

Symbiotic Relations Between Natural and Synthetic Rubber

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The relations between natural and synthetic rubbers are truly of a symbiotic nature. Many of the rubber products essential to world economy today are based on blends of both types selected to provide optimum properties for the specific end use. In each case, of course, economic considerations help to determine the final composition.

Tyres probably represent the ideal case, since each part is specifically engineered, from the standpoint of materials and design, to provide optimum performance. The quantity of natural rubber in tyres varies greatly, depending upon the type and intended use. Industrial rubber products are designed with the same concepts in mind, as well as foam rubber.

The rubber industry has grown vigorously because the symbiotic relations between natural and synthetic rubbers have been most rewarding. The future of the industry will be beneficially influenced if these relations remain favourable.

Symbiosis may be broadly defined as a mutually beneficial partnership between two organisms of different kinds. Many examples exist in nature, such as the lichens (alga-fungus pairs). The tubercle-forming bacteria symbiotically associated with the roots of leguminous plants, in some way not yet clear, capture and fix free atmospheric nitrogen. Symbiosis is more widespread than is generally realised, and may occur between two plants, two animals, or a plant and an animal. Thus the concept of living together in mutual aid, assistance and support is well established in nature.

A parallel can be drawn in the complex relations between natural and synthetic rubbers which have become such an important part of our modern industrial economy. Both similarities and differences exist which will be described in this paper to emphasise the interdependency that underlies many of their applications, despite their differing origins.

A contrast may be drawn in the sources of the two major classes of rubber. Natural rubber is a true product of chemurgy. It is obtained from a plant, *Hevea brasiliensis*, and as it is harvested, it is being constantly replenished, so long as the requirements for photo-

synthesis are met. Moreover, through the research efforts of the Rubber Research Institute of Malaya and similar institutions, remarkable increases in yield are being attained by hybridisation, so that in the foreseeable future a ten-fold increase in the 1967 world average yield of 380 pounds per acre (430 kilograms per hectare) seems possible (INTERNATIONAL RUBBER STUDY GROUP, 1967). This improvement must surely rank as one of the most economically significant achievements in plant breeding of all time.

In contrast, synthetic rubbers are based on petrochemicals from fossil fuels which are slowly but surely being depleted. New discoveries of petroleum and gas continue to add to the world's proved reserves, but consumption also continues to increase dramatically, and some day in the future may outstrip new sources. Most of these fossil fuels are used to generate energy. Since the amount converted into synthetic rubbers is probably less than 0.1 per cent of the total consumption of petroleum products, we should not become unduly alarmed about future sources of raw materials for synthetic rubbers.

Symbiosis is superbly illustrated in the instance of blends of natural and synthetic rubbers. Many factors, such as cost and quality considerations, determine the types and proportions of the various elastomers used in a particular rubber product. In many cases, the optimisation process requires constant re-evaluation of these factors to arrive at the particular composition used at any particular time — in other words, a *dynamic* equilibrium is maintained with a balancing of costs, properties and performance as the critical criteria. In fact, the cases of synergism where blends are superior to either component alone outnumber those where only one is indicated, particularly for today's tyre, which we shall discuss in more detail later.

A case for symbiosis can also be made in the synthesis of polyisoprene with natural rubber properties by the use of stereospecific catalysts to polymerise isoprene in solution. Perhaps this success encouraged Professor F. Lynen, as well as researchers at N.R.P.R.A., to work out a biochemical synthesis of rubber. The success of their efforts, in turn, has encouraged us to believe that stereoregular polymers can be synthesised in aqueous systems.

MOLECULAR STRUCTURE OF ISOPRENE POLYMERS

Unravelling the microstructure of natural rubber and other isoprene polymers has challenged the analytical chemist for decades. Until recently, based on infrared absorption measurements, the generally accepted structures were as follows (*Table 1*):

The difference in chemical structure of polyisoprene between the natural polymer and its synthetic counterpart, if there is any, is very slight and occurs mainly in the content of the 3,4- addition unit. However, the validity of the method for determination of the 3,4- unit in polyisoprenes containing small amounts of this structure has been disputed since the method was first developed. It now appears that the numbers in the 3,4- column may all be 2–3 per cent high. Both near infrared and nuclear magnetic resonance measurements by CHEN (1966) of our laboratories and others strongly substantiate this recently proposed

TABLE 1. STRUCTURES OF POLYISOPRENES

| Polymer | <i>Cis</i> -1,4 | <i>Trans</i> -1,4 | 3,4- | 1,2- |
|---|-----------------|-------------------|------|------|
| Natural rubber (<i>Hevea</i>) | 98 | — | 2 | — |
| Synthetic polyisoprene (Natsyn type) | 97 | — | 3 | — |
| Synthetic polyisoprene (Shell Li type) | 94 | — | 6 | — |
| Natural <i>trans</i> -polyisoprene (Balata) | — | 98 | 2 | — |
| Synthetic <i>trans</i> -polyisoprene (Vanadium catalysed) | — | 98 | 2 | — |

view, namely, that the polyisoprenes in natural rubber, balata and their synthetic counterparts (with the exception of the lithium-catalysed polymer) consist *only* of 1,4 type structures.

However, differences in polymer chain structure such as head-to-tail type variation as well as cyclic structure and branching may exist between the natural and synthetic polyisoprenes. But as it stands now, these are more or less speculations pending future experimental verification.

An interesting point on the chemical structure of natural rubber has been made by SEKHAR (1961). There is evidence that natural rubber contains 5 to 12 aldehyde groups per million molecular weight. The storage hardening of natural rubber is attributed to cross-linking reactions involving these functional groups. Reaction with hydroxylamine hydrochloride converts them to oxime groups which cannot participate in cross-linking reactions. Rubber so treated maintains a viscosity level on storage equal to that of the original plantation rubber. We have no evidence that synthetic polyisoprene (Natsyn type) contains such functional groups, supported by the additional fact that it does not harden on storage.

The close similarity in structure between the natural and synthetic polyisoprenes does not, however, imply that their physical properties must be entirely alike. Other factors besides

microstructure play a major role in the physical properties of polymer. These include gel content, molecular weight and the distribution of molecular weights. Chain scission occurs so readily in polyisoprene that the exact values of these macromolecular physical properties depend to a great extent upon the exposure to heat, light and mechanical forces prior to the time of measurement.

PROCESSING CHARACTERISTICS

It is axiomatic that processability is a key consideration in the fabrication of virtually every rubber product. Whether processing is excellent, good or poor is often difficult to define because the standards of the consumer may vary a great deal depending upon his facilities and the nature of the end use.

Natural rubber has been highly regarded because of its high initial Mooney viscosity, its easy breakdown to a usable plasticity, its tack and green strength, and, generally, its adaptability to the fabrication techniques of the rubber factory. However, natural rubber also has significant deficiencies. Not all consumers find that the breakdown characteristics suit their special needs. Some would prefer better retention of compounded Mooney viscosity, whereas others would prefer a faster breakdown without peptisers. All consumers would like to reduce the costs associated with pre-mastication.

The synthetic polyisoprenes do offer the advantage of lower initial Mooney viscosity to eliminate the breakdown portion of the processing cycle, but they still have the easy breakdown that is so characteristic of polyisoprene molecules. On the other hand, the synthetic polyisoprenes do not yet have quite the high green strength that is typical of natural rubber, although it is adequate for many applications. Greater green strength will be tomorrow's development.

Polybutadiene has a processing advantage, or disadvantage, depending on the point of view, in that it is quite resistant to breakdown on the mill. Thus a high molecular weight polymer can be plasticised with extending oil and then processed, without losing the inherent advantage of high molecular weight. This

advantage holds for both polybutadiene and SBR, whereas polyisoprenes are somewhat at a disadvantage because of their ready chain scission.

In most cases, the stereospecific polybutadienes do not have the excellent mill behaviour of natural rubber. However, the plasticising effect of styrene in SBR does contribute to processability, so that this copolymer is easily handled, especially after years of effort to develop varieties which provide maximum ease of processing without sacrifice in quality.

Polybutadiene is also characterised by extreme lack of nerve and tack, and a tendency to 'bag' on the mill. Despite this appearance of 'nervelessness', polybutadiene stocks do not flow easily in high speed extrusions, tending to give torn edges and high die swell. Thus it was inevitable that polybutadienes find their major applications in blends with other rubbers. In mixtures with SBR or with *Hevea* (or both), processability of the stock is improved to acceptable levels.

Most polybutadienes also suffer from poor tack, and nothing short of adding polyisoprene really solves this problem. There is, of course, extensive use of 'tackifiers', but most processors will only agree that these make rubber 'stickier'. There is a clear distinction between a strong, cohesive merging of like rubbers — which we call *tack* — and the surface softening, and *weakening*, that tackifiers provide.

The ethylene-propylene terpolymers (EPDM) possess a different combination of processing characteristics. On the mill, they undergo a thermoplastic softening without breakdown which helps that phase of factory operations. But the complete lack of building tack, the relatively slow rate of cure and the lack of cure compatibility with highly unsaturated elastomers are all processing disadvantages which EPDM has had to contend with in its efforts to gain acceptance in tyres. Considerable progress has been made toward solving some of these problems, but much more effort is needed.

In the years ahead, we may see dramatic changes in rubber processing resulting from

advances in polymer synthesis. One example is the Thermoplastic polymers commercially introduced by Shell (BAILEY *et al.*, 1966). These low molecular weight polybutadiene or polyisoprene rubbers, with blocks of polystyrene at each end of the rubbery chain, have some similarities to cured rubbers below the softening point of the styrene blocks. Above this temperature, they are very soft, injection mouldable materials. Such polymers can be processed without the conventional compounding and curing steps, and readily lend themselves to automated operations.

Similarly, we have seen the liquid, castable polyurethanes capturing larger markets as a result of their simple processing, despite materials costs far in excess of those of the usual rubbers.

If this trend continues, we can foresee the day when inexpensive liquid hydrocarbons will be end-linked and cured — in a manner physically analogous to that for thermoplastics and polyurethanes — so that the mills and Banbury mixers of today may no longer be the trademark of rubber processing.

RUBBERS IN TYRES

In tyres, we see symbiosis at work to a greater degree than anywhere else in the industry. Where once a single rubber dominated the entire scene, we have observed the evolution of a complex tyre, containing several rubbers in differing blends, each blend carefully designed to accomplish a particular task, and each compound perfected to provide its own contribution to the whole. Moreover, the inter-relationships with the fabric in the carcass and in the belt (where used), as well as design features in the tread and other sections of the tyre justify the statement that the tyre is one of the most highly engineered products on the consumer market today.

It appears that these evolutionary changes will continue as we learn to take fuller advantage of the diverse properties of newer rubbers and as the polymer chemist generates still newer types for evaluation. Today, rubber usage in U.S.A. tyres is more than 75 per cent synthetic, and predictions have ranged up to 85 per cent for 1975 (*Table 2*):

TABLE 2. TRANSITION IN ELASTOMER USAGE IN TYRES (U.S.A.)

| Elastomer | 1940 | 1950 | 1960 | 1965 | 1975 |
|------------|------|------|------|------|------|
| Natural | 100 | 60 | 40 | 30 | 15 |
| SBR | | 40 | 60 | 55 | 50 |
| Stereo | | | | 15 | 30 |
| Speciality | | | | | 5 |
| % Man-made | 0 | 40 | 60 | 70 | 85 |

Some reasons for the changing use of elastomers in tyres are indicated in this comparison of tyre properties (*Table 3*):

TABLE 3. TYRE POLYMER COMPARISON

| Property | Natural | Polyisoprene | SBR | Polybutadiene | EPDM |
|--------------------|---------|--------------|-----|---------------|------|
| Treadwear | 100 | 100 | 115 | 150 | 115 |
| Resilience | 100 | 100 | 75 | 95 | 85 |
| Heat durability | 100 | 100 | 150 | 150 | 150+ |
| Cold flexibility | 100 | 100 | 90 | 120 | 100 |
| Weather resistance | 100 | 100 | 115 | 100 | 150 |

Although there are differences between natural rubber and synthetic polyisoprene in the raw polymers and in their handling characteristics, these are largely levelled out during vulcanisation. Thus these two rubbers compete primarily on a processing and cost basis — in other words, on their total all-in cost *after processing* into a tyre.

The other rubbers offer unique advantages over the polyisoprenes. SBR has long been recognised for treadwear improvement and resistance to tread cracking, and it, in turn, has had to bow to a partial replacement by polybutadiene. Additionally, the high resilience of polybutadiene, coupled with its heat

resistance and flexibility, has made it popular as a carcass component.

As for EPDM, its outstanding weather resistance has moved it into tyre sidewalls in spite of its poor compatibility with the highly unsaturated rubbers normally used in tyres.

Perhaps the best way to picture the symbiotic relations of these rubbers is to examine in some detail the construction of a passenger tyre.

The carcass of a tyre is the main strength member — it is the mass of cord plies and rubber that must flex and twist to transform engine energy into vehicle motion and to absorb the shocks and vibrations of that motion.

The carcass compound must provide an excellent bond to the fabric, and, because of the rise in temperature, heat durability is a prime consideration. The current answer to these requirements is a low-black compound with a substantial amount of natural rubber or equivalent polyisoprene, along with SBR and polybutadiene. The polyisoprene contributes good processing, resilience and strength. The SBR and polybutadiene distinctly improve ageing, and the polybutadiene also helps resilience.

The tyre tread is that part of the tyre with which we are most familiar. If the average motorist knows little else about the tyres on his automobile, he usually is quite concerned about the rate at which the tread is wearing.

This factor — abrasion resistance — is the prime consideration in a tread compound. But there must also be freedom from groove cracking. And, of course, the principal function of the tyre is traction, which the motorist seldom thinks of — except when it is missing.

These requirements are satisfactorily met by compounds that are higher in black and extended with oil. The use of blends of SBR and polybutadiene in passenger tyre treads has become widespread in recent years. The polybutadiene content has ranged up to 40 or 50 per cent of the total rubber, but such treads do not have acceptable side-slip characteristics on wet roads. The compromise that gives superior treadwear without side slip seems to be near the level of 25 per cent polybutadiene.

In the United States today, inner tubes for

passenger tyres are seldom used. Instead, the tyres are made to seal at the rim without air leakage, and the tyre is lined with a compound resistant to air diffusion. Low air diffusion is, of course, the primary liner requirement. However, since this characteristic must last for the life of the tyre, resistance to reversion in the presence of hot air under pressure becomes very important. Such a liner may be compounded from blends of chlorobutyl and polyisoprene rubbers, with oil and resins as additional ingredients.

The sides of a tyre also receive considerable punishment, so it is necessary for some protection to be provided for the carcass. This is the true function of the sidewall. There is an esthetic factor as well, since the tyre must be sold in a highly competitive market. Thus, the tyre must present a pleasing appearance and must resist the effects of long-term weathering. More importantly, however, it must continue to protect the carcass against scuffs and bruises, and it must not fatigue from constant flexing.

Hot SBR, with its freedom from pro-oxidant catalysts, has been the preferred rubber for tyre sidewalls. Recently, EPDM has made its initial entry into tyres on a commercial scale by providing added weathering protection, which is further enhanced by the use of substantial amounts of anti-ozonants and waxes.

Thus in the whole tyre, there is now an assortment of rubbers, used in a variety of compounds, each designed to do its own job, yet each engineered to energetically balance with its neighbours for the elimination of points of stress within the structure. Each compound must also be so designed that processing is reasonably easy, that building can be conveniently accomplished, and that each part of the tyre will reach optimum cure at the same time.

Our attention has been directed largely to the passenger tyre, but similar considerations apply to other types, such as truck, off-the-road and aeroplane tyres. Natural rubber is used to a larger extent in these types, although recent developments permit the use of synthetic rubber in the treads of aircraft tyres for a greater number of landings before retreading becomes necessary.

Tyre engineering has become a highly sophisticated activity from the standpoint of both materials and design. Substantial improvements in treadwear and road-handling characteristics have been obtained recently by wide tread bias/belted constructions with fibreglass in the belt and polyester or other cord in the carcass. Such constructions appear to offer a happy compromise which includes the best features of both the bias-ply and the radial-ply constructions, and provide the motorist with a substantial reduction in tyre cost per mile.

RUBBER IN INDUSTRIAL PRODUCTS

Rubbers of all varieties are employed in that broad category commonly called industrial rubber products, which include hose, belts, gaskets, seals, rubberised fabrics and many others. Natural rubber is widely used in many of these products. In some products, the more expensive synthetic rubbers are used in whole or in part because certain performance specifications can be met in no other way.

With the low cost of natural rubber that has prevailed during the past year, one might expect that many products now made with synthetics, especially the non-oil-resistant types, would be converted to the use of natural rubber. Such changes are more difficult to make than it appears. Industrial products are established on the basis of tests and specifications to define their performance. Before a change can be made, a great deal of evaluation by the manufacturer and the customer is in order. Many processing changes may be involved, such as in compounding, milling, extruding, mould lubrication and a host of others.

An interesting recent example of the competition between rubbers is that which involved Neoprene and EPDM. Because of a shortage of supply of Neoprene a couple of years ago, a number of rubber products were changed over to EPDM as the basic rubber. These included automobile trunk strips, window channel strips, irrigation ditch liners and others. The working out of a proper cure of the new synthetic was difficult, but its lower price and suitable properties for these applications offered considerable incentive for solving

the problems encountered in production. Later, Neoprene became available in ample quantity, but EPDM appears to be holding on to some of the applications acquired during the Neoprene shortage.

Although synthetic rubbers with exceptional properties, such as oil resistance, weathering resistance, high-temperature resistance, etc., have found many specific applications, it should also be recognised that natural rubber continues to be a very important factor in the industrial rubber products area. The following are illustrations of such applications in which substantial amounts of natural rubber are used:

1. A roll of conveyor belting weighing 32 000 pounds and standing nearly 13 feet in height. It contains more than a quarter of a mile length of inch-thick, 42-inch wide belting to carry crushed limestone.
2. A network of conveyor belting which is stockpiling various sizes of sand and gravel at a Texas aggregate plant.
3. A rubber conveyor belt used in the cookie manufacturing line of a California bakery.
4. Belts 450 feet in length used as moving sidewalks to transport thousands of passengers daily at the San Francisco International Airport. They are the longest moving sidewalks in the United States.
5. Belts used as moving sidewalks at the Festival of Gas Pavilion at the recent New York World Fair. Eighteen of them were used to move millions of visitors from place to place.
6. A complicated conveyor system built and assembled at our new Marysville, Ohio plant, for sorting huge quantities of limestone rock used in road building.
7. A collapsible container, called a Van-Tank, filled with 1100 gallons of latex which is being loaded aboard a freighter at Baltimore Harbour.
8. Rubber sleeves manufactured in one of our Akron plants to be used as flexible connections between pipes.

9. Rubber treads for military vehicles such as tanks, manufactured in our plants at St Marys, Ohio and Muncie, Indiana.
10. Natural rubber mountings for hay rake teeth, with a several hundred percentage increase in life span.
11. Rubber dock fenders, 19 feet in length, to protect both ship and pier at Port Everglades, Florida.
12. Flexible highway posts, which will take bumps from a car with little or no damage to either the car or the post.
13. Fenders to protect the bow and sides of a deep sea tug. The ship illustrated was fitted with more than 16 000 pounds of fenders.
14. Truck seat and air-springs in combination to provide a comfortable ride for long periods. Neoprene and natural rubber are used together in the air-spring, with the natural rubber providing superior flex properties.

These are just a few of the illustrations one could mention of the use of natural rubber in a variety of rubber products. With all the compounding experience that has accumulated over the many decades that natural rubber has been used, it would be surprising to run into an entirely new compounding problem. However, in the example of tank treads just cited, the plant chemists called to our attention a porosity condition that existed in the centre of the rubber tracks. Many formulations from the available technical literature were evaluated with very little success. Finally, a team of research chemists and physicists tackled the problem and evolved a new concept of sulphur-accelerator ratio that not only produced the desired uniformity in cure but also improved other physical properties.

The unique shear and damping characteristics of vulcanised rubber are responsible for its application as bearings for bridges and highway structures. Natural rubber now shares with Neoprene the position of having been accepted for this application by the American Association of State Highway Officials.

The transformation of natural rubber into useful derivatives by chemical reactions has been carried out commercially in three areas —

cyclisation, hydrochlorination and chlorination. Cyclised natural rubber (Pliolite) is used as a moisture-resistant paper coating and rubber hydrochloride (Pliofilm) as a food-packaging film. Chlorinated rubber (e.g., Parlon) enjoys success in speciality paint applications. Despite the large amount of effort to develop other rubber derivatives, these three are the only ones to have enjoyed some commercial success.

APPLICATIONS IN FOAM RUBBER

The foam rubber industry, which started out about thirty-five years ago with natural rubber latex as its basic raw material, represents an excellent example of symbiosis. Most latex foam articles today are made from a blend of natural and synthetic rubber latices, designed to provide the desired properties at the lowest cost. The hot SBR latices available in the early 1950's did not penetrate this field to any great extent. Foam rubber required the high stress/strain values and excellent wet gel characteristics of natural latex to make a foam of good quality, and could tolerate only 10 to 20 per cent of the lower cost synthetic. However, the situation was changed when improved synthetic latex became available from the low-temperature polymerisation process.

Urethane foam, which had its early development in Germany, started to make inroads into the higher-priced latex foam. The rapid increase in use of urethane foam was encouraged by the dramatic decrease in price of its raw materials, especially TDI (tolylene diisocyanate), which dropped from more than \$1.00 per pound in 1955 to less than 40 cents. Substantial savings were also realised by substituting lower cost polyethers for the more expensive polyesters recommended in many of the original formulations.

As one might expect, companies that supplied latex foam also began to manufacture urethane foam, and in several cases dropped latex foam completely and either went out of the 'cushioning market' completely or turned to urethane foam. Goodyear was one company that maintained its interest in latex foam and also manufactured urethane foam. The interest in latex foam was strongly supported by the

timely development in their research laboratory of a new 'cold' polymerised, large particle size SBR latex which sold at a lower price than natural latex at the time, and made latex foam more nearly competitive with urethane foam. This latex, known commercially as Pliolite Latex 5352, was also sold to other manufacturers of latex foam to provide them with a lower cost raw material. In the United States natural rubber latex, which sold at a substantially higher price, lost its hold on the foam rubber market.

Foam manufacturers in Europe did not have these lower-priced, large particle size synthetic latices readily available and did not convert to them as quickly as did American manufacturers. The price of natural rubber latex then began to drop, so there was less incentive to change, and today foam rubber produced in Europe contains a higher percentage of natural rubber. In America the natural/synthetic ratio in latex foam averages 15/85, but in Europe it is approximately 50/50.

One question why a rubber foam manufacturer does not shift his raw materials more quickly to take advantage of lower cost latex. One very important consideration is mould size, which is related to shrinkage during gelation and subsequent vulcanisation. The excellent wet gel strength of natural rubber, which is a plus factor in almost all of its applications, is a negative factor in this case. In order to change to natural rubber latex, a foam producer has to increase the size of his moulds at substantial additional expense. Around the 50/50 natural/synthetic ratio, some adjustment upward to a 70/30 ratio is possible with little effect on the shrinkage ratio.

Foam rubber manufacturers would probably agree that a 50/50 natural/synthetic blend is optimum, but costly mould replacement would be required for those now making foam with a higher synthetic content to make the change.

After the foam industry learned to use the 'cold' polymerised large particle size SBR latex, the foam was found to have certain advantages such as better ageing, improved permanent set properties, and improved odour. Natural rubber is retained for improved cigarette burning resistance and higher stress/strain values. More

uniform gelling, which is a processing advantage, is attributed to the synthetic component.

The important physical properties of moulded latex foam made of 100 per cent natural rubber, 100 per cent SBR and a 50/50 blend of natural rubber and SBR, have been summarised in Table 4.

TABLE 4. PHYSICAL PROPERTIES OF MOULDED LATEX FOAM

| Property | Natural | SBR/ Natural | SBR |
|---------------------------|---------|-----------------|-----|
| Stock efficiency | 100 | 100 | 100 |
| Odour | 90 | 95 | 100 |
| Tensile/Elongation | 100 | 75 | 50 |
| Permanent set | 95 | 97 | 100 |
| Cigarette burn resistance | 100 | 100 | 95 |
| Flex life | 100 | 100 | 100 |

Ratings of 100 for different physical properties are found in each of the three types. The tensile/elongation rating of foam rubber containing 100 per cent natural is twice that of the 100 per cent SBR. In a few applications, this property is a significant advantage, such as when foam slab is being pulled around a rigid base in order to cushion the edge. However, for practically all applications the stress/strain properties of the 100 per cent synthetic foam are adequate.

Table 5 lists some of the processing characteristics of latices when converted to foam rubber. The volume shrinkage of SBR is less than that of natural, a property which allows easier stripping from core type moulds. The other properties, especially uniformity of processing, favour synthetic.

Urethane foam outsells latex foam by an approximate 2 to 1 margin based on volume, though the ratio is more than reversed, based on tonnage or weight. However, the higher quality cushioning properties of latex foam have enabled it to hold a substantial portion

TABLE 5. PROCESSING CHARACTERISTICS OF MOULDED LATEX FOAM

| Properties | Natural | SBR/ Natural | SBR |
|-------------------------------|---------|-----------------|-----------|
| Volume shrinkage, % | 30 | 20 | 15 |
| Cure rate (min at 100°C) | 14 | 12 | 10 |
| Maturing of latex compound | Yes | Yes | No |
| De-ammoniation | Yes | Yes | No |
| Processing uniformity | Good | Very good | Excellent |

of this market and this situation is likely to continue.

A new development relating to latex foam rubber has made its appearance in several American automobiles. This is an impact-resistant foam rubber cushion that is positioned behind the front seat of the automobile and which, in case of an accident, protects the heads and faces of people riding in the rear seat. Although latex foam rubber is well noted for its excellent resilience, this new type of foam has a completely opposite characteristic—it is shock-absorbent rather than resilient, and this property extends over a wide range of temperatures. The rebound characteristics change very little as the temperature varies from -20°F (-29°C), which is not too uncommon in the northern regions of North America, up to 120°F (49°C) which the interior of a closed automobile may reach in the summer. The shock-absorbing ability of this latex foam is much superior to that of its competitor, urethane foam. Although at present the composition of the shock-absorbing foam is 100 per cent synthetic, the formulation can be adjusted to accommodate up to 50 per cent natural rubber latex.

Another application for this foam is for head rests. Resilient foams are now used for this purpose but because of serious neck and back injuries resulting from 'backlash' in automobile collisions, there is a move in the direc-

tion of shock-absorbent foam for this application. Although these cushions are relatively small, an unusually high foam density is required for satisfactory performance. The higher density also requires a higher accelerator level to give a satisfactory cure in the same factory equipment as that used for flexible cushioning foam.

Several other products utilise natural rubber latex in spite of the increasing competition from synthetic sources. Rubber thread for clothing is one area which urethane, with its excellent ageing resistance, threatened to capture a few years ago. Natural rubber thread, with low permanent stretch and more constant modulus, is maintaining a substantial share of this market.

Scrium adhesives for carpeting are made with both natural and synthetic latices, in an application where maximum pigment loading is an important requirement. Natural rubber latex enjoyed all of this business until a few years ago when it was found that certain synthetic latices, especially the carboxylic types permitted even higher loadings of pigments and thus lowered overall costs—symbiosis at its best.

High density foam rubber as carpet backing is becoming a high volume application in America. Natural latex blended with synthetic and 100 parts or more of low-cost pigment comprise the basic ingredients for this stock, which has a finished density of 10 to 11 pounds per cubic foot (160 to 177 kilograms per cubic meter). This is an excellent example of the blending of the best qualities of both types—the mechanical stability of the synthetic latex and its ability to bind a large quantity of low-cost pigment, combined with the excellent tack and superlative tensile/elongation values of the natural component.

Fire and flame resistance will be increasingly needed in many foam rubber articles of the future. The world-wide trend toward greater safety in products used in the home and automobile will require flame-resistant cushioning materials, and development of satisfactory formulations by compounding is well under way. The work of the Natural Rubber Producers' Research Association reported several

years ago on the reaction of natural rubber latex with trichlorobromomethane is also significant (COCKBAIN *et al.*, 1963). Although foam rubber can be made flame-resistant by this modification, the cost is high and ageing properties are adversely affected.

RUBBER PROCESSING TECHNIQUES

It is encouraging to note the accelerated pace with which natural rubber producers are expanding their output of new process, technically specified forms of natural rubber. It is a sure indication of a magnificent job in improving technically to meet competition. BATEMAN (1968) has estimated that these improved natural rubbers will top the 100 000-ton mark in 1968.

The symbiotic relations between natural and synthetic rubber are well illustrated in our new venture in Sumatra which employs finishing equipment originally designed and supplied for our production of *cis*-polyisoprene and other stereopolymers made by solution polymerisation processes.

Cis-polyisoprene is prepared in an aliphatic hydrocarbon solvent and the viscous polymer solution is mixed into hot water with vigorous agitation to volatilise the solvent and unreacted monomer. At this stage the rubber is in large, loosely agglomerated lumps containing about 50 per cent water, resembling natural rubber as it comes off the washer.

The wet rubber is passed through a dewatering machine which consists of a barrel with longitudinal slits which allow the water to escape. The rubber is forced through the machine by screw action and passes through a perforated plate at the end. The squeezing and mechanical working of the rubber at this stage raises the temperature to 200–220°F (95–105°C). It leaves the machine as small lumps having a reduced water content of about 10 per cent.

The rubber now goes through a devolatiliser, which is a screw-type extruder operating at about 400°F (205°C). The rubber is exposed to these conditions for only a few seconds, and then is forced through another perforated plate where it virtually explodes, expelling the remaining water as steam. The rubber pellets are

then coated and baled. Similar finishing techniques and equipment are used for *cis*-polybutadiene and in some cases for SBR.

About ten years ago, our natural rubber technologists decided to study processing techniques of this type and their possible application on the plantation. The first experiments in Akron were with natural rubber made from preserved latex and from quantities of wet cup-lump sent from Sumatra and Costa Rica. Natural rubber was found to be tougher and built up more heat going through the drier. Synthetic polymer passed through the screw quite easily, but natural rubber tended to adhere in spots and build up into oxidised lumps. Working with several engineering companies, we finally developed a machine that would commercially dry natural rubber effectively. This equipment, preceded by a washing and dirt-removal unit, is now in operation at the Dolok Merangir Estate in Sumatra.

AID TO MEDICAL RESEARCH

Before terminating this discussion, I feel that I should inject one additional facet of rubber symbiosis, namely, that man has done much to make rubber better through the years, and rubber has in turn improved man's existence.

At Goodyear Research, we have one small but important project in which our rubber experts contribute their know-how in rubber compounding and fabrication to aid our nation's medical research teams. This work dates back to some of the pioneering efforts on developing artificial hearts, arteries and heart valves, starting about 1960. I might illustrate two or three projects.

Perhaps the smallest and simplest of these prosthetic devices is a tiny T-tube, about the size of a dime (or sixpence). These tubes are intended to assist in providing a new blood supply to damaged heart muscle when a blood clot has caused a heart attack.

The idea is to quickly insert the tube in the heart muscle as soon after the heart attack as possible, so that blood from the ventricle may flood the damaged area, until the body can supply a new system of blood vessels. The unit is now being tested in animals.

Another tiny but very important contribution deals with clot prevention during the implanting of small arteries. To date, there has been no possible replacement for these arteries, because the small tubes quickly develop clots which flake off and plug the arterial system involved. Our people made a tube of conductive rubber with an inner liner of Dacron velour. The velour, with its velvet-like pile surface, successfully builds a neo-intima lining from the blood stream without clot formation.

Artery segments of this size have previously developed clots within three or four hours of implantation in dogs. Now, the medical researchers replace these arteries with confidence that clotting will not be a problem.

The heart itself is, of course, the target for complete replacement by these doctors. You will recall the heart function, involving alternating relaxation and compression action, which brings venous blood into the right ventricle, then pressures it into the lungs, next accepts the oxygenated blood into the left ventricle, and finally pressures it into the arterial system.

This same type of action is accomplished by ventricle constructions where compressed air squeezes the blood-containing inner sac. Here, we have a combination of natural and urethane rubbers. The natural rubber provides the soft, flexible inner chamber, while a high

modulus urethane is used to provide a tough outer shell. This total replacement heart combines two ventricles, plus appropriate connections for pressure monitoring. The heart has been tested in animals, and it performs well.

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