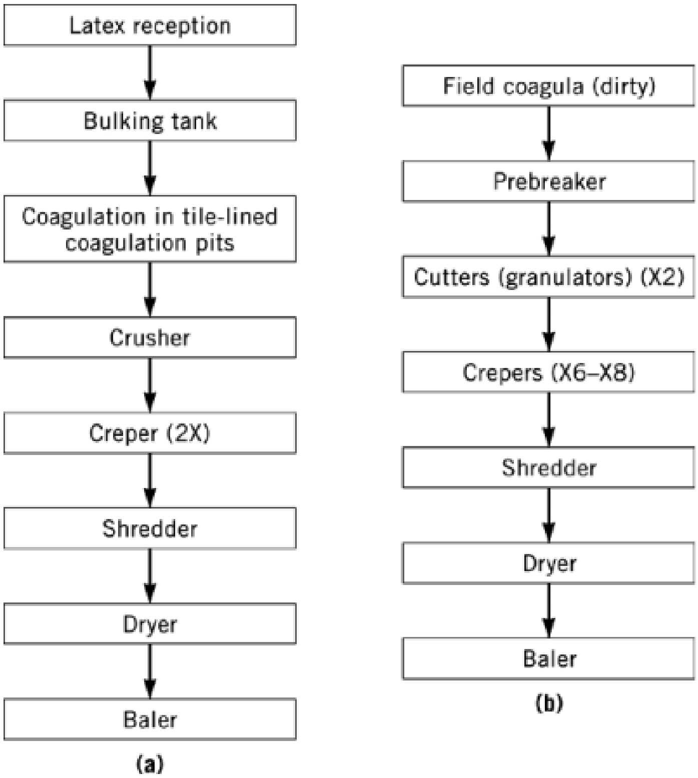

Fig. 3. Typical factory processing lines for (**a**) latex-grade rubber, and (**b**) field-grade rubber.

higher index values correspond to darker colors. Generally the specification for TSR L is a maximum Lovibond individual value of 6 and range $(\max) = 2$.

1.3.2.2. TSR CV. Natural rubber undergoes an irreversible increase in viscosity which occurs during transport and storage. This storage-hardening can be effectively inhibited by the addition of 0.15% hydroxylamine neutral sulfate (HNS) to ammonia-preserved latex prior to acid coagulation. The coagulum is then processed normally to produce TSR CV60 and TSR CV50 grades which have guaranteed Mooney viscosity ranges of 60 ± 5 and 50 ± 5, respectively.

1.3.2.3. TSR 5. Within the Malaysian scheme SMR 5 is restricted to rubber derived from sheet material prepared by conventional processes, ie, ribbed smoked sheet (RSS), air-dried sheet (ADS), and unsmoked sheet (USS) and presented in small bale form. Other countries may source different raw materials, eg, Indonesia produces SIR 5 from thin latex coagulum (14). SMR 5 prepared by pressing dry-sheet material into standard bales must be identified by the type of sheet material, eg, SMR 5RSS, on the test certificate as well as on the wrapping.

1.3.2.4. SMR GP. SMR GP is a general-purpose (GP) grade of viscosity-stabilized rubber made using a 60:40 mixture of latex-grade rubber sheet material and field coagulum. Its specifications are similar to SMR 10, with the additional guaranteed specification of Mooney viscosity ($65 + 7 - 5$). Not less than 20% (dry weight) must be latex or sheet material of SMR 5 quality, processed in an SMR factory or designated processing center. The balance of the sheet material may be USS or RSS. SMR GP can be produced by two methods, the wet process and the dry process. In the wet process, cleaned crumbs of field coagulum are mixed with latex containing HNS and coagulated by the addition of formic acid. The mixture is then processed in the normal way to produce crumb rubber. The dry process involves the application of HNS as a concentrated spray onto mixed dried latex and field-grade rubber, which are then blended in an extruder, followed by cooling and baling.

1.3.2.5. TSR 10 and TSR 20. These field grades consist predominantly of cup lump or field coagulum, where natural coagulation of the latex has been allowed to occur in the collecting cups. The raw materials are first soaked in water, blended, then fed through a series of creper-hammermills, granulators, and shredders (methods of size reduction depend on each factory) to produce clean crumbs which are dried, then baled. Specification testing of the final rubber is carried out to determine which grade is produced and cleaner rubbers usually end up as the TSR 10 grade. Knowledge of the source of raw material and experience of processing also help to determine each grade.

1.3.2.6. TSR 10CV and TSR 20CV. Certain producing countries make viscosity-stabilized grades (controlled viscosity, CV) from field coagulum. In recognition of consumer demand for these particular grades, Malaysia introduced SMR 10CV and SMR 20CV into the revised SMR scheme in 1991. Processing is carried out using the same methods and raw materials as for other nonstabilized field grades. Viscosity stabilization is achieved by spraying HNS solution onto dried crumb before passage through a prebreaker. The Mooney viscosities of SMR 10CV and SMR 20CV are at present not of specification status. They are, however, controlled by the producer to 60 $(+7, -5)$ and 65 $(+7, -5)$, respectively (see Table 1).

2. Properties of Natural Rubber

2.1. Crystallization

Raw natural rubber may freeze or crystallize during transit or prolonged storage, particularly at subzero temperatures. The rubber then becomes hard, inelastic, and usually much paler in color. This phenomenon is reversible and must be differentiated from storage hardening. The rate of crystallization is temperature-dependent and is most rapid at $-26^{\circ}\mathrm{C}$. Once at this temperature, natural rubber attains its maximum crystallinity within hours, and this maximum is no more than 30% of the total rubber.

During crystallization, rubber molecules associate into a crystal array. As the storage temperature is increased, thermal motion of the molecules restricts crystallization until, at temperatures above 20°C, the rate is near zero. Observed melting temperatures of natural rubber depend markedly on the temperature at which crystallization occurs. Figure 4 shows a general trend in which the higher crystallization temperatures result in higher crystal melting temperatures (17). The wide range of melting temperatures exhibited by rubber crystallized at low temperature is a reflection of a polycrystalline texture that contains a large number of small crystals. The generally accepted crystal melting temperature of natural rubber is 30°C. Crystals with high melting temperature are fewer and larger than those formed at lower temperatures and take a relatively long time to form.

Frozen rubber is normally thawed by storing in a hot room at 40–50°C. Because rubber is a relatively poor thermal conductor, melting is governed by the slow conduction of heat through the bale. As the rubber melts, distinct regions of thawed and frozen rubber become apparent and a sharp boundary can be distinguished between the two (18). Palletized frozen rubber can take a considerable time to thaw; in a hot room at 50°C it takes about two weeks for the center of the pallet to reach 30°C. Dismantling frozen pallets and thawing bales singly or in well-spaced stacks obviously helps, but this can be a costly operation. Methods of dealing with frozen rubber vary from factory to factory, and consumer experience determines conditions appropriate to particular needs or limitations.

2.2. Storage Hardening

Storage hardening is a slow, irreversible increase in the Mooney viscosity of natural rubber that occurs during storage and transport; an increase of some 30 Mooney units is typical for nonviscosity stabilized grades. Hardening is thought to result from the interaction between the nonisoprenic groups, such as aldehydes,

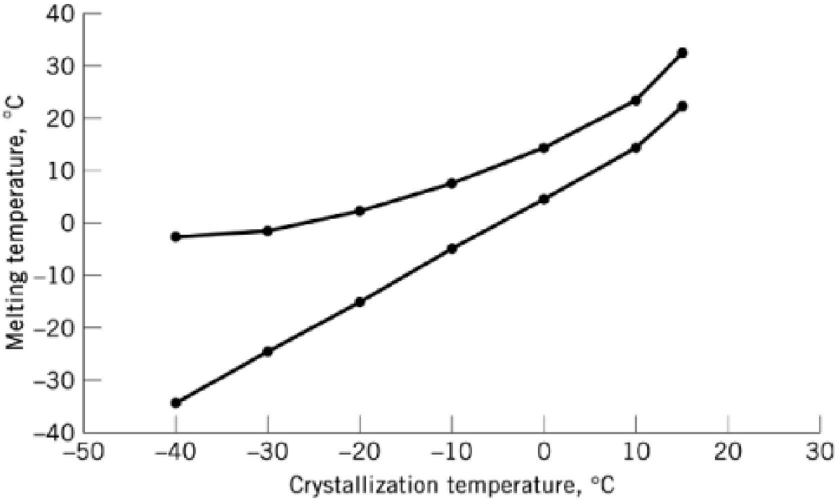

Fig. 4. Relation between crystallization temperature and melting temperature for natural rubber.

present on the rubber molecule to form cross-links, and as the rubber hardens, the extent of long-chain branching and gel increases. Storage hardening is also accelerated by high temperature and low humidity.

Many mechanisms of storage hardening are proposed and all have been reviewed (19). One of the most favored is the bimolecular aldol reaction between rubber aldehyde groups (5, 20). Nevertheless, the involvement of rubber-bound epoxide groups has also been postulated in cross-link formation (21–23), though this was later refuted (24). The hardening mechanism is certainly catalyzed by the presence of amino acids in the latex (25); however, the question of what constitutes a definitive mechanism for storage hardening has yet to be resolved.

Nevertheless, storage hardening can be effectively inhibited by the addition of a reagent such as hydroxylamine, which produces an oxime via a condensation reaction and thus blocks the cross-linking process (26). For viscosity-stabilized grades (CV) produced in this way, the viscosity increase during transit and storage is negligible.

2.3. Cure Characteristics

Methods of natural rubber production and raw material properties vary from factory to factory and area to area. Consequently, the cure characteristics of natural rubber can vary, even within a particular grade. Factors such as maturation, method and pH of coagulation, preservatives, dry rubber content and viscosity-stabilizing agents, eg, hydroxylamine-neutral sulfate, influence the cure characteristics of natural rubber. Therefore the consistency of cure for different grades of rubber is determined from compounds mixed to the ACS1 formulation (27). The ACS1 formulation is as follows: natural rubber, 100; stearic acid, 0.5; zinc oxide, 6.0; sulfur, 3.5; and 2-mercaptobenzothiazole (MBT), 0.5.

This is an activator-starved formulation and so is highly sensitive to the presence of nonrubbers that are capable of activating or accelerating vulcanization, and Table 2 illustrates the cure behavior of different grades of SMR (28). Cup lump grades show the highest state of cure and fastest rate of cure, whereas the stabilized grade, SMR CV, shows the lowest state of cure and slowest cure rate.

Although filled systems are not as sensitive to variations in this type of cure behavior, certain correlations can be made with practical vulcanizing systems (29).

Table 2. Cure Characteristics of SMR Grades Mixed to the ACS1 Formulation

	Monsanto rheometer,[a] 160°C, ±3° arc		
Grade	MHR–ML,[b] Jcm^2	T_{S2}[c], min	T_{90}[d], min
SMR CV	29.4	2.2	11.6
SMR L	33.9	1.8	9.7
SMR 5	37.2	1.5	7.8
SMR 10	40.0	1.3	6.8
SMR 20	41.1	1.2	6.8

[a] See Rheological measurements.

[b] MHR = maximum stiffness during cure minus minimum stiffness, both in a rheometer. To convert J/cm^2 to lbfin., divide by 0.0175.

[c] T_{S2} = Scorch time.

[d] T_{90} = Fractional modulus (90% of MHR–ML).

2.4. Plasticity Retention Index

The oxidation behavior of natural rubber may affect both the processing characteristics and final vulcanizate performance, and the plasticity retention index (PRI) test can be used to give an indication of both. Natural antioxidants present in natural rubber give some protection and a measure of the efficacy of protection is given by PRI. PRI% = $P_{30}/P_0 \times 100$, where P_0 is the initial Wallace plasticity and P_{30} is the plasticity after aging in an oven at 140°C for 30 min. During mastication, rubber with high values of PRI tends to break down less rapidly than rubber with a low value; normally there is little significant difference between rubbers with a PRI above a value of 60%. PRI can also be correlated with the aging performance of natural rubber vulcanizates (30). For example, raw rubber with a large PRI value gives better high temperature aging resistance, even in a formulation containing two parts of *p*-phenylenediamine antioxidant.

3. Chemistry and Technology

Natural rubber as obtained from *Hevea brasiliensis* is *cis*-1,4-polyisoprene with small amounts of nonrubber produced by the tree. Although the double-bond structure is useful for chemical modification purposes, it does not benefit natural rubber's heat resistance. Natural rubber is relatively unstable compared to the more modern almost fully saturated elastomers, such as EPDM rubber (see Elastomers, synthetic–ethylene–propylene–diene rubber). In terms of physical properties, the strain crystallizing nature of natural rubber gives it high tensile and tear strengths, and it exhibits both low heat buildup and low rolling resistance. These latter two features make it especially attractive for tire manufacture. However, unless modified, it shows extensive swelling in oils, is relatively permeable to gases, and is not generally suitable for damping applications. In the majority of applications, natural rubber is used in blends and, until fairly recently (31), remarkably little was known about the distribution of cross-links in such blends. Modern techniques have been adapted to look into this subject, with a consequent improvement in properties brought about by achieving a better balance of cross-links in the blend. In latex applications, a large proportion of the industry has moved out to the Far East, for example to Malaysia, if only because it is logical to ship the final product to the end user country rather than the latex, which contains 40% water. In general terms, the proportion of natural rubber in the total rubber market is slowly increasing (ca 1996), partly because it is technically necessary in tires for radial sidewalls, low rolling resistance, and low temperature behavior, and partly because the rubber industry is moving to the Far East, where the bulk of natural rubber is grown and is more easily available.

3.1. Vulcanization

Natural rubber is generally vulcanized with a sulfur-based system, the mechanism of which is extremely complex and has been studied for many years by a number of workers (32–35). Basically, a high sulfur, low accelerator (2.5 parts phr of sulfur and 0.5 part of sulfenamide) system results in a mainly polysulfidic cross-linked rubber that has a high tensile strength and exhibits good dynamic performance, but has relatively poor aging characteristics, even with an antidegradant present (Table 3). On the other hand, an efficient vulcanizing (EV) system based on low sulfur and high accelerator levels (see Table 3) leads to a mainly monosulfidic cross-linked network with consequent improvement in compression set and aging characteristics, but less good tensile and tear properties and inferior dynamic performance. Between them there are a multitude of semi-EV systems that fall between the high sulfur–low accelerator and low sulfur–high accelerator recipes and give a compromise in properties, as indicated in Table 3. For maximum heat resistance, as distinct from oxidative aging, there are also the Peroxide and Novor systems. The peroxide vulcanizing agents, eg, dicumyl peroxide [80-43-3], give direct carbon–carbon cross-links for extreme thermal stability. However, such systems have little or no scorch safety, unless a free-radical trap is incorporated, and they tend to require very long cure times. For example, about six times the half-life of the peroxide is needed to ensure complete decomposition; otherwise, aging performance is reduced (36). Further, *p*-phenylenediamine-type antioxidants are to be avoided, as they reduce efficiency of the cure. The virtue of peroxide vulcanization of natural rubber lies in improved heat resistance and good aging, creep, and compression set. In general, however, the vulcanizates suffer from poor low temperature crystallization performance compared to a conventional sulfur cure, and also have inferior tensile and tear properties. Urethane cross-linking systems (37), eg, Novor 950 (see Table 3) are also extremely heat resistant, but exhibit inferior tensile and dynamic properties compared to conventional sulfur-cured vulcanizates. One added virtue is that they can be used in conjunction with sulfur systems to produce an excellent compromise according to the ratios used (38).

In summary, there are a range of vulcanizing systems which can be used for natural rubber, and the choice is dependent on the combination of properties required. No single one offers ideal, all-around properties combined with good heat resistance. The end user has to be selective, according to the properties required for the final application. Certain properties such as oil resistance and gas permeability have been omitted from Table 3, because in regard to these properties natural rubber is substantially inferior to synthetic rubbers such as acrylonitrile rubber and halobutyl rubber (see Elastomers, synthetic; Rubber compounding).

3.2. Protective Systems

As in the case of sulfur vulcanization, there have been many research workers in the field of natural rubber oxidation and its protection (39, 40). The principal problem has always been to find an antioxidant that provides protection against flex-cracking, and yet does not stain. None has been found as of the mid-1990s, hence it is best to categorize the various types according to their capabilities.

The principal category of protective agents is the staining antidegradants, which protect against oxygen, ozone, and flex-cracking (see Antioxidants; Antiozonants; Amines, aromatic; Rubber chemicals). By far the most effective are the *p*-phenylenediamines. These are the *N*-alkyl-*N′*-phenyl, *N,N′*-dialkyl, and *N,N′*-diaryl compounds. As a general rule, those with the lowest molecular weight are the most reactive, but also the most volatile, most easily extracted, and the worst staining. The second category is staining antioxidants with anti-flex cracking capability only. Examples of these are diphenylamine–acetone condensates and naphthylamine derivatives. They are good antiflex cracking agents, but not as effective as the *p*-phenylenediamines. The condensates are good as general-purpose antidegradants and are used in tire compounds. The third type is made up of the low staining amine antioxidants, which include polymerized 2,2,4-trimethyl-1,2-dihydroquinoline, di-β-naphthyl-*p*-phenylenediamine, and alkylated or aralkylated diphenylamines. These impart good protection

Table 3. Properties of Carbon Black-Filled Natural Rubber Vulcanizates With Various Cure Systems[a]

Property	Cure system				
	Conventional sulfur[b]	Semi-efficient sulfur[c]	Efficient sulfur[d]	Peroxide[e]	Novor 950[f]
other components, phr					
oil	4	4	4	3	
zinc oxide	5	3.5	5	5	5
stearic acid	3	2.5	2		1
hardness, IRHD[g]	65	65	67	61	70
relaxed modulus at 100%, MPa[h]	2.08	2.22	2.34	2.28	2.60
tensile strength, MPa[h]	28.8	30.1	24.2	21.4	24.0
elongation at break, %	515	485	390	310	460
Dunlop resilience,[i] %	70	77	67	72	66
ring fatigue, 0–100%, kHz	223	106	68	51	90
Goodrich HBU,[j] °C	29	32	36	34	
compression set, 24 h at 70°C, %	27	14	10	11	
retention of tensile strength after 7 d at 100°C, %	27	46	76	51	70

[a] 100 phr SMR 5; 50 phr N330 carbon black.

[b] Plus sulfur, 2.5 parts; *N*-*t*-butyl-2-benzothiazolesulfenamide, 0.5 part; Santoflex 13, 2 parts.

[c] Plus sulfur, 1.2 parts; *N*-cyclohexyl-2-benzothiazolesulfenamide, 0.8 part; tetramethylthiuramdisulfide, 0.4 part; Santoflex 13, 2 parts.

[d] Plus sulfur, 0.33 part; 2-morpholinothiobenzothiazole, 3.0 parts; tetramethylthiuramdisulfide, 2.0 parts; Santoflex 13, 2 parts.

[e] Plus dicumyl peroxide, 2.5 parts; Flectol H, 2 parts.

[f] Plus Novor 950, 6.7 parts; Caloxol, 5 parts; zinc 2-methyldithiocarbamate, 2 parts; zinc 2-mercaptobenzimidazole, 2 parts; 2,2,4-trimethyl-1,2-dihydroquinoline (polymerized), 2 parts.

[g] IRHD = International Rubber Hardness Degrees (ISO 48).

[h] To convert MPa to psi, multiply by 145.

[i] A measure of rebound resilience (BS903: Pt. A8: 1990, Method A).

[j] HBU = heat buildup, a measure of temperature rise and resistance to fatigue (ISO 4663/3).

against heat and oxygen, and the *p*-phenylenediamine is also effective as a metal deactivator. All stain less than most of the other amine antioxidants.

Among nonstaining antioxidants, the least staining and discoloration is given by the phenolic antioxidants, such as the phenol-alkanes, hindered phenols, and hydroquinones. These give reasonably good antioxidant protection, but some are susceptible to pinking on exposure to light. For nonstaining protection against ozone attack under static conditions, waxes (qv) are used. The type of wax is determined by the service condition involved and the temperature. In general, the melting temperature of the wax should not be less than 20°C above the maximum temperature that the surface of the product is likely to reach. The wax must bloom to the surface and form a coherent layer to work satisfactorily. Finally, it is well known that traces of certain metals such as copper, manganese, and iron act as catalysts in the oxidation of natural rubber vulcanizates. Many amines and some phenolics are effective inhibitors of metal-catalyzed oxidation. Here again, *p*-phenylenediamines are particularly effective, providing their staining can be tolerated. Blends of antioxidants are also used and 2-mercaptobenzimidazole or its zinc salt have been found to be very effective.

3.3. Modified Forms of Natural Rubber

Because of the limitations in the properties of natural rubber itself, many workers, even before synthetic rubber was produced, attempted to change its structure to broaden its use into new applications. Several of these were only scientific curiosities such as, for example, hydrogenated natural rubber (41, 42) and ethyl

Table 4. Grades of Superior Processing Natural Rubber

Grade[a]	Vulcanized phase, %	Raw rubber phase, %	Oil, %
SP20	20	80	0
SP40	40	60	0
SP50	50	50	0
PA57	80	20	40
PA80	80	20	0

[a] PA = processing aid.

N-phenylcarbamoylazoformate (ENPCAF) modified natural rubber (43). However, these led the way to more practical materials such as chlorinated natural rubber (44, 45) for chemical- and heat-resistant paints and coatings, and cyclized natural rubber (46) for shoe solings, hard moldings, and industrial rollers. Although these have virtually disappeared, poly(methyl methacrylate)-grafted natural rubber, superior processing natural rubber, and epoxidized natural rubber are available. The first of these, poly(methyl methacrylate)-grafted rubber (MG rubber), is made by the polymerization of vinyl monomers with the rubber (47) to produce a material of increased modulus or hardness according to the percentage of grafting. The overall result is a modified natural rubber, which is a hard flexible material combining high rigidity with complete recovery from impact (48). MG rubber is used for hard impact-resisting rigid articles and as an adhesive. The latter use is because it contains within its molecular structure both polar poly(methyl methacrylate) and nonpolar polyisoprene components and these make it an attractive material for bonding unlike surfaces, eg, natural rubber with poly(vinyl chloride) (PVC). The second modified form of natural rubber readily available (48, 49) is superior processing rubber. This group consists of intimate mixtures of cross-linked and uncross-linked materials prepared by blending vulcanized latex with diluted field latex in proportion to percentage of vulcanized phase required. There are generally five grades available, as shown in Table 4.

As is implied by their name, superior processing (SP) rubbers provide significant manufacturing advantages. Their two-phase structure increases the stiffness and Mooney viscosity of rubber mixes and at the same time improves flow behavior. The result is faster production rates and greater throughput. Of course, the other advantage of these SP rubbers is that, unlike some other processing aids, these do not affect the final vulcanizate properties, being modified natural rubber themselves. They are used to assist in calendering, extrusion, and reworking and to reduce or eliminate air-trapping problems. They are particularly advantageous in the liquid curing or salt bath process. Here the normal practice is to extrude the rubber at as high a temperature as possible to ensure rapid vulcanization on entering the salt bath. This inevitably results in a soft extrudate liable to collapse, along with porosity problems. Replacement of half of the rubber with PA80 eliminates these problems, and also reduces die swell (see Table 4).

The third and newest modified natural rubber available is epoxidized natural rubber (ENR). This modification was actually discovered as early as 1922 (50), although the elimination of ring opening and side reactions to give a purely epoxidized material took another 50 years or so to achieve (51). The resulting polymer is a new material, with properties totally different from natural rubber, as indicated in Table 5.

Epoxidized natural rubber is still a strain crystallizing rubber and therefore retains the high tensile strength of natural rubber. However, as can be seen from Table 5, in other respects they have very little in common. The epoxidation renders a much higher damping rubber, a much-improved resistance to oil swelling (insofar as a 50 mol % modified natural rubber has similar oil resistance to a 34% nitrile rubber), and much-reduced air permeability. This latest form of modified natural rubber therefore widens the applications base of the natural material and enables it to seek markets hitherto the sole province of some specialty synthetic rubbers.

Table 5. Physical Properties of Black-Filled Epoxidized Natural Rubber[a]

Properties	NR	Epoxidized	
		25%	50%
hardness, IRHD[b]	59	56	59
modulus at 300%, MPa[c]	7.8	6.9	8.8
tensile strength, MPa[c]	27.1	25.9	27.8
elongation at break, %	550	590	560
compression set, 24 h at 70°C, %	17	15	17
Dunlop resilience, 23°C, %	78	60	25
Goodrich HBU,[d] ΔT, °C	44	46	52
volume swelling, 70 h at 70°C, %			
ASTM No. 1 oil	66	73	−5
ASTM No. 2 oil	114	28	6
ASTM No. 3 oil	191	108	21
air permeability at 23°C, $m^4/(sN) \times 10^{18}$	27.0	8.0	1.98

[a] Filler: N220 black, 30 parts phr.
[b] IRHD = International Rubber Hardness Degrees.
[c] To convert MPa to psi, multiply by 145.
[d] HBU = heat buildup.

Table 6. Typical Properties of Hard Blends of Thermoplastic Natural Rubber

Property	Blend		
flexural modulus, MPa[a]	700	900	1100
stress at yield, MPa[a]	16	19	24
tensile strength, MPa[a]	30	33	34
elongation at break, %	650	700	630
Izod impact strength at −30°C, J/m[b], [c]	>640	250	120

[a] To convert MPa to psi, multiply by 145.
[b] To convert J/m to ftlbf/in., divide by 53.38.
[c] 1-mm notch tip radius.

3.4. Thermoplastic Natural Rubber

Thermoplastic elastomers are probably the fastest-growing sector of the polymer market in the 1990s because of their easy processibility, efficiency in reuse of scrap or out-of-spec moldings, and general recycling capability. Natural rubber thermoplastic materials are based on blends of natural rubber and polypropylene (52, 53). Basically, there are two types: those with a low natural rubber content, which are really only rubber toughened forms of polypropylene, and the softer grades with high natural rubber content, which are truly classed as thermoplastic elastomers. The latter have high strength and good recovery properties, better aging than conventional natural rubber vulcanizates, and excellent ozone resistance. These materials all have to be processed on thermoplastic machinery, and 180°C is regarded as the minimum melt temperature.

The hard (low natural rubber content) grades are best regarded as rubber-modified polypropylenes. Their main attribute is impact resistance, especially at low temperatures, for any given stiffness, as shown in Table 6.

By employing additives to improve interfacial adhesion and the cohesive strength of the rubber phase, natural rubber can compete with ethylene–propylene rubbers as an impact modifier for polypropylene. These hard grades, containing between 15 and 25% natural rubber, have the potential for use in the automotive and domestic markets, eg, in bumpers, spoilers, grilles, electrical connectors, and floor tiles.

Table 7. Typical Properties of Soft Blends of Thermoplastic Natural Rubber

Property	Blend				
hardness, Shore A	50	60	69	80	90
modulus at 100%, MPa[a]	3.1	4.1	5.3	6.3	8.2
tensile strength, MPa[a]	6.5	8.8	11.2	13.2	15.3
elongation at break, %	285	315	340	370	505
tear strength, Die C, N/mm[b]	22	31	38	43	51
tension set, %	9	10	14	18	23
compression set, 24 h at 70°C, %	30	35	36	41	55
retention of tensile strength after 7 days at 100°C, %	96–98	96–98	96–98	96–98	96–98

[a] To convert MPa to psi, multiply by 145.
[b] To convert N/mm to ppi, divide by 0.175.

Table 8. Effect of Reprocessing Thermoplastic Natural Rubber

	Percentage retention				
Property	1 Recycle	2 Recycle	3 Recycle	4 Recycle	5 Recycle
modulus at 100% extension	94	92	90	87	84
tensile strength	105	103	103	99	100
elongation at break	104	107	109	108	112

The more important grades of thermoplastic natural rubber, which fall into the olefinic class of thermoplastic elastomers, are prepared with the natural rubber phase partially cross-linked during blending, a process known as dynamic vulcanization. The hardness of the soft blends is controlled by the natural rubber content, and typical properties of those of 50–90 hardness (Shore A) are shown in Table 7.

The good strength properties of the natural rubber thermoplastic blends may relate to the natural rubber phase undergoing strain-induced crystallization, as there is a distinct upturn in the stress–strain curve of the natural rubber blend which is not seen with other olefinic thermoplastic elastomers. It may be noted too that the natural rubber blend exhibits good recovery properties with compression set values of the softer materials not too dissimilar to that of a conventional high sulfur vulcanizate (see Table 3). Thermoplastic natural rubber, when correctly compounded, has excellent aging characteristics, as shown in Table 7, and ozone resistance is also high. Even the softest grades with the highest natural rubber content exhibit no cracking after exposure to 100 pphm ozone for 7 d at 40°C and 20% strain. Its recyclability is demonstrated in Table 8 where the retention of tensile strength and modulus is shown after reprocessing five times.

These thermoplastic natural rubber elastomers have a place in the modern world, where recycling has become so important, and when excessive heat is not found in service. Thus, footwear, glazing seals, sports goods, hose, domestic products, and a whole range of automotive products have already been identified for such use. It must be noted, however, that tires are not a potential market for these materials, because of the high temperatures which result from emergency braking.

3.5. Natural Rubber–Rubber Blends

The majority of natural rubber is used in blends with other elastomers. This has been common practice for many years, and most of the formulations employed by the manufacturers of rubber products have been derived empirically. It was not until 1988 that there was a method of measuring cross-link density in blends (31, 54). Using a swollen-state nmr spectroscopy technique, it has been found possible to not only measure cross-link density in natural rubber itself, but also in the individual phases of vulcanized blends. This technique has enabled studies to be made of a range of natural rubber–synthetic rubber blends and, as was expected to be

Table 9. Average Polymer Composition of Truck Tire Components,[a] %

	Tread			Sidewall			Ply/belt		
Year	NR	SBR	BR	NR	SBR	BR	NR	SBR	BR
1974	45	21	34	48	37	15	71	20	9
1981	60	12	28	44	19	37	84	11	4
1983	77	7	16	58	6	36	100		
1985	86	5	9	62		38	100		
1990	86	5	9	75		25	100		
1994	100			60		40	100		

[a] NR = natural rubber, SBR = styrene – butadiene rubber, and BR = butadiene rubber.

the case, has also shown a total imbalance of cross-link density in incompatible blends such as natural rubber and nitrile rubber (55). However, the ability to measure individual cross-link densities in such a blend and effectively confirm that the natural rubber phase is under-cross-linked enables changes to be made to redress the imbalance. Thus, by careful selection of suitable curatives, which are likely to be more soluble in the natural rubber phase, a much more even distribution of cross-links between the two polymers has been achieved, with the resulting improvement in physical properties such as tensile strength. The technique is being applied to other natural rubber–synthetic rubber blends, and it seems likely that improvements will even be made in blends of natural rubber with EPDM. This will be of immense benefit, because a combination of the virtues of these two polymers, the strength and resilience of natural rubber and the oxidation resistance of EPDM, will provide a material much sought-after by the manufacturing industry.

4. Applications

In the same way that natural rubber is predominantly used in blends, it is also predominantly used in tire manufacture. Its excellent building tack, low heat buildup, low rolling resistance, and good low temperature performance make it the polymer of choice for many parts of tire construction, for both passenger and truck vehicles. The effects of radialization and demand for low rolling resistance and good low temperature performance have all tended to benefit natural rubber, especially in truck tire construction, as shown in Table 9.

A large proportion of the circa 3.7×10^6 t/yr of natural rubber used in tires is consumed in truck tires, off-the-road tires, and aircraft tires, all of which demand a low heat buildup performance. The retreading of truck tires was also the province of natural rubber until the precured process was developed. Prior to the advent of this technique, the tack of natural rubber was essential for the unvulcanized rubber to adhere onto the buffed carcass, and the thickness of the shoulder region was such that the low heat buildup of natural rubber was essential to ensure that no failure occurred in service. With the precured tread process neither of these attributes were necessary and, synthetic rubber, which was and continues to be used, was found to give particularly good wear performance under low severity conditions, especially in the United States. However, work (56) has shown that natural rubber-based formulations can be developed which give a similar order of wear performance to the all-synthetic rubber tread, but with the additional benefit of lower rolling resistance, and hence better fuel economy.

Natural rubber was also used extensively in its oil-extended form in winter tires in the 1970s (57). Use of oil-extended natural rubber treads, found to have excellent traction on ice and snow, superseded studded synthetic rubber treads when studs were banned in certain countries and states owing to the damage they cause to partially cleared roads. This concept has been extended into all-season tires, which account for over 75% of original equipment and replacement tires in the United States. It has been shown (58) that part replacement

Table 10. End Uses of Natural Rubber

Use	Amount, 10^3 t	Percent of total
tires and related products	3800	71
latex products	585	11
footwear	210	4
nonautomotive engineering	200	4
belting and hose	80	1.5
automotive (nontire)	80	1.5
wire and cable	15	<1
other	360	7
Total world natural rubber consumption	*5333*	*100*

of styrene–butadiene rubber (SBR) in the formulation of all-season tire tread compounds with oil-extended natural rubber increases ice and snow traction, reduces rolling resistance, and has no effect on normal wet grip. Also, there is only a minor trade-off in wear performance, because below a tire surface temperature of approximately 32°C, the wear of natural rubber is superior to SBR, whereas above this temperature the reverse is true (59). Thus, wear of an all-season tire ultimately depends on the surface temperature of the tread over its annual cycle of temperatures.

Other than tire use, there are few other significantly large application areas for natural rubber that can be identified, as indicated in Table 10. The use of natural rubber in latex products covers items such as gloves, condoms, balloons, catheters and other dipped goods, latex thread, foam and carpet backing, and rubberized coir and hair. In total, latex goods consume about 11% of world rubber production. Thereafter, there are four categories: footwear, nonautomotive engineering, belting and hose, and nontire automotive applications, which consume 1.5–4% each. Footwear is self-explanatory, with the market for athletic shoes, especially those made in the Far East, tending to keep natural rubber in this market. Nonautomotive engineering applications cover the use of natural rubber in civil engineering products such as bridge bearings, off-shore oil field equipment, and the growing market for rubber–metal-laminated bearings to protect buildings against earthquakes (60, 61). This relatively new application was born out of the early work on metal-laminated natural rubber bearings for bridges, which later spawned the use of natural rubber bearings to protect buildings against ground-borne vibrations, eg, from the London Underground. This in turn developed in the 1980s into natural rubber bearings to protect buildings against earthquakes, a technique fast developing around the world in earthquake-prone areas, notably Japan, New Zealand, Italy, and the state of California in the United States. Another significant use of natural rubber is in belting and hose, where natural rubber's high strength, resilience, and fatigue performance still help to maintain its use as a premium rubber for these applications.

The nontire automotive sector includes engine mounts, where natural rubber is still regarded as the preferred polymer, and the many other rubber bearings, seals, grommets, washers, and boots used in the automotive industry for which oil-resistance is not required. It is likely that some of these items will change to thermoplastic materials, including thermoplastic natural rubber, in coming years as the demand for total recyclability of automobiles takes hold (see Recycling). The wire and cable industry has continued to use less natural rubber over the years because of its poor durability as compared to PVC and ethylene–propylene rubbers. However, improvements in blend technology may well reverse this trend if natural rubber/ethylene–propylene rubber blend properties can be optimized for the cable market.

The other miscellaneous uses of natural rubber cover a multitude of applications, none of which of themselves consume a large tonnage. Many of these are traditional uses such as pipe seals, medical closures, rollers, small solid tires, mountings for a whole range of domestic and commercial appliances, rubber balls and tubing, milking inflations, and other agricultural-based applications. In total these make up approximately another 7% of natural rubber usage, which for 1993 had a total market share of some 5.33×10^6 t.

5. Natural Rubber Latex

5.1. Preparation

Natural rubber latex has a pH of 6.5–7.0 when it emerges from the tree. Its rubber content is between 25–40% depending on the clone soil conditions, weather conditions, and time of tapping. From the moment the latex comes in contact with air, bacteria and enzymes act to reduce the pH and destabilize it. If left unchecked, the bacterial action causes the latex to coagulate within hours. A preservative must therefore be added either to the cup prior to tapping or during collection soon after flow has ceased. The traditional, and still widely used, field preservative is ammonia, which is added to the latex as a small quantity of a fairly concentrated solution. The drawback of ammonia is that it evaporates from aqueous solution, which can be unpleasant for users and can lead to changes in concentration during storage and transport. Ammonia is only effective as a bactericide above a concentration of about 0.2%; below 0.1% concentration it can actually promote bacterial growth (62). For these reasons, a 1:1 mixture of tetramethylthiuram disulfide and zinc oxide (TZ) has been used increasingly as a field preservative.

At the processing factory, the field latex is bulked into batches of at least several tons and ammoniated to a level of about 0.5%, usually with ammonia gas. Bulking has the effect of ironing out variations in rubber content and other properties of latex from various sources. Ammonia has the role of preservative, but also raises the pH of the latex which promotes hydrolysis of some natural lipids to release stabilizing fatty acid soaps. Diammonium phosphate can be added at this stage to precipitate any magnesium ions in the latex as magnesium ammonium phosphate, which settles as a sludge (61).

5.2. Concentration

The most common method of concentrating field latex is centrifugation. The two widely used types of centrifuge are the de Laval and Westfalia. Both operate by spinning the latex at high speed between a set of closely spaced conical disks. Because rubber is less dense than the water-based serum, the rubber particles tend to be concentrated toward the center of the centrifuge and the serum toward the outside. In a continuously running machine, the rubber content of the concentrate depends on the rubber content of the incoming latex and the feed rate. The output from the low rubber side of the centrifuge is called skim and generally contains about 5% rubber. This is coagulated and processed to produce skim rubber, which is considered a low grade of dry rubber owing to its high ratio of nonrubbers to rubber. After centrifuging, the rubber content of the concentrate is adjusted to 60% and final preservation is carried out. This consists of either raising the ammonia concentration to 0.7% to produce high ammonia (HA) or full ammonia latex, or keeping the ammonia level low (LA) to about 0.2% and adding a secondary preservative. The most common secondary preservative is TZ (LATZ latex) (63). The use of others, such as boric acid (LA–BA latex) and sodium pentachlorophenate (LA–SPP), has declined owing to concerns about toxicity of these products.

Although more than 90% of all latex concentrate is centrifuged, small quantities are produced by creaming and evaporation. Creaming takes advantage of the natural tendency of the rubber particles to rise to the surface of static latex. Commercially, creaming agents such as ammonium alginate are added to increase the rate of creaming (64). The process is of necessity a batch process, and it can take several weeks to achieve the required concentration.

Evaporated latex is produced in continuous evaporators, which use a combination of heat and reduced pressure to remove water from the latex. The main distinguishing features of evaporated latex is that 100% rubber recovery is achieved, but unlike the other methods, the nonrubbers are also concentrated. The most well-known evaporated latex is Standard Revertex (trade name from Revertex).

5.3. Latex Properties

Almost all latex concentrates are produced to meet an international standard, ISO 2004 (Table 11). This standard gives minimum requirements for rubber content and sets limits on some other latex properties. One of the most important properties is mechanical stability, which gives an indication of the resistance to flocculation or coagulation during processing of the latex. Mechanical stability rises naturally, particularly during the first month after concentration, owing to the chemical action of ammonia on some latex compounds (65). It can also be raised artificially by the addition of soaps to the latex. Copper and manganese concentrations are limited because of the severe degrading effects of these metals on finished products. The volatile fatty acid (VFA) number gives an indication of bacterial activity and thus shows how well the latex has been preserved (66). This is a particularly important test for low ammonia latices, which have no minimum requirement for ammonia content. For all five types in Table 11, the VFA specification (ISO 506) is as agreed by the interested parties, but not to exceed 0.20. The KOH number (ISO 127) for all five types is as agreed by the interested parties, but not to exceed 1.0. If the latex contains boric acid, the KOH number may exceed the specified value by an amount equivalent to the boric acid content as determined according to the method specified in ISO 1802. Color and odor specification are as follows: on visual inspection there should be no pronounced blue or gray; and after neutralization with boric acid, there should be no pronounced odor of putrefaction. The most important latex properties not covered by ISO 2004 are latex viscosity, magnesium content, and stability in the presence of zinc ions (67, 68).

5.4. Processing and Products

The main distinguishing feature of rubber products made from latex rather than dry rubber is the rubber thickness, which is limited to a few millimeters. The diffusion of water through rubber is so slow that the drying times of thicker-walled products would be impractically long.

In producing latex products, the chemicals required for vulcanization, stiffening, coloring, antioxidant protection, or other purposes are added as solutions, emulsions, or fine dispersions to the latex before forming the product. Because no heat is generated during this mixing, it is possible to use ultrafast accelerators that would cause scorch problems in dry rubber compounds. Indeed, it is desirable to use ultra-accelerators in latex products because it allows lower vulcanization temperatures to be used, which reduces the potential of oxidative degradation in these thin-walled products. The most widely used accelerators for latex products are the dithiocarbamates, particularly zinc diethyldithiocarbamate (ZDEC) and zinc dibutyl dithiocarbamate (ZDBC or ZBUD). Thiazoles such as zinc mercaptobenzothiazole (ZMBT) are often used as secondary accelerators with dithiocarbamates, and thiurams such as TMTD are sometimes used in place of dithiocarbamates, especially where low sulfur systems are required. Another effect of wet mixing of chemicals that distinguishes latex products from dry rubber products is that mastication does not occur and hence the original high molecular weight of the polymer is retained.

The most important group of latex products are the dipped goods, which account for more than 50% of all latex concentrate usage. Dipped goods are produced by dipping a shaped former into a suitably formulated latex compound, and then withdrawing it. The latex deposit is dried and vulcanized in hot air to give the product, which is then stripped from the former. There are three main variations on the dipping process, ie, straight, coagulant, and heat-sensitive dipping. Straight dipping gives the thinnest deposits and is used to produce condoms. The thickness is dependent primarily on the latex viscosity and rubber content. In coagulant dipping, the former is dipped in an inorganic salt solution prior to the latex dip. Thicker deposits can be produced this way and the final thickness is dependent on the latex dwell time, as well as other factors. Medical, household, and industrial gloves are produced by this method, as are many other products, such as balloons, bladders, catheters, and other medical devices. Heat-sensitive dipping is used to make the thickest latex products, such as baby-bottle nipples. It requires hot formers to be dipped into a suitably compounded heat-sensitive latex.

Table 11. ISO Specifications for Natural Rubber Latex Concentrates

	Limits					
Characteristic[a]	Type HA	Type LA	Type XA	Type HA, creamed	Type LA, creamed	Method of test
total solids content[b], %	61.5	61.5	61.5	66.0	66.0	ISO 124
dry rubber content[b], %	60.0	60.0	60.0	64.0	64.0	ISO 126
nonrubber solids[c],%	2.0	2.0	2.0	2.0	2.0	
alkalinity (as NH_3),% on latex concentrate	0.60 min	0.29	0.30 min	0.55 min	0.35	ISO 125
mechanical stability[d], s	650	650	650	650	650	ISO 35
coagulum content,%	0.05	0.05	0.05	0.05	0.05	ISO 706
copper content, mg/kg of total solids	8	8	8	8	8	ISO 8053
manganese content, mg/kg of total solids	8	8	8	8	8	ISO 7780
sludge content,%	0.10	0.10	0.10	0.10	0.10	ISO 2005

[a] Value is maximum unless otherwise specified.
[b] The requirement is for either total solids content or dry rubber content. Value is minimum.
[c] The difference between the total solids content and dry rubber content.
[d] A minimum mechanical stability may be required which is greater than the minimum value specified.

Aside from dipping, the other main products produced from natural rubber latex are elastic thread and foam products. Latex thread is produced by extruding a suitable latex compound under gravity through a tube of the appropriate diameter into an acid bath. On coming into contact with the acid, the latex gels. It is then taken through washing baths and a drying/vulcanization oven in a continuous process that results in reels of thread. This thread is used primarily in the garment industry. Latex foam is produced by mechanically incorporating air into a stabilized latex compound until the required density is achieved. The foam is gelled by either a delayed action chemical or by a heat gelation process before vulcanization and drying. The main applications of latex foam are in molded products such as mattresses and cushions, and spread foam for carpet backings. Unlike the dipped products industry, the latex foam industry has suffered from competition from synthetic styrene–butadiene rubber (SBR) latex. Many foam products can be made from either NR, SBR, or blends of the two.

Natural rubber latex is also used in adhesives for tape, packaging, envelopes, and in the footwear industry. It is used in the carpet industry as a binder for backing compounds, but this is another area in which synthetic SBR latex has competed effectively. There are a number of relatively small and specialized applications for natural rubber latex including rubberized coir or hair and cast products such as toys. Latex sheeting which is used in dental dams and for numerous other purposes can be made by dipping or casting onto a continuous belt.

5.5. Latex Allergies

Since the late 1980s there has been a great deal of attention given to the problems of allergic reactions to latex products. One reason for this is that a sharp increase in consumption of latex products in body contact applications occurred, notably medical gloves and condoms, largely as a result of concern about the spread of AIDS. In addition, there may well have been an increased incidence of sensitization to the latex allergy as a result of some poor-quality products being produced to meet the sudden upturn in demand. These factors, combined with a general increase in susceptibility of Western hemisphere populations to allergies, and a spread in awareness caused by a few publicized cases, caused an apparent eruption in this problem despite the fact that latex products of essentially the same composition had been around for decades previously.

There are two types of allergy that can be caused by latex products. Type I allergy or immediate hypersensitivity reactions are mediated by Immunoglobulin E (IgE), which is produced in the body of susceptible individuals in respect to contact with the allergen. Individuals carrying latex-specific IgE are considered to be sensitized to the allergy, and subsequent contact with latex products is likely to induce an immediate allergic response (69). The clinical manifestations of the reactions range from urticaria (nettle rash), which is the most common symptom, to anaphylaxis, which is rare but can result in loss of consciousness (70). It is clear that the components of latex products which elicit the Type I allergy are proteins and protein residues which remain in the product after manufacture. These substances do not contribute in any significant way to the properties or performance of the product but are a result of natural origin of the material. Latex product manufacturers have therefore put considerable effort into finding ways to remove or reduce the levels of allergenic proteins (71). Extensive washing or leaching, chlorination, and polymer coating of the surface are some of the main ways in which this has been achieved.

Because of the importance of residual proteins in causing Type I allergies, methods for their analysis have also been an area of great interest. Extractable proteins in latex products can be determined either chemically or by immunological methods. The chemical methods, such as the Bradford and Lowry assays, do not distinguish between allergenic and nonallergenic proteins, whereas the immunochemical methods are specific to either allergenic or antigenic proteins. Of the chemical methods of analysis, a modified Lowry method (72) has gained widest acceptance and one version of this method has been adopted by ASTM (73). Immunological methods of analysis such as radioimmunosorbant assays (rast) and enzyme-linked immunosorbant assays (elisa) are more specific and much more sensitive than the chemical methods, but require a large, homogeneous, and representative pool of sera from sensitized individuals in order to give consistent results.

The other type of allergy that can be attributed to natural rubber latex products is a Type IV allergy. This allergy also requires sensitization of the individual but the allergic response when a sensitized person comes into contact with the allergen is delayed by hours or days. The reactions are limited to localized skin complaints but the reaction can be sufficiently uncomfortable to prevent a sufferer from using natural latex products. The causes of the Type IV allergy are accelerators and antioxidants, particularly the dithiocarbamate accelerators, which are added to the latex during product manufacture. Products containing very low levels of residual accelerators have been described as hypoallergenic; however, the use of this term is discouraged, because it does not distinguish between the two types of allergy.

6. Economic Aspects

Malaysia, Indonesia, and Thailand are the three main rubber-producing countries in the world; in 1994 they contributed 73% to the world's natural rubber production, which was some 5.7×10^6 t (74). In the early 1990s the relative consumption of natural rubber has remained fairly constant at 38–39% of total rubber consumption, despite competition from synthetic rubber.

Figure 5 shows natural rubber production from 1980 to 1994 split between the three principal producing countries, Malaysia, Indonesia and Thailand, and "others." The others constitute production from (in alphabetical order) Brazil, Cambodia, Cameroon, China, Côte d'Ivoire, Gabon, India, Mexico, Nigeria, the Philippines, Sri Lanka, and Vietnam, all of which produce a varied amount of natural rubber. Figure 5 shows that Malaysian production peaked in 1988 at 1.66×10^6 t and is down to just over 1×10^6 t/yr. This has been brought about by many years of low prices causing smallholders to abandon their trees and seek employment in the fast-developing downstream industries in Malaysia, combined with a general labor shortage in the country. This has allowed Thailand to become the No. 1 natural rubber producer, with an output of 1.72×10^6 t in 1994, compared to Indonesia at 1.36×10^6 t, and Malaysia at 1.10×10^6 t. Thailand is also industrializing and it is likely to reach a peak in production in the latter half of the 1990s. Indonesia still has considerable land available for rubber planting and a plentiful labor supply, so production there is likely to increase. Nevertheless, it

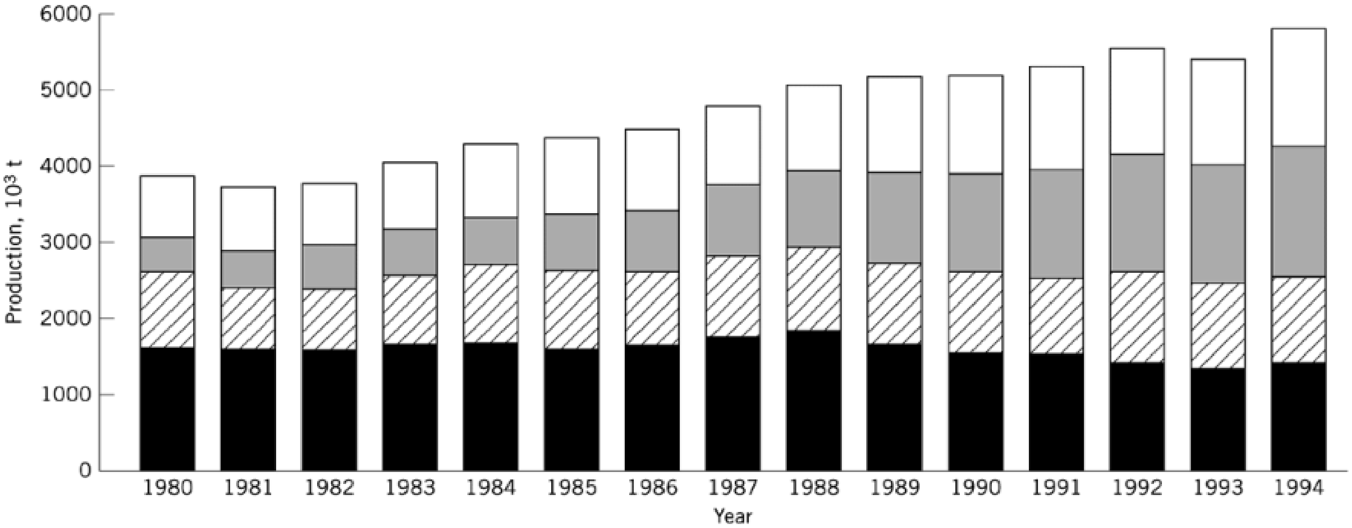

Fig. 5. Natural rubber production, where (■) represents Malaysia; (▨) Indonesia; (▣) Thailand; and (□) other.

is difficult to see where the extra natural rubber required for the year 2000 will come from, with a predicted consumption by then of some 6×10^6 t. However, world demand for natural rubber will no doubt control its price, which in turn will dictate the volume produced. Much will depend on the world economy and whether there continue to be further International Rubber Agreements prior to the year 2000.

The natural rubber industry is important in the producing countries, providing work and earning money from exports. Natural rubber and rubber products earned 4.1% of the export income for Malaysia in 1994, of which 2.1% was derived from natural rubber. A total of 1.7×10^6 ha of land were under rubber but only 1.1×10^6 ha yielded rubber, owing in part to a labor shortage. In Malaysia, about 84% of the total area planted with rubber was tapped by smallholders, who produced 72% of the rubber, with the rest produced by estates (75, 76). Indonesia (77) has a similar proportion of land (83%) cultivated by smallholders. Smallholders are becoming increasingly important for rubber production, and account for 73% of the total world area under rubber cultivation with Thailand almost 96%, and Sri Lanka, 56%. Rubber smallholders are typically self-employed farmers who depend on their land to support their families and also plant other crops to supplement their income. Estates are self-contained units owned by individuals or large companies, and large estates carry out all stages of rubber production. Smaller estates may send their rubber to other factories for processing before export.

6.1. Consumption of NR Latex

The total world consumption of natural rubber latex was 585,000 t in 1993, more than double that of 10 years earlier. The proportion of total natural rubber used as latex concentrate also increased from 7% in 1983 to 11% in 1993. Malaysia remains the dominant latex concentrate producing country in the world (Table 12). Its decline in exports during the 1980s and early 1990s has been partly compensated by an increase in consumption within the country (Table 13). Since the 1970s there has been a gradual shift in latex consumption from the traditional consumers in Europe and the United States to Asian countries. In 1994 Malaysia consumed 175,000 t of latex, more than the combined consumption of Western Europe and the United States (see Table 13).

Table 12. Net Exports of NR Latex, 10^3 t

Country	1989	1990	1991	1992	1993	1994
Malaysia	241	192	190	152	120	119
Liberia	106	40	19	28	3	1
Thailand	26	46	61	69	137	132
Indonesia	34	32	59	39	40	35

Table 13. Consumption of NR Latex, 10^3 t

Area	1989	1990	1991	1992	1993	1994
Malaysia	83	112	125	149	151	175
United States	77	74	65	82	73	73
Western Europe	94	78	71	68	67	71
China	42	31	36	54	49	80
India	36	39	35	51	52	54
Korea	29	29	26	25	24	26
Taiwan	25	24	36	32	23	19

BIBLIOGRAPHY

“Rubber, Natural” in *ECT* 1st ed., Vol. 11, pp. 810–826, by T. H. Rogers, Jr., The Goodyear Tire & Rubber Co., Inc.; in *ECT* 2nd ed., Vol. 17, pp. 660–684, by T. H. Rogers, The Goodyear Tire & Rubber Co., Inc.; in *ECT* 3rd ed., Vol. 20, pp. 468–491, by D. R. St. Cyr, Goodyear Tire & Rubber Co., Inc.

Cited Publications

1. P. R. Wycherley, *The Planter* **44**, 127 (1968).
2. H. N. Ridley, *Agric. Bull. Malay. Pen.* **7**, 136 (1897).
3. P. D. Abraham and R. A. Tayler, *Trop. Agriculture*, **44**, 1 (1967).
4. A. Aziz bin and S. A. Kadir, *Rubb. Chem. Technol.* **67**, 537 (1994).
5. A. Subramaniam, in A. Aziz bin S. A. Kodir, ed., *Proceedings of International Rubber Technology Conference*, Kuala Lumpur, 1993, Rubber Research Institute of Malaysia (RRIM), p. 19.
6. A. Subramaniam, *Technology Bulletin No. 4*, Rubber Research Institute of Malaysia, 1980.
7. J. B. Gomez, *Physiology of Latex (Rubber) Production*, MRRDB Monograph No. 8., Malaysian Rubber Research & Development Board, Kuala Lumpur, Malaysia, 1983.
8. *RRIM Training Manual on Tapping, Tapping Systems and Yield Stimulation of Hevea*, RRIM, Kuala Lumpur, Malaysia, 1980.
9. P. D. Abraham and co-workers, *J. Rubb. Res. Int. Malaya, Pts. I, II, and III* **23**, 85, 90 and 114 (1971).
10. “The Green Book,” *International Standards of Quality and Packing for Natural Rubber Grades*, Rubber Manufacturers Association, Inc., Washington, D.C., 1975.
11. R. Tharmalingam, M. C. S. Perera, and R. Gunathilake, in R. Tharmalingam, M. C. S. Perera, and R. Gunathilake, *Proceedings of IRCIND Conference*, India, 1980.
12. M. C. S. Perera, T. A. S. Siriwardene, and H. K. D. C. S. Jayawardene, *Plast. Rubb. Process. Applic.* **12**, 153 (1989).
13. *Revisions to Standard Malaysian Rubber Scheme, SMR Bull.* **11** (1991).
14. Indonesian Ministry of Trade Decree No. 184/Kp/VI/88, Jakarta, 1988.
15. ISO 2000, *Rubber, Raw Natural—Specification*, International Organization for Standardization, Geneva, Switzerland, 1989.
16. ISO 4660, *Rubber, Raw Natural—Color Index Test*, International Organization for Standardization, Geneva, Switzerland, 1991.

17. E. H. Andrews and A. N. Gent, in L. Bateman, ed., *The Chemistry and Physics of Rubber-like Substances*, Maclaren & Sons Ltd., London, 1963, p. 225.
18. G. M. Bristow and A. G. Sears, *NR Technol.* **13**, 73 (1982).
19. D. R. Burfield, *J. Nat. Rubb. Res.* **1**, 202 (1986).
20. D. R. Burfield and T. C. Tan, *Polym. Comm.* **28**, 190 (1987).
21. D. R. Burfield, *Nature* **249**, 29 (1974).
22. D. R. Burfield and S. N. Gan, *J. Polymer Sci. Polym. Chem. Ed.* **13**, 3725 (1975).
23. D. R. Burfield and S. N. Gan, *J. Polymer Sci. Polym. Chem. Ed.* **15**, 2721 (1977).
24. A. Subramaniam and W. S. Wang, *J. Nat. Rubb. Res.* **1**, 58 (1986).
25. M. J. Gregory and A. S. Tan, in M. J. Gregory and A. S. Tan, *Proceedings of International Rubber Conference*, Kuala Lumpur, Malaysia, Vol. **IV**, 1975, p. 28.
26. B. C. Sekhar, *J. Polym. Sci.* **48**, 133 (1960).
27. ISO 1658: *Natural Rubber - Test Recipes and Evaluation of Vulcanization Characteristics*, International Organization for Standardization, Geneva, Switzerland, 1973.
28. *Rubb. Devel.* **39**, 23 (1986).
29. G. M. Bristow, *NR Technol.* **11**, 59 (1980).
30. G. M. Bristow, *Rubb. Devel.* **43**, 24 (1990).
31. P. S. Brown, M. J. R. Loadman, and A. J. Tinker, *Rubb. Chem. Technol.* **65**, 744 (1992).
32. D. K. St. Cyr, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Vol. **14**, Wiley-Interscience, New York, 1988, 687–716; M. Porter, and co-workers, in N. M. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, Vol. **12**, John Wiley & Sons, Inc., New York, 195–210.
33. A. V. Chapman and M. Porter, in Roberts, ed., *Natural Rubber Science and Technology*, Oxford University Press, Oxford, U.K., 1988, 511–620.
34. A. Y. Coran, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Vol. **17**, Wiley-Interscience, New York, 1989, 666–698.
35. M. R. Krejsa and J. L. Koenig, *Rubb. Chem. Technol.* **66**, 376 (1993).
36. C. S. L. Baker, in C. S. L. Baker, *Symposium Proceedings Session B: Materials and Compounding*, Swedish Institution of Rubber Technology Fall Meeting, Boras, Sweden, 1979.
37. C. S. L. Baker, *Kaut. Gummi Kunstst.* **36**, 677 (1983).
38. C. S. L. Baker, *Vulcanization with Urethane Reagents*, NR Technical Bulletin, Malaysian Rubber Producers' Research Association, Brickendonberry, U.K., 1978.
39. R. W. Keller, *Rubb. Chem. Technol.* **58**, 637 (1985).
40. D. Barnard and P. M. Lewis, in Ref. 33, p. 621.
41. H. Staudinger and W. Feisst, *Helv. Chim. Acta* **13**, 1361 (1930).
42. D. R. Burfield, K. L. Lim, P. K. Seow, and C. T. Loo, in J. C. Rajarao and L. L. Amin, eds., *Proceedings of International Rubber Conference*, Kuala Lumpur, Malaysia, Vol. **2**, 1985, p. 47.
43. D. Barnard, K. Dawes, and P. G. Mente, *Proceedings of International Rubber Conference*, Kuala Lumpur, Malaysia, Vol. **4**, 1975, p. 215.
44. D. E. Woods, *J. Soc. Chem. Ind.* **68**, 343 (1949).
45. G. F. Bloomfield, *The Applied Science of Rubber*, Edward Arnold Ltd., London, 1961, 112–121.
46. G. F. Bloomfield and S. G. Stokes, *Trans. Inst. Rubber Ind.* **32**, 172 (1956).
47. P. W. Allen, in Ref. 17, p. 97.
48. *High Performance Natural Polymers*, Leaflet by Asiatic Development Berhad, Wisma Genting, Jalan Sultan Ismail, Kuala Lumpur, 1993.
49. Rubber Research Institute of Malaya, *Planters Bull.* **32**, 83 (1957).
50. R. Pummerer and P. A. Burkard, *Ber.* **55**, 3458 (1992).
51. I. R. Gelling, *J. Nat. Rubb. Res.* **6**, 184 (1991).

52. I. R. Gelling and A. J. Tinker, in L. L. Amin and L. K. Thong, eds., *Proceedings of the International Rubber Technology Conference*, Penang, Malaysia, 1988, p. 212.
53. D. J. Elliott, *Thermoplastic Elastomers from Rubber–Plastic Blends*, Ellis Horwood Ltd., Chichester, U.K., 1990, 102–129.
54. A. J. Tinker and M. J. R. Loaman, *Rubb. Chem. Technol.* **62**, 234 (1989).
55. P. S. Brown, S. Cook, S. A. Groves, M. V. Lewan, and A. J. Tinker, "Natural Rubber Blends," paper presented to the *ACS Rubber Division Meeting*, Orlando, Fla., Oct. 1993.
56. "Development of Natural Rubber-Based Truck Tyre Retreading Compounds," in M. E. Cain, and Siti Zubaidah bte Mohd Rashid, eds., *Proceedings of a UNIDO-sponsored Workshop*, Kuala Lumpur, Malaysia, Malaysian Rubber Producers' Research Association, Hertford, U.K., 1992.
57. J. McLellan, *Rubber Devel.* **24**, 77 (1971).
58. R. Newell and I. R. Wallace, *Kaut. Gummi Kunstst.* **45**, 380 (1992).
59. K. A. Grosch, *J. Inst. Rubber Ind.* **1**, 35 (1967).
60. V. A. Coveney, C. J. Derham, K. N. G. Fuller, and A. G. Thomas, in Ref. 33, 938–957.
61. V. A. Coveney, K. N. G. Fuller, and A. G. Thomas, *Int. Const.*, **31**, 21 (1992).
62. W. L. Resing, in T. H. Messenger, ed., *Proceedings of the Rubber Technology Conference, London*, W. Heffer & Sons, Ltd., Cambridge, U.K., 1954, p. 50.
63. C. J. John, M. Nadarajah, P. S. Rama Rao, C. M. Lau, and C. S. Ng, *Proceedings of the International Rubber Conference*, Vol. **4**, Kuala Lumpur, Malaysia, 1975, p. 339.
64. I. H. Duckworth, in I. H. Duckworth, *Proceedings of Planters Conference*, Vol. **12**, Kuala Lumpur, Malaysia, 1964, p. 134.
65. H. M. Collier, *Trans. IRI* **31**, 166 (1955).
66. D. H. Taysum, *Proceedings of Natural Rubber Conference, Kuala Lumpur*, Vol. **1**, Rubber Research Institute of Malaysia, 1960, p. 834.
67. A. D. T. Gorton and T. D. Pendle, in J. C. Rajarao and L. L. Amin, eds., *Proceedings of the International Rubber Conference*, Kuala Lumpur, Malaysia, Vol. **2**, 1985, p. 468.
68. A. D. T. Gorton and T. D. Pendle, *J. Nat. Rubber Res.* **1**, 122 (1986).
69. K. Turjanmaa, K. Laurila, S. Makinen-Kiljimen, and T. Reunala, *Contact Dermatitis* **19**, 362 (1988).
70. D. A. Levy, D. Charpin, C. Pecquet, F. Leynadier, and D. Vervloet, *Allergy* **47**, 579 (1992).
71. S. J. Dalrymple and B. G. Audley, *Rubb. Devel.* **45**, 51 (1992).
72. Y. Faridah and H. Y. Yeang, *J. Nat. Rubber Res.* **7**, 206 (1992).
73. *ASTM 5712-95*, American Society for Testing and Materials, Philadelphia, Pa., 1995.
74. *International Rubber Study Group (IRSG) Statistical Yearbook*, London, 1995, p. 2.
75. *Economic Report*, Ministry of Finance, Kuala Lampur, Malaysia, 1994/95.
76. *Statistics on Commodities*, Ministry of Primary Industries, Malaysia, July 1995.
77. The Economist Intelligence Unit, *Rubber Trends*, 1994, 1st Qtr., p. 18.

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