

Functional Materials (Chemical Edition)

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1. Introduction

In the iron-making business, which makes extensive use of blast furnaces, manufacturing coke as a source of fuel for the furnace is indispensable. At Nippon Steel Corporation, the development of new chemical products using coal tar and coke oven gas (COG), etc. obtained from the coke manufacturing process had been carried out under the leadership of the Chemicals Research Center of the Advanced Technologies Research Laboratories inaugurated in 1981. At first, from the standpoint of supporting the existing chemical business of the company and developing new products with coal tar as the principal raw material, the Center pressed ahead with research on pitch-based carbon fibers, composite carbon fiber materials, carbon materials, functional resins and functional chemical products in response to the changes and needs of the market. In the 16 years until 1997, when the Center was reorganized, the basic research started by the Center led to the commercialization of new chemical products and the foundation of a new chemical company.

In the meantime, the company accumulated diverse component technologies in many different fields from synthesis to chemical engineering processes, including those for pitch-based carbon fibers, LCD inks, protective membranes using cardo polymers with a fluorene skeleton as the core technology, etc. Those component technologies have been handed down to the appropriate business divisions of the company. In this technical review, we describe our approach based on chemical materials science to the complex system called "black chemicals," such as pitch-based carbon fiber and pitch coke, and the chemical products that have been commercialized by Nippon Steel Chemical Co., Ltd., with the focus on fundamental research on carbon blacks.

2. Research and Development on Carbon Blacks

2.1 Background of R&D—commercialization of high-function carbon black for tire tread

Carbon black (CB), an example of effective utilization of tar, is manufactured and sold by Nippon Steel Chemical Carbon Co., Ltd. (split off from Nippon Steel Chemical in 1997). Every year, about 700,000 tons of CB are manufactured almost equally by five domestic companies. Until around 1990, the CB products of Nippon Steel Chemical were mostly of general-purpose grade, since the company had not yet commercialized high-value-added, fine-grain CB products as represented by Super Abrasion Furnace (SAF) and Intermediate Super Abrasion Furnace (ISAF) for tire tread. In those days, commercializing CB for tire tread was a symbol of high technology. Nippon Steel Chemical and the Chemicals Research Center started

joint research and development to upgrade their basic technology to design rubber properties and commercialize CB for tire tread.

2.2 Mechanism of reinforcement of rubber by CB—importance of interaction at interface between CB and rubber

Generally speaking, rubber is mixed with various substances so as to manifest the desired properties as a "rubber composition." Table 1 shows examples of rubber compositions for tires.

Natural rubber, Styrene Butadiene Rubber (SBR), Butadiene Rubber (BR), etc. which have high elasticity, mechanical strength and wear resistance have CB—a reinforcing agent—added for sulfur curing. The overall performance of rubber is adjusted by using various additives, such as curing agents (accelerators/supplementary accelerators) and antioxidants. The typical rubber composition ratio is rubber 100, CB 40-60, and sulfur, etc. 10 (in terms of weight). Since CB accounts for about a third of the rubber composition, it is considered to have a significant influence on the rubber properties.

The purpose of mixing CB in rubber is to improve (enhance) the mechanical strength of the rubber. Rubber for tire tread is the best example of this. CB improves various properties of rubber for tire tread, including enhancing the rubber's strength, wear resistance and adhesion (braking performance) and the reduction of rubber rolling resistance (for better fuel efficiency).

The rubber reinforcing mechanism of CB is outlined below. Fig. 1 schematically shows the structure of CB (ISAF) used for tire tread. The properties of the rubber composition are determined by the size and structure of the particles, the size of the graphene forming the surface, and the functionals/radicals that exist at the edges. Qualitatively, the mechanism of rubber reinforcement by CB can be grasped as follows. In the small-strain region, it is assumed that the rubber is a fluid and that the increase in viscosity of a fluid with filling material added occurs with the CB-added rubber as well. This is expressed

Table 1 Typical contents of tread-rubber compounds

Contents	Typical compound
Rubber	Natural rubber (NR), SBR, BR
Vulcanizing agent	Sulfur, organic curing agent
Vulcanization accelerator	Thiazole derivatives
Accelerator activator	Zinc oxide, stearic acid
Anti-oxidant	Amine, phenol derivatives
Reinforcing agent	Carbon black, silica
Filler	Calcium carbonate, clay
Softener	Petroleum processing oil, aromatic oil
Coloring agent	Titanium oxide, zinc oxide

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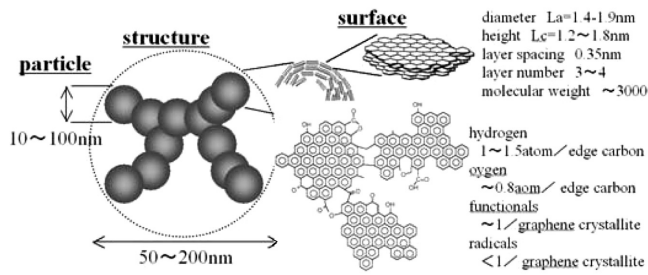


Fig. 1 Schematic structure of carbon black (ISAF)

by the following Guth-Gold equation that is an expansion of Einstein’s viscosity theory. (The value of ϕ varies according to the particle structure.)

$$E/E_0 = a\phi + b\phi^2 \quad \phi : \text{apparent volume of CB}$$

In the large-strain region, the stress relaxation resulting from the separation and slip of the rubber at the CB surface prevents the breakdown of rubber particles and increases the breaking strength of the rubber (see Fig. 2). Looking at the mechanism this way, the important factors in the reinforcement of rubber by CB can be classed into: the “form” of CB that determines the apparent volume of CB (particle size and structure); the “surface properties” that determine the interaction between the rubber and CB; and the “state of dispersion of CB in the rubber.” Of those factors, the state of dispersion basically depends largely on the rubber mixing process, including the rubber manufacturing equipment: it depends little on material development, although the CB particle strength has something to do with it. Concerning the form of CB, various efforts have been made to

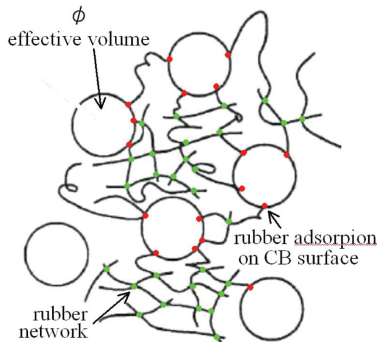


Fig. 2 Schematic structure of rubber-CB compounds

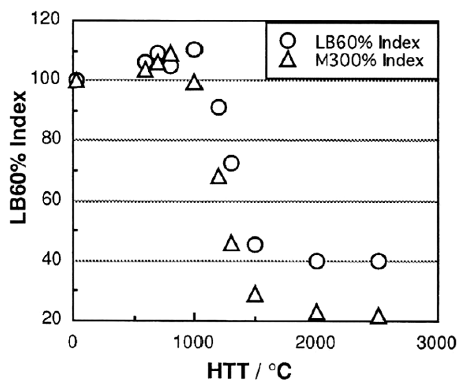


Fig. 3 Lambourn abrasion (LB60%) and Young modulus (M300%) vs. heat-treatment temperature (HTT)

optimize it, with the focus on the particle size and structure, in order to meet specific needs. At present, the optimization of particle structure is studied with the aim of improving fuel efficiency.

On the other hand, the surface properties significantly influence the reinforcement of rubber by CB. As shown in Fig. 3, when a HAF-class CB available on the market is heat-treated in nitrogen to cause the distribution of functionals on the surface to change, the properties of the rubber composition change markedly. In particular, the properties of the rubber composition are strongly influenced by the change in distribution of oxygen-containing functionals on the CB surface caused by heat treatment in the neighborhood of 700°C to 1,000°C and by the change in hydrogen content at temperatures between 1,000°C and 1,500°C. Below, we introduce some of our R&D focusing on improvements in properties of rubber compositions mainly by functionals on the CB surface.

2.3 Analysis of interaction at interface between CB and rubber—relationship between adsorbed rubber and rubber properties¹⁾

The rubber polymers that are adsorbed on the CB surface show a movement and entanglement behavior which differ from those of bulk rubber polymers further from the CB. The rubber adsorbed to the CB is generally called bound rubber, which can roughly be evaluated quantitatively from the T_2 of proton NMR. In the present research, as a more accurate evaluation method, we studied direct quantification of the amount of bound rubber from the residue in a solvent used for extraction. Fig. 4 shows the concept of bound rubber.

We defined bound rubber that could not be removed from the CB surface even when the dissolving strength was increased as shell rubber, which was further divided into adsorbed rubber and chemisorbed rubber by utilizing their different solubility. From the correlation between those indexes and rubber properties, we succeeded in attributing several of the representative properties of rubber to a specific type of shell rubber.

Fig. 5 shows that there is a strong correlation between the amount of adsorbed rubber and the abrasion characteristic (Lambourn Abrasion: LB, slip ratio = 10, 25, 60%) of the rubber composition. The higher the slip ratio, the greater the abrasion becomes. From Fig. 5, it can clearly be seen that the abrasion with lower slip ratios shows a tendency to decrease when the amount of adsorbed rubber is large, whereas the abrasion with higher slip ratios shows a tendency to decrease when the amount of adsorbed rubber is small (the amount of chemisorbed rubber is large). It is estimated that under the abrasion with low slip ratios whereby the degree of rubber deformation is small, the breakdown of rubber is restrained by the slip of rubber molecules at the rubber-CB interface, and that under the abrasion with high slip ratios, the breakdown of rubber is restrained by the strong bond (chemisorption) between the rubber and CB.

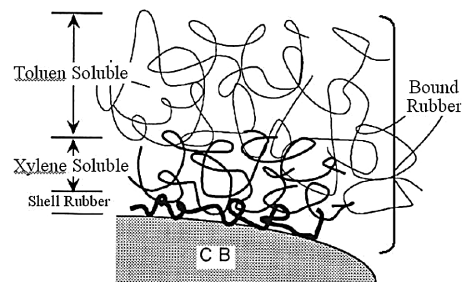


Fig. 4 Schematic picture of bound rubber

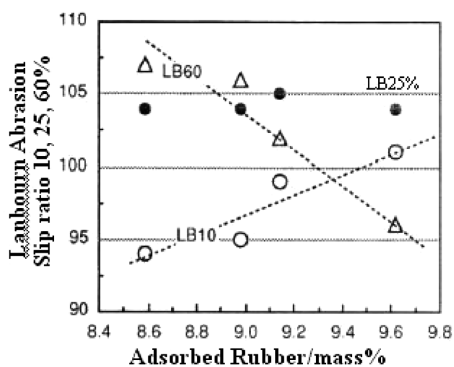


Fig. 5 Strong correlation between Lanbourn abrasion and adsorbed rubber

In addition, it became clear that there was a strong correlation between the increase in the amount of chemisorbed rubber (shell rubber—adsorbed rubber) and the $\tan \delta$ restraint. Generally speaking, when one end of a long, narrow strip of rubber is subjected to a sinusoidal vibration, the other end vibrates with a phase retardation (δ). This phase retardation corresponds to the amount of internal loss (heat generation) of the rubber composition, which loss (heat generation) is indicated by $\tan \delta$ for convenience' sake. It is considered that $\tan \delta$ is essentially due to the slip/separation of rubber molecules on/from the CB surface. Namely, it is estimated that $\tan \delta$ is small when the rubber molecules are chemisorbed to the CB surface but that $\tan \delta$ is large when the rubber molecules are largely adsorbed to the CB surface.

2.4 Example of improvement of rubber properties by CB surface modification

As an example of improvement of the properties of a rubber composition by CB surface modification, Fig. 6 shows how much the Lanbourn abrasion with a slip ratio of 60% and 25%, respectively, changed when the CB surface was subjected to various types of modifications.

Since the CB abrasion mechanism (mode) differs according to the slip ratio, it had been considered difficult to design a CB following general guidelines. Recently, however, it was found possible to vary the direction of change in rubber properties by various types of chemical modification of the CB surface, specifically, the control of components, including hydrogen-enriched functionals (H-func), oxygen-containing functionals (O-func) and nitrogen-containing functionals (N-func), activation (surface roughing: Activated), and

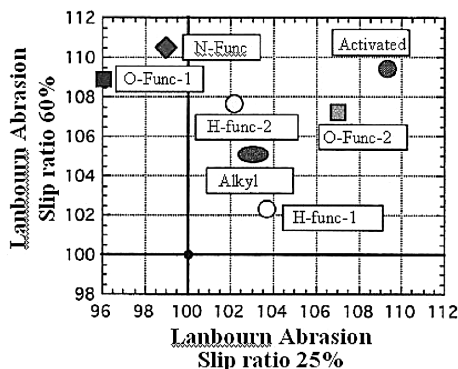


Fig. 6 Lanbourn abrasion property of various CBs with controlled surface functional groups

the introduction of alkyl groups (esterification: Alkyl). By using those indexes of surface activity, it is possible to obtain design guidelines for development of products that meet customer needs. Regrettably, at present, it is difficult to control the above surface activities (surface functionals) independently of one another in an actual furnace. However, the advantage of being able to press ahead with product development in the future in accordance with established design guidelines is no small technical asset.

2.5 Results of development—startup of a new-type furnace and commercialization of CB for tire tread

From the studies on production of fine-particle CB using a small experimental furnace carried out by the R&D group of Nippon Steel Chemical, it became clear that with the existing CB manufacturing furnaces, the structure of fine-particle CB for tire tread could not be controlled completely. Therefore, the company carried out its R&D with the aim of designing equipment for a furnace to produce a high-grade CB and determining the final operating conditions. The correlations between CB colloidal characteristics (industrial indexes of shape and surface activity of CB) and rubber properties were almost clarified in about five years, and test samples for small furnaces that had been required by tire makers to develop new rubbers for tread could be obtained.

At the same time, technology for computer simulation of the combustion reactions and fluid motions in a furnace had been established in cooperation with a university. In 1998, Nippon Steel's support for the above R&D ended as an original new manufacturing furnace (for fine-particle grades) was completed at Nippon Steel Chemical Carbon. Using its new furnace, Nippon Steel Chemical Carbon succeeded in commercializing an ISAF abrasion-resistant grade in 2004 and SAF grades for truck/bus tire tread in 2009. On the other hand, in 2000, capitalizing on its furnace design technology, the company successfully introduced a new type of furnace for manufacturing soft carbon black (high-function grade of intermediate particle size) used in various industrial rubber products.

2.6 New application of CB technology—developing new catalysts for fuel cells

The technology for controlling the microscopic surface structure of CB that was developed during the R&D on CB has been applied to research on the electrodes of polymer electrolyte fuel cells (PEFCs) since 2000. The PEFC electrode is a composite structure (called a catalyst layer) consisting of a catalyst—CB carrying Pt particles of several nm—and a proton conductive polymer. The CB structure and surface construction significantly influence the electrode performances, including gas diffusion. Controlling the wettability of the electrode is another important factor determining the performance

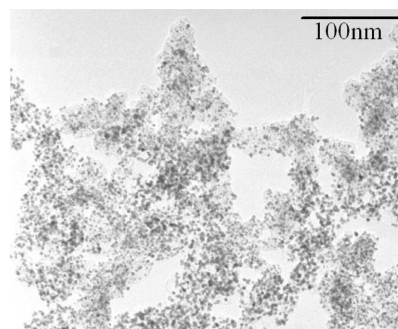


Fig. 7 TEM photograph of Pt supported carbon black

of PEFC. On the other hand, the porosity of CB and the refinement and dispersion of particles of Pt, which have a direct bearing on the electrode performance, can be controlled by the surface construction of CB. Thus, the key technology for CB helps enhance the performance of the latest fuel cells (see Fig. 7).

Incidentally, the performances of coal-based pitch coke/pitch-based carbon fibers can be enhanced by controlling the structure of pitch through coal tar fractional distillation,²⁻³⁾ thermal polymerization/condensation, dry distillation, hydrogenation, etc. The raw material for CB is an example of effective use of a by-product from the above process. The Nippon Steel Group's technology relating to "black chemicals" is sure to progress steadily in the future.

3. Introduction of New Products of Nippon Steel Chemical

3.1 Guidelines on product design

The functional products of Nippon Steel Chemical began with basic chemical products derived from tar by applying techniques to "separate," as represented by distillation and crystallization. Then, techniques to chemically "impart" specific functions to materials, such as imparting reactive functionals or polymerizing monomers, and techniques to physically "add" new functions to those materials by combining them together or integrating them with other materials have been used in combination to develop and manufacture new functional products.

The current functional products include: "ESPANEX", which is a flexible material for printed circuit boards composed of layers of aromatic polyimide and copper foil stacked layer on layer without using any adhesive; "ESFINE", which is a resistance material for the color filters of liquid crystal displays (LCDs) with an aromatic functional polymer in the main chain; and "SILPLUS", which is an original hybrid material containing cage-type silsesquioxane structures in an organic matrix. Nippon Steel Chemical is expanding the market for the above functional products.

3.2 Resistance materials for LCD color filters (ESFINE)

In the LCD color filter, a black matrix is used to improve the contrast of the display and prevent the light leaking by shielding the light passing between the RGB pixels. Formerly, a thin deposit of metal, such as chromium, was used as the black matrix (BM). Although a thin metallic deposit has good dimensional accuracy and opacity, it requires a vacuum vapor-deposition process, such as sputtering. With the increase in size of the glass substrate so as to improve productivity, the material for BM has been switched from metal to resin (see Fig. 8).

Although the functions required of BM differ according to the liquid crystal driving system, those which are required of the resin BM in In-Plane Switching (IPS) system—the representative wide viewing angle technology—are as follows.

- (1) Shielding the backlight to improve the display contrast (improved optical density: OD).

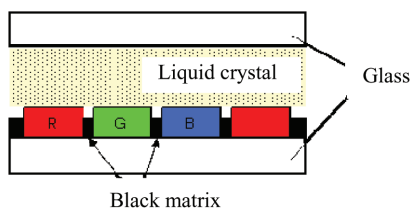


Fig. 8 Schematic of liquid crystal display unit

- (2) Preventing the mixing of RGB colors to restrain any deterioration in color purity and improve the surface flatness of the color filter (matrix thickness/taper shape control).
- (3) Securing a specified (or higher) level of aperture ratio (line width, dimensional accuracy).
- (4) Keeping the lateral electric field free from confusion to drive liquid crystal molecules in a horizontal plane (electric non-conductance).

The material of BM is composed of resins, monomers, polymerization initiators and pigment dispersants. As the resin, the cardo-type resin that was developed in the Chemicals Research Center of the Advanced Technologies Research Laboratories is used (Fig. 9). The cardo-type resin has a hinge structure in which four aromatic rings are bonded to one carbon atom. Since this polymer intrinsically contains many aromatic rings, the molecular refraction is high, making the total refractive index high. In addition, since the aromatic rings in a cardo structure face in different directions to one another, the optical anisotropy of the polymer as a whole is canceled out and the birefringence is low. Thus, in addition to excellent heat resistance and transparency, the polymer has a number of good characteristics required of an optical material.

Besides, the polymer has an advantage over a commonly used (meth) acrylic resin binder of low molecular weight in that it efficiently adsorbs to the dispersed carbon pigment thanks to the interaction of the aromatic rings. Furthermore, it offers a high variance in BM pattern profile control through a good balance of mixing with monomers (Figs. 10 and 11).

By making the most effective use of the properties of the cardo-type resin co-developed by Nippon Steel Corporation and Nippon Steel Chemical Co., Ltd., it has become possible to secure the dispersibility of carbon pigment and the advantage of shape/dimensional control in order to guarantee the prescribed OD value (opac-

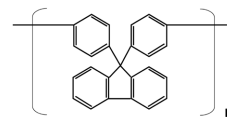


Fig. 9 Basic structure of cardo resin

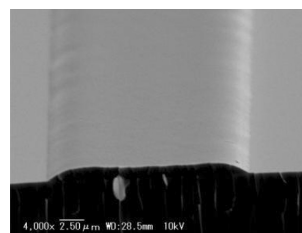


Fig. 10 Quonset type black matrix

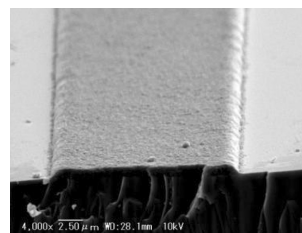


Fig. 11 Perpendicular type black matrix

ity) and electric non-conductance properties. On the other hand, with the continual increase in scale and speed of the photolithographic processes of our customers, we are required to constantly improve the properties of the BM materials, such as conformity for the high-speed resistance coating process, high sensitivity and high developability. Thus, it has become necessary to implement a well-balanced design of those performances that are apparently incompatible with one another, such as control of the viscosity and design of the pigment dispersant.

3.3 Organic-inorganic hybrid material (SILPLUS)

As materials with properties which cannot be obtained from either organic or inorganic materials alone, organic-inorganic hybrid materials have been actively studied in diverse fields.

Among them, new polymers containing silicon, especially those with a polysilsesquioxane structure, are expected to replace inorganic silicon compounds in the fields of electronics and photonics, etc.

“Silsesquioxane” is a network-type polymer or a polyhedral cluster, the structure of which is $(\text{RSiO}_{1.5})_n$. It can be obtained by hydrolysis and condensation of tri-halosilanes or tri-alkoxysilanes. Polysilsesquioxane with a cage-type structure, which imparts rigidity to flexible siloxane-based materials and which facilitates introducing organic functionals, is a very useful unit for creating organic-inorganic hybrid materials (see Fig. 12).

The process for manufacturing silsesquioxane, which has reactive functionals, was developed by the Chemicals Research Center of the Advanced Technologies Research Laboratories. Since then,

Nippon Steel Chemical Co., Ltd. has optimized the combination of silsesquioxane with an organic matrix. As a result, it is attracting attention as an organic-inorganic hybrid material. The basic properties of SILPLUS are shown in Table 2.

SILPLUS is far inferior in rigidity and dimensional stability (coefficient of thermal extension) to ordinary inorganic glass. In terms of optical properties and pencil hardness, however, it is almost comparable to inorganic glass. In addition, the specific gravity of SILPLUS is about half that of inorganic glass. This is advantageous from the standpoint of making a lighter device. Compared with polymethylmethacrylate (PMMA) and polycarbonate (PC), which are typical organic glass materials, SILPLUS has superior heat resistance, optical isotropy and pencil hardness. Taking advantage of the above properties of SILPLUS, Nippon Steel Chemical Co., Ltd. has been promoting sales of SILPLUS®Film and Sheet mainly for peripheral components on display devices, including (1) the front protective window for LCD panels of mobile devices, and (2) the upper layers of touch panels.

At present, organic-inorganic hybrid materials lie between inorganic glass and organic polymers in their properties. In the future, it is necessary to improve specific material properties for specific uses. Developing hybrid materials that are much closer to glass in properties might be one direction to take. However, we are now planning to come up with new hybrid materials that have properties hardly obtainable with glass and that are very flexible and can easily be made into the desired shapes.

4. Conclusion

In response to the changes and needs of the market, research and development on chemical systems made from coal tar, coke oven gas, etc. occurring in the process of production of coke which is indispensable for the iron-making business has brought about pitch-based carbon fibers, carbon fiber-based composite materials, carbon materials, functional resins, and functional chemical materials one after another. Today, those materials are widely used in diverse fields, including electronics.

Since the Great East Japan Earthquake that occurred on March 11, 2011, the energy demand structure has changed noticeably and the search for new materials has begun. Under those conditions, carbon materials are once again attracting attention as materials which are capable of storing energy. On the other hand, the modern-day information society employs rapidly progressing high technology. At present, there is growing demand for Smartphones and tablet PCs along with improvements in the cloud computing system. It is expected that the new chemical products of Nippon Steel Chemical

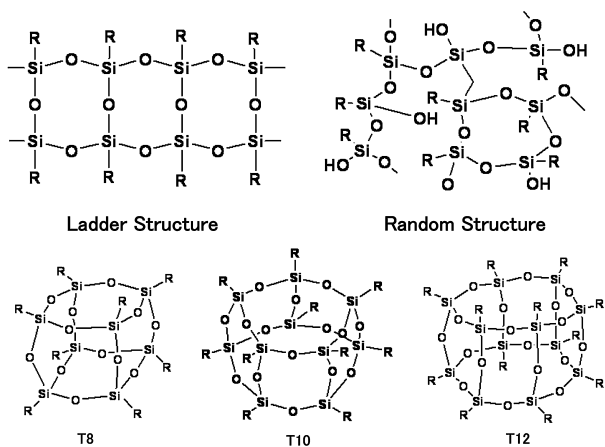


Fig. 12 Structure of Silsesquioxane

Table 2 Properties of various transparent materials

		Inorganic glass	SILPLUS Type-A	SILPLUS Type-B	PC	PMMA
Bending modulus	GPa	70-80	3	2	2	3
Elongation (at break)	%	0.1	2	5	200	5
Transmittance (total)	%	90-91	91	91	90	92
Refractive index	-	1.42-1.92	1.53	1.53	1.59	1.49
Retardation	nm	< 5	< 3	< 1	40-80	< 20
Tg	°C	500-1000	> 300	> 300	140	105
CTE	ppm/K	3-10	40	70	70	70
Pencil hardness	-	9H	9H	3H	2B	3H
Specific gravity	g/cm ³	2.5	1.3	1.2	1.2	1.2

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Co., Ltd. will be increasingly used in those information terminals.

In relation to R&D on chemical materials rooted in the iron-making business, the Nippon Steel Group intends to continue forging ahead with the development of new processes and new products while promptly and accurately grasping the needs of modern society.

References

- 1) Patent Application Publication No. 11-060799, 11-060800, 11-060984, 11-060985
- 2) Mochida, I., Mitsuguri, Y.: Carbonization Chemistry for Mesophase Control. Carbon. 116, 35 (1984)
- 3) Arai, Y.: Pitch-Based Carbon Fibers. Carbon. 241, 15 (2010)



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