There are a lot of difficult problems related to thermal energy when trying to solve global warming, heat dissipation from electronic devices, and the shortage of electricity during summer 2011. The integrated thermal management materials of Hitachi Chemical are applicable to solving these problems. In this paper, the features and applications of thermal management materials, such as those used in thermally conductive materials, thermally insulating materials, and thermoelectric modules and devices, are explained. Finally, our approach to the environmental thermal problem is discussed.

Heat, similar to potential energy and electrical energy, is a form of energy. The thermodynamics - academic inquiry into heat - began at the time of Watt’s invention of the steam engine and was established in the early 20th century by questioning “What is thermal energy?” and “How can thermal energy be maximally utilized?”

1,2) The laws of thermodynamics state that the total sum of energy in an isolated system is constant, and when processes are irreversible, entropy must increase. However, the speed of heat flow and the rate of entropy increase in a system are not determined. We can easily control the speed of heat flow and the rate of entropy increase to a certain extent by changing the system’s size, structure, and materials. Thermal management materials, the topic of this paper, are materials that bring about various effects by using this controllability appropriately. The targets of this research are primarily to solve thermal problems and to develop materials related to electrical equipment, automobiles, and housing. Because their heat generation density is relatively low, it is easy to control the speed of heat flow of these products with thermal management materials. In this paper, the functions and features of these materials created by Hitachi Chemical, which are useful in controlling heat flow, are described.

Now, when faced with today’s problems, such as urban heat islands, global warming, and the Fukushima nuclear power plant accidents as a result of the Great East Japan Earthquake and the ensuing lack of electricity, one cannot help but feel the difficulty in controlling heat. However, we must not stand paralyzed in the face of these problems. We still hope that we can contribute something. Our efforts to address these problems are discussed below.

First of all, heat dissipation materials to control heat flow are discussed. Heat dissipation materials are critical for recent compact electrical devices and hybrid cars. Because the temperature of these products must be kept below certain levels, thermal management materials are used to dissipate the heat produced by CPUs or power semiconductor devices. As shown in Figure 1, our heat dissipation technologies consist of 1) nano-structure control (molecular design of epoxy resin with a mesogen structure) and 2) orientation control.

In collaboration with Hitachi, Ltd., we have developed highly thermally conductive epoxy resin with a mesogen structure3,4). By combining this resin with our hardening agent technology and technology for high loading of ceramic fillers, we have developed an adhesive insulating sheet that can achieve thermal conductivity of 5–10 w/mK5-7). The typical properties of this sheet are shown in Table 1. The sheet not only has outstanding thermal conductivity, it also has high heat resistance and strong adhesion. These technologies were described in detail in the last issue6). We have begun to mass produce the sheet and it has been applied to power modules and LEDs.

The orientation control technologies that control the orientation of graphite particles arranged vertically in a sheet of 150-500 µm thickness, as shown in Figure 1b, are our proprietary. Using our original graphite particles with high thermal conductivity in flake form and elastic resin, we developed a new process that orients the graphite vertically in the sheet. As a result, the sheet exhibits thermal conductivity more than several ten times than that of sheets using spherical graphite particles or sheets using horizontally oriented graphite particles in scale form8-9). Besides being used to dissipate the heat from the CPUs in high-end servers, the sheet is also being used to reduce the thermal resistance of thermoelectric converter modules, as described below.

By combining our original materials and technologies, we have also brought various thermally conductive materials into the market. Besides of heat dissipation, distinguished feature that these technologies have in common is additional functions. These materials are briefly described below.

The change from incandescent and fluorescent lamps to LEDs is accelerating due to the recent demand for saving energy.
HT-5100M, a metal based substrate using the high thermal conducting epoxy resin, and MCF-5000I, a thin and flexible substrate with high heat dissipation ability and good workability, are applicable to LED lighting. Both of them are introduced in the "Report" section of this issue. Their additional function gives numerous features, such as enabling products to be made thin and light. Also, HT-9000ITM, a flexible heat-dissipating substrate composed of a heat-resistant adhesive layer laminated beforehand to MCF-5000I, can simplify the substrate production process by omitting the conventional process of attaching adhesive to separated substrates. These products can be applied not only to LED lighting, but also to compact batteries, automobiles, and clothing that take advantage of curved surfaces.

We have also developed a flexible and transparent heat-conducting sheet. The sheet is produced using our pattern plating transfer method. It has a high degree of transparency with a transmittance of 90% of visible light. Also, because the sheet has...
fine copper mesh wiring on surface of flexible polymer film, as shown in Figure 3, its thermal conductivity in the horizontal direction is 6 W/mK, 30 times that of conventional resin sheets, while it exhibits the same flexibility as conventional polymer films. This additional functions of this product are transparency which can be applied to lighting surface of LEDs and shielding ability of electromagnetic wave. Currently, we are investigating the application of this product to areas in which both a high transparency and high thermal conductivity are demanded.

We have also developed a metal based substrate that features flexibility in addition to thermal conductivity. Because it can reduce the stress on the solder balls of the mounted devices, it has been used more than 10 years as an in-vehicle substrate. This technology is widely applied to the process of attaching materials with different coefficients of thermal expansion. Its application is being widely extended to die bonding films and encapsulant films.

We propose a variety of heat dissipation materials suitable for each application. However, because of the difficulty in heat dissipation to outside in recent small electronic devices and LED lighting devices, the problems of overheating of the entire device have risen.

For such cases, it is necessary for heat to be dissipated from the chassis by radiation. Because thermal radiation follows the Stefan–Boltzmann law, it is desired to coat the surface of a high-temperature body by a high emissivity material (thermal radiation paint). Hitachi Chemical and Hitachi Chemical Industrial Materials Co., Ltd. have developed HC-001, an environmentally friendly water-based coating with superior emissivity and heat resistance. This material can be coated on uneven surfaces by spraying.
and forms a hard film after drying. Figure 4 shows an example of the heat sink of an LED light bulb painted with HC-001. The temperature at the heat sink dropped by 10 °C. The temperature at the substrate mounted on the LED dropped by 7 °C. This reduction is expected to greatly extend the life of products.

In the future, it is expected that there will be the need to secure heat dissipation paths not only by using high thermal conducting materials but also by combining various materials. Therefore, not only materials but also technologies for measuring basic physical properties related to heat, simulation technologies based on these measurement technologies, and technologies to combine materials are essential. We have begun to extend MSS (Material System Solution), the technology we have been applying to the electronic packaging materials for a long time, to the thermal management materials and have started the proposal of the optimum combination of materials. By making such proposals for a variety of electronic devices, we can shorten the time of selecting appropriate materials.

3 Heat Insulating Materials: A Group of Materials for Suppressing the increase of Entropy

In this chapter, heat insulation, the complete opposite of heat dissipation discussed above, is discussed. The most important issue is to lower the electrical energy consumed by air-conditioning and heating. The term “saving energy” is frequently used today. However, because the first law of thermodynamics states that the total energy of an isolated system is always constant, the energy cannot be saved completely. The essence of “saving energy” is to thermodynamically control the inflow and outflow of heat between different systems and to inhibit the increase of entropy. We have a group of materials which are effective to suppress the entropy, based on our resin processing technology. Some of these materials are introduced below.

In order to suppress heat inflow and outflow between systems, heat insulating - controlling of heat transfer, convection, and radiation - is important. As shown in Figure 5, we have developed cross-linked polyethylene foam called Hiethylene S\(^{10}\). The expansion ratio of Hiethylene S is 10 to 40. By controlling the expansion ratio, the suitable insulation and shock absorbing characteristics can be selected. In addition to basic product, Hiethylene S has various versions, such as, flame-retardant version and heat-resistant version. One of these products is Hitachi Chemical’s “Mildy” sheet, composed of Hiethylene S laminated with antibacterial and insect repelling nonwoven cloth. As a mat used during emergency evacuations, it suppresses the hardness and coldness of wooden or concrete floors of gyms and other facilities used as shelters. Because it improves the livability of shelters, it gained attention as an anti-disaster resource in the aftermath of the Great East Japan Earthquake.

Because our heat insulation paints\(^{16}\) contain many particles that function as heat insulator, they exhibit twice of the insulation ability of ordinary paints. They are water-based epoxy paints, so they can form an outstanding insulation layer only by drying at room temperature. Their use is not limited to only buildings but is expected to be applied to small devices such as smartphones.

The group of materials described above restrain heat flow in accordance with Fourier’s law (heat flux is proportional to the gradient of temperature). While they have excellent heat insulation functions, they do not have a function to maintain a constant temperature in a room by controlling heat flow. We have an intelligent material that can control the temperature of a system by controlling heat inflow. By controlling the orientation of heteromorphous particles in microcapsules, our light control film\(^{17}\) can reversibly change the color tone from dark blue to transparent. By regulating the incoming light to the room, it can simultaneously control the heat inflow (see Figure 6). In other words, our light control film is a product that proposes a comfortable living...
space. Light control glass, which has the light control film laminated to glass or polycarbonate board, is already being used as window glass in buildings and airplanes. Because the film confers a high sense of design and also effectively controls temperature, it is expected to be used in a variety of applications, such as automobiles, ships, and trains\textsuperscript{19}.

The group of materials stated above can control the amount of heat flow in a wide variety of ways. However, in the end, thermal energy is not reused and migrates to a different low-temperature system. In other words, any usable energy is not obtained and the entropy increases in vain. Thus, it is necessary to convert thermal energy into electrical energy and reuse it by exploiting the temperature difference created when the thermal energy moves to a low-temperature region.

Together with Hitachi Powdered Metals Co., Ltd., and the Central Research Institute of Electric Power Industry, Hitachi Chemical has developed a thermoelectric conversion module enclosed in an airtight case by applying powder metallurgy technology\textsuperscript{19,20}. An example of the product is shown in Figure 7. Besides an SiGe module that exhibits superior power generation efficiency at a heat source temperature of 600–1,000 °C (8.4 W@▵T=630 °C), we are also developing modules, using Mg\textsubscript{2}Si, that use common elements and show better performance than SiGe at 300–600 °C. Because of the outstanding reliability of thermoelectric converter modules, they have been used as the power source of deep space probes. However, in order to use them for automobiles or homes in the future, further improvement in performance and invention to simplify installation and to lower the cost are required. Since the electricity produced by the thermoelectric converter is determined by the temperature difference, it is essential to minimize the thermal resistance between the heat source and the module and maximize the thermal resistance inside the module. For the module to be in direct contact with the heat source, a method to lower the thermal resistance by inserting the flexible graphite-oriented sheet described above between the heat source and the module is in practical use. We plan to further increase the thermal resistance inside the module by lowering the thermal conductivity of the materials used in the module.

Figure 7 Encapsulated thermoelectric module and device
A thermoelectric module in a vacuum metal case has excellent reliability.
Efforts on Environmental Issues

An overview of Hitachi Chemical’s thermal management materials, mainly applied to electronic devices, is described above. Finally, We would like to discuss how Hitachi Chemical’s materials contribute, albeit humbly, to reducing CO₂ gas and addressing the problem of global warming.

Solar heat reflection paint used on rooftops is an example of a thermal management material that supports the environment. It is well-known that half of the energy emitted by the sun is light in the infrared region. Thus, the temperature increase in a room can be held down by reflecting the sun’s infrared rays. Hitachi Chemical Industrial Materials Co., Ltd.’s solar heat reflection paint Hi-star Shataro24 including special pigments that block infrared rays shows an infrared reflectivity of greater than 90%. Because this paint is water-based, it is gentle to the environment. Its workability is also good because it requires a short drying time of about 30 minutes. The effects of this solar heat reflection paint are shown in Figure 8. Compared to general paints, the reflectivity of the infrared region is three times higher. This paint can thus reduce the temperature of the painted surface. In experiments simulating exposure to sunlight during the summer period, Hi-star Shataro lowered the temperature of the surface by 25 °C compared to an unpainted surface and lowered the temperature by 20 °C compared to a surface painted with conventional paint. The combination of this paint with the heat insulating paint and polyethylene foam described above would further prevent the inflow of heat from the roof.

Furthermore, in addition to heat dissipation materials, Hitachi Chemical is providing numerous materials for electronic devices, including substrate materials, and die bonding films25. The evolution in electronic devices and information technologies is expected to reduce CO₂ emissions by 5% in 2020 (compared to 2000, reduction of 8.6 million tons) by:

1) reducing the use of physical materials - paperless office, electronic transaction, electronic money.
2) constructing efficient distribution systems - advanced traffic system, improved fuel efficiency, electronic tags, etc26. Simply doing these things will not reach the Japanese government’s reduction targets (25% reduction by 2020 compared to 1990). However, 5% is a large part of 25%. Although the direct contribution of packaging materials, including thermal management materials, to the fight against global warming may be small, their indirect contribution is large. Thus, Hitachi Chemical’s materials have numerous direct and indirect benefits for measures against global warming27.

Meanwhile, our material development and production-related business activities themselves, of course, produce heat, CO₂, and waste. The time has come to take these points into consideration when thinking about how to be beneficial to the environment. We can quantitatively understand business economic activities and the environmental load by applying an input output table (Leontief model)28,29. We have been investigating the use of linear programming in a system that simulates the effects and environmental load at material design. This system enables early-stage determination of the worth of productization30-28. This R&D effort is still at its early stages. However, we think it provides an indispensable perspective for truly contributing to solving thermal problems.

Basic academic questions related to quantitatively understanding thermal disputes problems on a global scale, such as global warming, belong to the field of thermodynamics. Although there are various disputes on environmental issues including global warming, the time has come for accurate and objective debates based on thermodynamics. Hitachi Chemical has been humbly yet definitively contributing to environmental thermodynamics, including co-sponsoring the 21st International Conference of the International Union of Pure and Applied Chemistry (IUPAC)39. The event was held last year, and its theme was the contribution of thermodynamics to environmental problems. Hitachi Chemical exhibited its thermal management materials at the conference’s reception event, which was attended by the Emperor and Empress. Collaborative research has started with result of discussions between domestic and foreign researchers based on the discussion at the conference.
Conclusion

Dr. Toru Atake, professor emeritus of the Tokyo Institute of Technology and chairman of the IUPAC conference mentioned above, has observed that, compared to the 20th century, the 21st century will be an era of thermal energy. Electrical energy that can be easily converted and transported and stored in batteries is called “high energy.” In contrast, thermal energy, which has poor conversion efficiency and is difficult to store, is called “low energy.” We are now in an era that requires using heat, a difficult form of energy to handle, without waste and skillfully carrying out heat dissipation and maintenance. We want to propose as many thermal management materials as possible that will be beneficial to this era. We also want to contribute directly and indirectly to fighting environmental problems, including the energy problem and global warming.

(Prof. Atake, who mentored us in our studies of thermal management materials, passed away on August 31, 2011. I sincerely pray that his soul may rest in peace.)

[References]
29) International Union of Pure and Applied Chemistry 21” International Conference on Chemical Thermodynamics (ICCT-2010) drafts, program reports, etc. (2010)