Yuko Ikeda · Atsushi Kato
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Rubber Science

A Modern Approach

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Preface

Rubber is polymeric or macromolecular, and rubber science is unquestionably an important branch of polymer or macromolecular science. Note that the two words, macromolecule and polymer, are interchangeably used widely. In most polymer science textbooks, however, there has not been adequate description of rubber to appropriately introduce readers to rubber science. If any, brief mention of rubber research by H. Staudinger, the first Nobel Prize winner from the macromolecular science arena, is made in an introductory chapter owing to the crucial contribution of rubber research in establishing the macromolecular theory. His researches on rubber were decisive in having negated the colloidal association theory of macromolecules, together with his tireless argument that one covalently bonded macromolecule could be colloidal (without any association) due to its high molar mass, i.e., macromolecular theory.

One reason for such neglect of rubber science at present might be because rubber science has been regarded as a traditional scientific area highly oriented to technical applications. Two historical events, i.e., invention of rubber vulcanization by C. Goodyear in 1839 and the beginning of mass production of pneumatic rubber tires early in the twentieth century, occurred well before the establishment of polymer science in the 1940s. That is, the rubber industry was established without much systematic assistance from the achievement of polymer science. In this historical context, the progress in rubber science has been highly dependent upon huge number of trial-and-error trials, often not much based on any modern scientific methodology for research and development.

However, the maturing of relevant disciplines including polymer and analytical science has recently created a new trend among the traditional sciences including rubber. That is, the utilization of modern and more or less sophisticated techniques has stimulated the spread of state-of-the-art methods to be used in rubber research at both university and private company laboratories. Increasing numbers of scientists and technologists are now interested in rubber not as a traditional field but as a promising one for applying the most modern scientific achievements, both theoretically and experimentally. Unfortunately for them, however, few books describing such latest scientific achievements on rubber are available, because almost all textbooks on rubber tend to describe conventional and traditional results in detail not much on the modern approaches. At the same time, this shortcoming in essence may be a continuing negative aspect of rubber science that may continue well into the middle of the twenty-first century, against its necessary and possible contribution to the sustainable development of the modern transportation society in this century.

This volume is the first trial to overcome that deficiency. It is neither conclusive nor comprehensive, but it may serve as a pilot version to meet the recent demand particularly among individuals working in rubber. It includes a few structural topics that have been disseminated in this century using X-ray scattering techniques from a modern synchrotron facility and neutrons from a nuclear reactor, plus the most recent advanced studies in the mechanics of tire manufacture. The results elucidate both the network structure and the vulcanization mechanism. Further, the most recent three-dimensional imaging technique applied to transmission electron microscopy, i.e., 3D-TEM, is used to elucidate nanofiller distribution in the rubbery matrix, which may give rise to important results for revealing the mechanism of rubber reinforcement. These techniques have recently been fundamental in lots of scientific areas and are the most urgent ones in rubber arena. The authors have done excellent work for the systematic presentation of these recent achievements, not simply to mentioning them as technical examples.

We are confident that this pilot version of a modern resource on rubber is extremely worthwhile for the future progress of rubber science in the twenty-first century. We hope that our trial efforts here will be soon followed by similar ones but from a different standpoint than ours. We are hopeful, too, that ours and other such versions will, in combination, accelerate the progress of rubber science, ultimately resulting in its much greater contribution to the sustainable development of the transportation society during this century.

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Chapter 1
Introduction to Rubber Science

1.1 Rubber and Elastomer

1.1.1 Materials and Matters

Just before studying rubber science which is a branch of materials science, we have to know the difference between material and matter. Scopes of the two words are shown in Fig. 1.1 as per the set theory, which suggests that the matter forms a larger set (ensemble) than the material. This figure also indicates that any materials are contained in the matter. (In Fig. 1.1, fact and information are shown, too, which are to be explained later.) Then, leaving the mathematical set theory, we have to ask what is the indicator or the index to qualitatively differentiate the two words? The answer is the social utility for us. In other words, usefulness is an essential property of materials, while the matter may be either of use or of no use [1–3]. In our everyday life, we use thousands of products made from various materials. Materials are either naturally occurring or synthetic. The latter materials are usually manufactured industrially via mechanical and chemical conversion processes. Surely, one of the hallmarks of modern industrialized society after the Industrial Revolution is our increasing extravagance in using synthetic materials. Currently, materials science is regarded to be among the three major technologies together with information science and biotechnology. Or, more recently, major technologies would be four, when environmental science is to be included.

On the other hand, the essence of matter (or often "substance" is used in chemistry arena) is the objective existence itself in this world, in accord with a priori assumption that the majority of natural scientists, technologists, and engineers hold unconsciously or without much thinking [1, 4–7]. The existence of matter does not have the raison d'être. In other words, it does not need to have a justification for existence [5–7], which is one of the basic features of modern science. In addition, the matter is philosophically assumed to be indestructible as a whole [6, 7]. That is, matter may be converted to the other matter, but be never nullified. This

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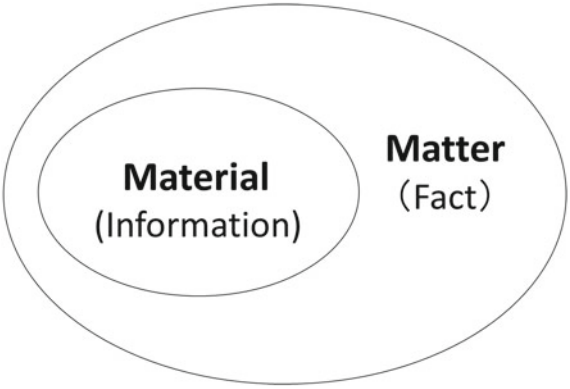


Fig. 1.1 Relationship between material and matter

philosophical understanding is related with scientific establishment of the atomic theory and the law of energy conservation by the end of nineteenth century [4, 5, 7–10]. The law was extended to accommodate matter or substance as well as energy, through the Einstein's relationship:

$$E = mc^2$$

where E is energy, m is mass, and c is the velocity of light. By the modern scientific understanding, materials are matters of use for the human beings, as explained by Fig. 1.1. In this book, rubber is described as a matter from a basic scientific standpoint, and it is also treated as a material from materials science viewpoint.

1.1.2 Materials Have Afforded the Grouping of the History of Us

Since the materials are useful for us, history of the human beings has been divided into three periods by what kind of material is mainly used at each era: the Stone Age, the Bronze Age and the Iron Age. About seven million years ago, an ape-man (*Pithecanthropus*) appeared on the earth, and it evolved into a hominid, i.e., the primitive human race, about two million and a half years ago. The human race began using a flake tool made from the stones. That is, the Paleolithic Age was started, followed by the Neolithic Age when a polished stone tool became popular. During the Stone Age, the human race learned the use of fire at about two million years ago, not only to warm their bodies but also to cook various food materials later. The importance of this event gave rise to a Greek myth that Prometheus, who had stolen the heavenly fire and gave it to a man, was punished to be chained to the mount Kavkaz by the order of Zeus. He was liberated only by Zeus's son, Herakles. Cooking a meal is basically a process of chemical change by using the fire, with some physical or mechanical changes of food materials. Combined with the invention of earthen wares as a container, the cooking extended the range of food materials and the storage time of food. Through these discoveries and inventions, the hominids were evolved into *Homo sapiens*, the present human beings. And eighty to seventy thousand years before, they began to spread worldwide from the East African Valley [11–13]. The odyssey might have ended when they arrived at the southern tip of the South American continent around twenty thousand years before.

The last glacial era was ending about twelve thousand years before the Christ (BC), when culturing of grains, specifically wheat, was started at the Crescent in the Middle East. This is the beginning of a full-scale agriculture [12–14]. Progress of agriculture necessitated more and more sophisticated stone and earthen wares. The agriculture also made constant migration of people unnecessary, to result in settling down of people permanently at a suitable place for agriculture. When they had been chasing animals and collecting fruits and nuts, they were obliged to move constantly or at least seasonally. The grains were much preservable among food materials and stored in an earthen vessel. Therefore, the supply of food became much more stable under the agricultural economy than under the previous hunting and collecting economy. The progress of agriculture at the Neolithic Age gave way to the civilization. Thus, via the short Bronze Age, the Iron Age began about four thousands BC. The spread of ironwares was, particularly, effective in bringing about civilization among many human races [15–20], together with agricultural production of food materials.

The importance of ironwares in a society is due to the versatile nature of iron as a material, and its significance is understood by the fact that the society of not yet using ironwares is often called “uncivilized.” Additionally, using ironwares has enabled mankind to make use of various materials other than iron. Under these diversification trends, the Mayan and Inca civilizations, where the ironwares were not so widely used, discovered natural rubber (NR) and manufactured rubber balls [21]. The games using the rubber ball might be of religious and/or political meanings. It is notable that Mayan and Inca civilizations were lacking ironwares and their diets lacked any wheat. Their main diets were maze and potato. Therefore, the civilizations were holding a unique position: The use of NR may be one of their peculiarities. The utilization of NR in these civilizations was, however, not much technical, and the use had been quite limited even after the encounter with European people in the sixteenth century. NR had to wait for the invention of vulcanization in 1839 by C. Goodyear (see Sect. 2.2) for its wide technical uses. In combination with the invention of pneumatic rubber tires, the rubber has been developed into an indispensable material supporting the modern transportation society, up to now [21].

The above discussion has been based on the general idea that rubber science is a branch of material science, and our history so far may be that of materials. A little mentioned transportation society is assumed to be the last stage of Materials Ages to continue to the end of this century [21], followed by the Information Age. In other words, “We are moving from the Age of Materials to that of Information” [22]. In this book, we still assume the former would be the case, at least to the end of this century. Tendency toward the Information Age might have already been recognized, coexisting with the Age of Materials. For a moment, however, materials are still more important: The most recent trend of Internet of Things (IoT) gives a support to the above recognition.

1.1.3 Science on Rubbery and Elastomeric Materials

In the twentieth century, demand of rubber for automobile tires was highlighted with the spread of automobiles: Famous Ford Model-T was marketed as early as in 2008. The price of NR was skyrocketed, which induced a strong interest in chemical preparation of synthetic rubbers, at synthetic chemistry arena [21]. Full-scale development of synthetic rubbers, however, was observed at the 1930s and the 1940s, and urgent, mass-scale developmental activities of synthetic rubbers were followed by their industrial mass production during the World War II, which did decisively open the era of present coexistence of NR and synthetic rubbers [21, 23–25]. With the increase of rubber use, the word “elastomer” has gained a frequent usage particularly in the synthetic rubber arena [24].

Quite often elastomer has been used interchangeably with rubber. However, elastomer, the origin of which is an adjective word “elastic,” means elastic materials, and it includes cross-linked rubber and thermoplastic elastomer (TPE, see Sect. 3.5.3). On the other hand, rubber includes raw rubber, rubber adhesives, and rubber glues, which are not cross-linked rubber products. More importantly, rubber is used in the technical words expressing the state and property of matter, such as “rubber elasticity”, “rubbery state”, and “rubbery matrix”. Hence, rubber is a much more versatile word than elastomer.

At present, science or learning, which is nowadays almost equivalent to science, is broken down as shown in Table 1.1.[1] (Some humanity and social scientists still do not like to use the word “science”. They prefer “learning” or “Wissenschaften” in German. For them, science means natural science only). The following two points are noteworthy in the table:

(i) Philosophy is a science to study how to understand this world and the mankind in general, while mathematics is concerned with quantity of all that are extant in this world (including our brain or mind). Hence, the two are an independent part of science. This claim is nowadays more acceptable: Philosophy on science and technology is recognized as one of the most important areas in the modern philosophy, and the use of mathematics has been increasingly popular in lots of human and social science areas, too.

(ii) Engineering, agriculture, and medicine have been recognized among natural science so far. However, they are placed separately under technology in the table. They are on technics, but science on technics had not been considered to be independent; they had been considered as an application side of mathematics, physics, chemistry, or biology.

Table 1.1 Breakdown of science in accordance with object of the study

Philosophy	View of the world	**Natural science**	Nature
Mathematics	Quantity of everything	Physical science	
Humanity science	Humanity	Physics	
Historiography		Chemistry	
Geography		Astronomy	
Literature		Geoscience (geology)	
Psychology		Biological science	
Social science	Society	Biology (botany, zoology)	
Economics		**Technology**	Technics
Jurisprudence		Engineering	Industrial technique
Sociology		Agriculture	Agricultural technique
Pedagogy		Medicine	Medical technique

This is still a traditional tendency, which is surely due to the historical reason [26, 27]. In the classical society (Greek and Roman), technical works were handled by slaves, not at all by the free citizens. Then, the philosophers (roughly equivalent to scientists nowadays) tended to be proud of not engaging in technical works: The spiritual activity, i.e., metaphysics, is for the citizens, while physical labors are for only slaves, not for citizens. This prejudice had persisted through the medieval period, and general recognition of the importance of technics was delayed until the progress of the Industrial Revolution. Steam engine was invented to give rise to industrial manufacturing, which essentially demanded the presence and supervision of engineers, not simply a manager [4, 17–20]. At the final stage of Industrial Revolution, technology, a science on technics, was recognized to be a separate subject from the natural science arenas: Technology is the science concerned with technics that are mediating between nature and the mankind (see Fig. 1.3 shown later), and it should be based on human and social sciences as well as on natural science.

Here, it is notable that the social importance of technology was first recognized not in Britain where the Industrial Revolution was developed first, but in France, then in Germany and in the USA, followed by Japan. These countries were trying to catch up Britain in terms of industrialization, and in need of as many engineers as possible. In France, the revolutionary government established *Ecole centrale des travaux* publics in 1794 in order to educate military and civil engineers, which was renamed to be famous "*Ecole polytechnique*" in 1795. "*Technische Hochschules*" and A & M (agriculture and mechanical engineering) universities were established in Germany and in many states of the USA, respectively, during the 2nd half of the nineteenth century. In Japan, a few faculties of engineering and agriculture were set up in its Imperial Universities by 1900. In Britain, many traditional universities which were established long before the Industrial Revolution (including Cambridge and Oxford) did not like to include technological colleges, since technology was regarded as the technics itself: Technology was not for learning, but was supposedly the skills simply to be practiced, for the majority of professors then, particularly in England.

Recently, the requirement of independent technology is renewed, i.e., technology as an independent science has increasingly been acknowledged by many people due to the importance of sustainable development (SD) for the future of us. In other words, further development of technology is the most urgent assignment on us for the success of SD of our modern society. In Table 1.2, a few technologies that have been established or are establishing at present are shown. The rubber science described in this book is a branch of materials science (see Sect. 3.1 for the origin of materials science), where nanotechnology is recently in a fashion as a promising subject. Some impressive results at nanoscale are presented in this book on rubber, too.

Information, an object of information science, is shown in Fig. 1.1. Facts in the world are too many to account all. Among so many facts, we have been trying to find out or to select those of much use for us to get knowledge. Then, the assembly of such knowledge is the basics for us to think. “I think, therefore I am” is correct, and it is essential for our thinking to have an assembly of the knowledge of useful facts. Both information and material are assumed to be useful for the human beings, and in order to judge their utility for us and for society, it is needed to place their science at technology arena. This process of choosing matter and fact of use, i.e., selecting materials and information, necessitates good considerations based on social and humanity studies. This is the reason of our classification materials science (and information science) into technology, not into natural science.

Biotechnology may be a very recent technological arena covering wide developmental studies in biological, agricultural, medical, and pharmacological sciences. Biomaterials are mostly soft and elastic, and rubber science is expected to play an important role in this arena, too. The more recent comer is environmental science. Environmental issues were as old as the history of mankind, but one of its beginnings as a branch of modern science is assumed to be the publication of “*Silent Spring*” in 1962, authored by Rachel Carson (1907–1964), who warned the wide environmental pollution by synthetic chemicals [28]. In Japan, the rapid industrial development in the 1950s and the 1960s often damaged the environments

Table 1.2 New technology and its object

Materials science	Material
Information science	Information
Biotechnology	Life-related technique
Environmental science	Environment

so much that in many industrial cities atmospheric air and environmental water (sea, lake, and river) were polluted to give damages to the healthy life of the inhabitants. Having recognized these negative factors of civilization, the movement involving inhabitants and scholars has pressured to create a new science, i.e., environmental science particularly in Japan [29]. Unhappy globalization of these pollution problems has accelerated the necessity of environmental science all over the world. It is still establishing itself, but from the SD viewpoint, its further progress might be uniquely crucial for the future of us.

Besides the ones listed in Table 1.2, there have appeared lots of new technologies, since the last quarter of the twentieth century. Many of them are more or less modeled after the engineering science, but have encountered a difficulty in systematizing and rationalizing themselves into the unified format from a theoretical viewpoint. Even the cybernetics, which is the oldest among them and has once enjoyed the strongest support as a novel promising scientific discipline, seems to have been absorbed into information science and biotechnology at present.

On the innovation of rubber science, too, there have been much efforts paid by many rubber technologists. Still, we have much to do for the sake of its establishment as a branch of not the traditional but of the most modern science. Rubber as a matter was turned out to be a material of much use by the invention of vulcanization in 1839, which was achieved by C. Goodyear. And the industrial manufacturing of bicycle and automobile rubber tires from NR began during the last decade of the nineteenth century, and it was established as a modern industry in the first quarter of the twentieth century, while the science of rubber was not established yet. The establishment of the macromolecular theory by H. Staudinger was in the 1930s, most probably around 1940, particularly due to the classical rubber elasticity theory (see Sects. 2.3.2 and 2.3.4). These historical facts seem to have impressed a seal of “traditional” on the science and technology of rubber as a branch of polymer science. We, rubber scientists or engineers, have to take lessons from the progress in chemistry: During the secession of several scientific disciplines such as geology, botany, geography, and anthropology into modern sciences from the traditional natural history, chemistry was establishing itself as a branch of modern science on the basis of the return of ancient atomic theory [30], with absorbing the alchemy of the Middle Age [31]. Of course, during the process of establishing chemistry as a modern science, extraordinary efforts by many scientists, such as R. Boyle (1627–91), J. Black (1728–99), J. Priestly (1733–1804), A. Lavoisier (1743–94), J. Dalton (1766–1844), and J. Berzelius (1779–1848), to name several, are surely to be noted [32–34].

The traditional “rubber science and technology” has to be innovated by adapting more modern techniques in chemistry and physics for its future progress while maintaining the essence of the traditional scientific aspects of rubber technology. The present text is intended to contribute to the progress toward the modernization of rubber science, which is to be discussed again later in Sect. 1.3.3 together with the discussions on what are technics and technology in general.

1.2 Natural Rubber: A Unique Biopolymer

1.2.1 Characteristics of Natural Rubber

Natural rubber (NR), the main chemical component of which is *cis*-1,4-polyisoprene, is a biomass; hence, it is renewable and carbon neutral, i.e., it is biosynthesized from carbon dioxide as a carbon source, and does not contribute to the increase of it in the atmosphere [21, 35–38]. Among lot of biomasses, NR is now enjoying one of the most wide industrial uses as a soft and tough material. Its unique qualities may be summarized [38] as follows.

Firstly, NR is biosynthesized in *Hevea* trees (*Hevea brasiliensis*), and the exudate, i.e., latex containing NR is collected after the incision of the trunk. These operations are called tapping, which is manually done using a special knife to give a cut on the tree trunk, a skillful operation needing a special proficiency [21, 37]. By the way, the *Hevea* tree was once named as the "Para rubber tree" which was originated from the Para port situated at the Amazon River just before flowing into the Atlantic Ocean. NR tapped at the Amazon Valley was exported via the port to the world. And the name is still widely used among botanists and agricultural scientists. Interestingly, the situation is very similar to that of "Mocha coffee": African coffee was exported through the Mocha port at the Arabian Peninsula to be known as Mocha coffee. Return to the first point, however, the fact that NRs being collected from a single species, *Hevea brasiliensis*, is recently considered to be a disadvantage from the viewpoint of biodiversity and biosecurity [21, 38–41]. We are going to face this problem of NR in a near future.

Secondly, from the nineteenth century on, the synthetic organic chemists have been successfully synthesized many natural products. However, the chemical (not biochemical) synthesis of NR has not done yet. One of the reasons is the highest stereo-regularity of *cis*-1,4-polyisoprene in NR: It contains only two or three *trans*-1,4-monomeric units at a terminal end of the linear polymeric chain. When we assume 3 *trans* units in a polymeric rubber chain, the degree of polymerization of which is one thousand (a relatively low value of NR), the ratio of units other than *cis*-1,4 is only 0.3%. Additionally, the three *trans* units are situated at one of the terminal ends of the chain. Such a stereo-regular *cis*-1,4-polyisoprene has not chemically synthesized yet [21, 39]. This high regularity gives rise to the specific feature of NR, i.e., unique strain-induced crystallization (SIC) behavior of NR (see Sect. 3.4), which is of utmost importance in evaluating most physical properties of NR. SIC is in fact a corollary of the high stereo-regularity of NR.

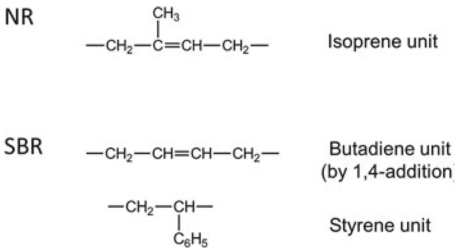
The tread rubber of tires for aircraft, which is of course an organic substance, is exposed to the harshest conditions when taking off and landing in terms of mechanical dynamic stress and friction (hence very high temperature) during the dynamic contact with the road surface of the air field. Yet, rubber tires, cap tread rubber of tire (see Chap. 5 for tread rubber) in particular, have managed to enable safe movements of aircraft on the surface of the earth, while arresting the destruction of them. SIC is regarded to be one of the responsible characters of NR for usages under so harsh a condition, together with wearing/abrasion properties of NR [38–41].

Thirdly, the elasticity of rubber is uniquely originated from entropy [21, 42]. The elasticity observed in usual matters is thermodynamically an energy originated. Other than rubber, inorganic glass is also amorphous (not crystalline, see Sect. 1.3), but its low elasticity is due to energy. In terms of elasticity, rubber has close relation with gas, the elasticity of which is entropic, too. The pneumatic rubber tires are a uniquely invented product by putting rubber and air together, to have enabled the automobiles to be driven in safety on the roads, not on the rails [21].

From these characteristics, rubber is considered to be a material of utmost importance for the sustainable development of the modern transportation society. It is fortunate for human beings to have found NR in the natural world, before the invention of synthetic rubbers. Also from the chemists' point of view, it is challenging that we have not yet succeeded in chemical synthesis of this natural product, NR.

1.2.2 *Synthetic Natural Rubber?*

NR is biosynthesized in a *Hevea* tree, and the tapping of the latex-bearing cortex of *Hevea* trees makes NR latex to exude through the incision. The latex contains the solid NR in the so-called rubber particle, and we get the solid-state NR by casting the latex onto a plate to obtain a NR thin film after evaporating the dispersant, or by coagulating the latex using aqueous acidic solution to obtain a NR bulk. Since the 2nd half of the nineteenth century, many organic chemists have challenged to the chemical synthesis of NR. However, the perfect chemical synthesis is still to be investigated in this century. Styrene-butadiene rubber (SBR) was developed in the 1930s and was industrially manufactured during the WW II. It is still mass-produced for tire rubbers of passenger cars and so on, and is one of the main rubbers for general purposes now. The chemical structure of it is shown in Fig. 1.2 with that of NR.



$$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-$$

$$-CH_2-CH=CH-CH_2-$$

$$-CH_2-\underset{\underset{\displaystyle C_6H_5}{|}}{CH}-$$

Fig. 1.2 Chemical structure of NR and SBR

In Fig. 1.2, the isoprene monomeric unit of NR is in *cis* configuration, and the chemical name of NR is *cis*-1,4-polyisoprene. SBR is a random copolymer of styrene and 1,3-butadiene (here only 1,4-addition unit is shown). Many grades of SBR are available in the market, and their properties are dependent on the content of styrene units, addition modes of 1,3-butadiene (1,2 or 1,4), *cis* or *trans* configuration of the C=C double bond, to result in covering a wide range of properties. The most popular one is manufactured by emulsion polymerization technique with styrene content of 23.5%, which is a general-purpose rubber as popular as NR (see the table in "Appendix").

Isoprene rubber (IR) was developed in the 1960s, which has almost the same chemical structure as that of NR shown in Fig. 1.2. It is uniquely called "synthetic natural rubber". Some of its properties are more or less similar to those of NR, but the stereo-regularity of IR is between 95 and 98% of *cis*-1,4, compared with almost 100% of NR. This apparently "small" difference in the stereo-regularity results in the difference between NR and IR: Several important physical properties of IR are not as good as NR, mainly due to less tendency for strain-induced crystallization (SIC, see Sect. 3.4.2). IR still remains to be a substitute of NR so far.

1.3 Rubber and Elastomer as Amorphous Polymers

1.3.1 Amorphous

Different from a crystalline state, the amorphous does not have structural regularity at the nanometer scale [43]. Gas and liquid, except liquid crystal, are amorphous. Exactly as Ziman claimed generally in his book [44] on polymeric materials, "few macromolecules form regular crystalline states, and they display complicated topologically randomized states to give rise to difficulty in analytically describing the state of them." As a matter of facts, it may not be easy to differentiate the assembly of fine crystallites and/or the para-crystals (crystals with lots of defects) from the amorphous state of polymers without using X-ray diffraction analysis. Specifically, the wide-angle X-ray diffraction (WAXD) pattern displays isotropic clear ring, and the orientation of the crystallites is random, which is the case for spherulitic crystals (see Sect. 3.4.3). When the pattern shows isotropic ring-shaped halo, the amorphous state is proved (see Sect. 3.4.1). On an amorphous phase, the random network model by Zachariasen [43–46] has been well known, and the most suitable example of it may be the rubber. For example, SBR is a random copolymer of styrene and 1,3-butadiene, and is not amenable to crystallize due to the structural randomness at nanometer scale. Additionally, even stereo-regular NR is also amorphous due to the active micro-Brownian movement of the polymeric chains. In the case of NR, however, it may crystallize (low-temperature crystallization) if kept standing at lower temperature for a long time. Also, the cross-linked NR crystallizes upon stretching, which is called strain-induced crystallization (SIC), and SIC is the origin of unique high performance of NR products. Note that SIC is reversible on stretching and contracting, and they are amorphous unless under a high strain (see Sect. 3.4 for the details of NR crystallization).

From a structural standpoint, amorphous states do not have a solid–solid interface due to the absence of a crystalline region, and hence, they apparently afford the homogeneous matrix at least macroscopically. This is a base of the statement, "Rubber is a polymeric solvent, though its viscosity is high." This liquid-like amorphous property of rubber affords much accommodating ability to rubbery matrix, enabling mixture with various powdery solids and liquids including various fillers and many reagents, ultimately soft composites of superior properties.

1.3.2 Glass Transition Temperature

Solid-to-liquid transition occurs when the crystalline materials are heated to their melting temperature (T_m). Amorphous means the absence of melting, but the rubber is soft and more or less liquid-like at room temperature. It is apparently a solid, but such appearance is due to its very high viscosity, and years of standing may display its liquid-like nature (cold flow). Combined this liquid-like nature of rubber with the amorphous nature of rubber, the rubbery matrix is known as a polymeric solvent, which can accommodate various additives, for example, carbon black as a reinforcing filler. When brought to a lower temperature than its glass transition temperature (T_g), it is exactly an amorphous solid. Heating of it to above T_g turns it to a soft polymeric solvent again (see later Sect. 2.4.1 for more detailed discussion on T_g).

Any polymeric materials whose T_g is lower than room temperature are a candidate for rubber. Therefore, T_g of rubber is somewhat equivalent to T_m of crystalline materials. Commercially available rubbers are listed in the table in "Appendix" with their specific features. Their lowest usable temperatures are closely related to their T_g's, all of which are below room temperature. Thus, T_g is an industrially very important index of rubber for practical usages. For example, so-called snow tires are made from the rubber the T_g of which is well lower than −30 °C to make them workable on snow or ice.

1.3.3 The Age of Soft Materials and Soft Technology

The twenty-first century, when the Iron Age seems to be just passing its zenith, may be the century of seeing the start of Age of Soft Materials. Rubbers are surely one of the earliest items to be recognized its utility among soft materials, which suggests us a reason to study rubber science in this century. Rubbers, polymer gels, colloids, and liquid crystals are expanding their utilization in accordance with the modern technological trend of devices that are soft, flexible, lightweight, and still being of tenacity. For example, the robots for industrial uses and in particular those for uses under dangerous conditions in emergency are already recognized their usefulness. The further development direction of the robotics may recently be suggested, the robots of much more humane characters. Next-generation robots are the ones that people want to hold in his or her hands or to be embraced by them. To realize such a humane character, it is mandatory to develop the devices with soft touch of the surface, highly deformable muscles, and flexible joints and so on.

As shown in Fig. 1.1, when we use them not as a material but as a matter, the Age of Soft Matters is the name to use from a basic scientific viewpoint. Also, this century may be that of entropy, while the twentieth century was that of energy. Entropy is to determine not only the elasticity of rubber and gas but also the quality of energy. The second law of thermodynamics is a principle of increasing entropy, and in an isolated system, the state is simply tending to be randomized toward chaos, which is measured by the increase of entropy [47, 48]. By our consumption of energy, the quality of energy is decreasing on the earth, i.e., the entropy of the system is constantly increasing. We are now not in energy crisis but in entropy crisis! The significance of studying rubber science includes possibly our understanding entropy more. From the viewpoint of materials science, the present state of our science on rubber and elastomer is not advanced enough to surpass the limit of a trial-and-error methodology. By publishing this textbook, we have tried to summarize the technical results on rubber which have been accumulated in the last century, and to advance one step toward the establishment of modern rubber science, based on the methodology in sciences of soft matters and of entropy.

Having this long picture in mind, let us learn a little more on technology. Actually, the term “technology” has now dual meanings; it means either technic itself or science on technics. In this chapter and later in Chap. 6, however, technology is employed for science on technics: Originally, “-logy” means learning or theory and technology is conceptually a branch of science. Therefore, often used phrase “science and technology” is problematic, and “science and technics” is recommendable from the present viewpoint. On this standpoint, what is the technic is considered first. Its origin is a few tools that our ancestors used for working on nature. That is, the mankind began to separate from the other species by using some tools, not directly using his or her hands on the natural world in order to work for survival [20]. Their use of tools had changed the nature in a long time to form the environment around the place where the human beings were living. In other words, environment is a nature more or less changed by the human activities. Utilization of tools had promoted the evolution of the human beings, and the progress of simple tools into various machines ultimately enabled mankind to industrialize our society. The result of these considerations on technics is schematically shown in Fig. 1.3.

The humankind had possibly used a chipped stone tool when working on nature for their survival, and such activities of them later resulted in invention of the polished stone tools, etc, were followed by the gradual conversion of nature to environment. In a sense, the environments are the artificial nature. During the Stone Age, human being learned how to use fires, sophisticated stone tools, and began even metals by chance for their survival and to progress civilization. This is the

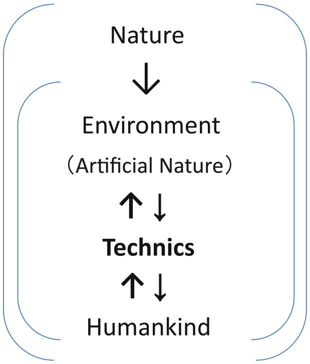


Fig. 1.3 Technics are intermediating between human beings and environment, and all are within nature in its broad sense

most important difference of humans from all the other living things. Actually, the use of a tool, an origin of technical instruments and later evolved into machines, was the accelerating factor for the ape-men to evolve into human beings, and the usage of technics by the humankind in working on nature had given rise to civilization. L.H. Morgan (1818–1881), an early anthropologist in America, who had conducted extensive sociological field research on native American Indians, wrote in the first chapter of his book “Ancient Society” [49] as follows:

> The latest investigations respecting the early condition of the human race, are tending to the conclusion that mankind commenced their career at the bottom of the scale and worked their way up from savagery to civilization through the slow accumulations of experimental knowledge.

Here, “experimental knowledge” is reasonably interpreted as the primitive technics on manufacturing and effective utilization of various tools (initially stones and woods) accumulated through their activities such as hunting, gathering, and culturing. That is, the technics, however primitive they might be, is the driving force for civilization [50].

Nowadays, we are encircled not by the nature but by the environment. The progress of mankind has been accelerating and so is the global widening of environment. Through the Industrial Revolution [4, 20, 51], in particular, the development and worldwide spread of modern technics were much accelerated, and the trend has not diminished until now [40, 52–54]. Recent international race to the Red Planet, Mars, is even leading to be the human’s next big mission to colonize Mars [55]. In other words, our environment is even expanding to the outsides of the Earth! B. Russell (1872–1970), a famous English mathematician and philosopher, wrote in 1955 as shown below which appeared at the top of his chapter entitled “Science and Human Life” of the book [56]:

> Science and the techniques to which it has given rise have changed human life during the last hundred and fifty years more than it had been changed since men took to agriculture, and the changes that are being wrought by science continue at an increasing speed.