Resin Technology

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Since the establishment of our business a century ago, resin technology comprising various kinds of resin has been used for many products. For products with high thermal conductivity and insulation, we have developed new epoxy resin with higher order structures and higher thermal conductivity. Moreover, thanks to our new analytical technique, we have clarified the thermally conductive property by revealing the interaction between the filler and resin, which has enabled us to design advanced products. Furthermore, the development of new analytical techniques, such as the detection of a minute amounts of accelerator in the thermosetting composite and analysis of the polymerization initiation mechanism of the UV curable resin system have also supported new product design. Recently, we have been studying biomass resin technology, including lignin resin for thermosetting materials, and silk fibroin for cosmetic applications. These resin technologies are expected to help develop our new business, providing new resin materials and new analytical techniques for the new era in future.

1 Introduction

We started research work into insulation varnish for Japan-made motors in a corner of the Hitachi Works of Hitachi Ltd., the birthplace of our business, a century ago (1912), which subsequently became the root of our resin technology.

Our research into resin material, initially focused on insulation varnish, has eventually progressed to include phenolic and epoxy resins used as materials for molding, printed circuit boards and encapsulation. The “molding” technology was the springboard for multiple new businesses and technologies, including molding material technology applicable to automobiles, FRP businesses and expanded polystyrene. Moreover, the functional capability of the “coating” insulation varnish was a catalyst for coating resin product lines and the acrylic resin technology eventually developed as a result became the cornerstone for research into photosensitive resins; used in photosensitive films for printed circuit boards. Conversely, the scope of the function to “adhere” has spread to include the development of alkyl phenolic and acrylic resins for bonding agents and adhesive compounds. Further, “coating” technology, an extension of photosensitive film coating technology, has come to materialize in the form of protective film for electronic equipment, electro-conductive anisotropic film for display terminals and optical waveguides, etc.

As just described, our history includes the use of various resins for our products. We believe the potential of our accumulated technologies in thermoset, photo-curable and thermoplastic resins will be invaluable in helping us expand our business into new fields in future.

2 Development of Resin Technology

Thanks to the following features, we introduce our current ventures involving the development of resin technology in new fields:

2.1 Control resin structure

The concept of high thermal conductive resin, which incorporates a self-aligning mesogenic structure we developed, is shown in **Figure 1**[1]. A high-order structure can be easily formed within this resin, which contains numerous highly ordered crystals at micro level. Furthermore, via a thermosetting reaction, this resin solidifies and stabilizes, randomly oriented at macro level and with isotropic thermal conductivity. Currently, attempts are being made to deploy newly developed epoxy resin for applications in electric/electronic devices in hybrid cars and LED lighting parts. However, high product performance cannot be accomplished simply by replacing existing resin with a new alternative. First of all, we must understand the structure of the resin itself. Moreover, it is also important to clarify the actual structural state in a product incorporating such resin and its effectiveness in boosting product performance. Accordingly, once the correlations between the resin structure and its characteristics are established, this paves the way for optimum product design and swift on-target improvement.

For example, although mixing a large amount of high heat conductive inorganic fillers requires a material using the resin with high heat dissipation and high insulation properties, as shown in **Figure 1**, these properties vary significantly subject to the selection of fillers, its dispersion or differences in the thermo-setting process.

Figure 2 shows the XRD (x-ray diffraction) analysis of mesogenic epoxy resin/ hexagonal boron nitride (hBN) crystal with high thermal conductivity (omnidirectionally 40 W/ m · K or higher) and insulation property (60 kV/mm or higher) [4].

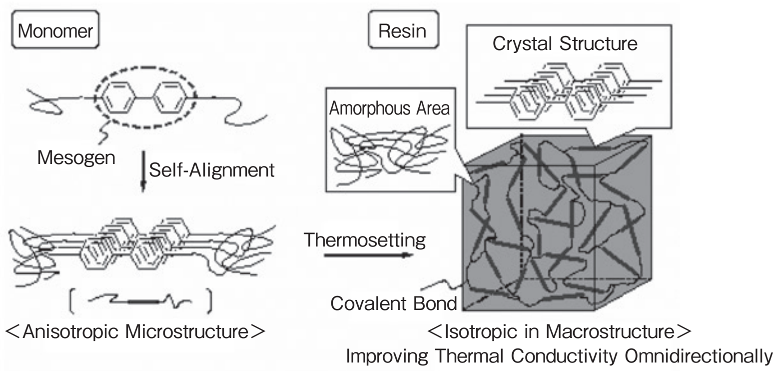


Figure 1 Concept of Thermal Conductive Epoxy Resin

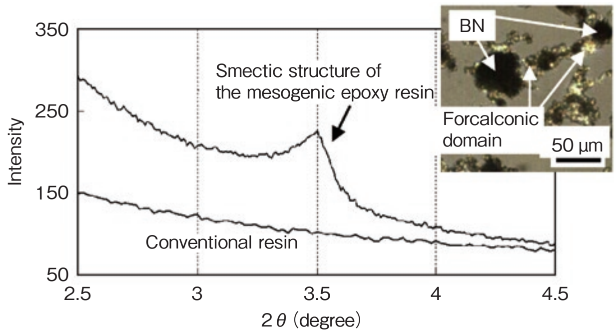


Figure 2 XRD Analysis of the Mesogenic Epoxy Resin / BN Filler Composite with High Thermal Conductivity

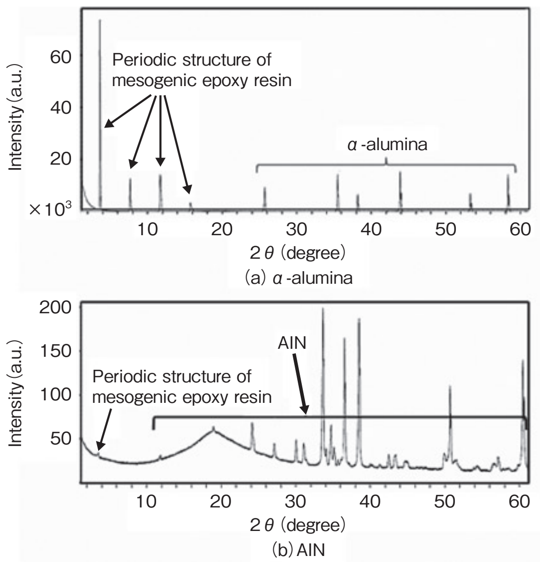


Figure 3 XRD Patterns of the Thin Mesogenic Epoxy Resin Layers Cured on (a) α-alumina and (b) AIN Plates

Observation of the high-order structure in the composite containing mesogenic epoxy resin is not possible using a polarization microscope or AFM due to the disturbance caused by added fillers. However, XRD analysis showed a peak of around 2θ = 3.5°; indicating a periodic structure and suggesting the formation of a high-order (smectic) structure in the resin. Furthermore, with the addition of fillers, its measured thermal conductivity of 0.45 W/m · K exceeded the 0.33 W/m · K of resin without fillers. **Figure 3** shows XRD analysis of the thin mesogenic epoxy resin layer cured on α-alumina and AIN plates [5]. α-Almina (a) showed strong high-order diffraction peaks due to the 2.2 nm pitch periodic structure; conversely, AIN (b) showed weak regularity of the periodic structure, suggesting AIN has difficulty in aligning mesogenic epoxy resin. In conclusion, it was clarified that alignment of mesogenic epoxy resin varies widely depending on the fillers used. By optimally exploiting analytical technology, the degree of interactions between epoxy resin and fillers can be converted to actual data. This allows us to directly access important information, which can then be utilized for product development, including the selective property of fillers and need for surface treatment.

2.2 Analytical Techniques Supporting Resin Technology

To develop a new resin, as mentioned above, as well as material composition, the type of functional groups, volume/amount, molecular weight and selection of modified materials, the application of resin technology backed by high level analytical technique is absolutely essential. We have been constantly engaged in developing new analytical techniques, which have boosted the progress of our new product development.

Here is an analytical example of UV curable resin. UV curable resin is used in a broad range of applications, including coating material, photosensitive film, OCA (Optical Clear Adhesive) for display, etc. **Figures 4** and **5**, and **Table 1** show the results of investigations into the initiation mechanism of polymerization by terminal group analysis using MALDI-TOFMS in the photopolymer systems of acrylic acid-2- phenoxyethyl acrylate (PEA), using highly sensitive oxime ester compound (OXIME-01) as a photo-polymerization initiator[6]. New findings confirmed that methanol,

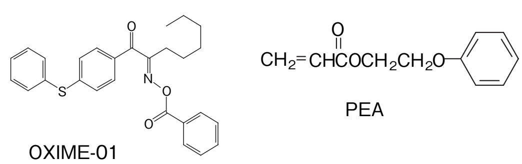


Figure 4 Structural Form of OXIME-01 and PEA

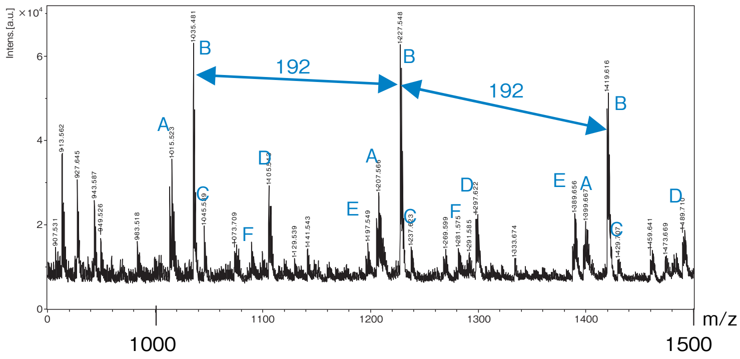


Figure 5 MALDI-TOFMS Spectra of PPEA

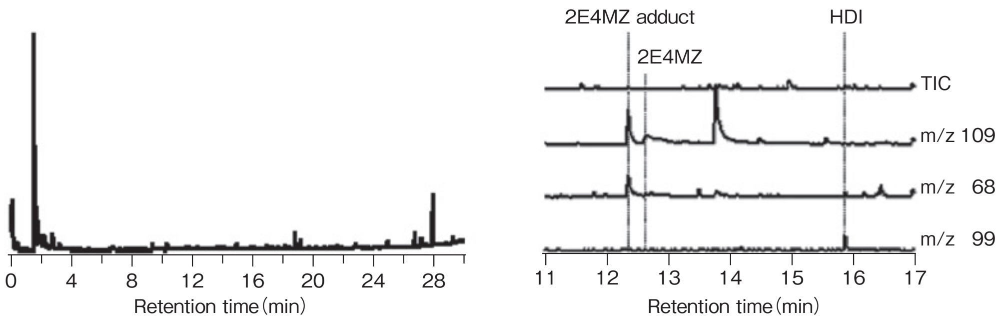
Table 1 Results of Terminal Group Analysis for OXIME-01

Peak group	Molecular Ion Peak	
	General formula	Assigned
A	32+192n	HO-CH_2-(PEA)n-H
B	244+192n	HO-CH_2-(PEA)n-(phenyl)-S-(phenyl)-C(=O)-
C	62+192n	HO-CH_2-(PEA)n-CH_2-OH
D	122+192n	(phenyl)-C(=O)-O-(PEA)n-H
E	214+192n	(phenyl)-S-(phenyl)-C(=O)-(PEA)n-H
F	106+192n	(phenyl)-C(=O)-(PEA)n-H

a solvent, functioned as a chain transfer agent, that methylol radicals become initiation species, and also confirm the existence of benzoyloxy and benzoyl radicals. These findings clarified the magnitude of the impact on the reaction rate of various radicals and helped us when designing new products.

Also, developing a standout analytical technique which is capable in itself of manifesting our technologies at a high level, is effective in preventing unwarrantable counterfeit goods of our products, the development of which required strenuous efforts.

The example shown in **Figure 6** illustrates the analytical results of curing accelerators and modifiers used in a curing formulation for epoxy resin mounted on a printed circuit board and identified in the final cured product[7]. Since the amount of curing accelerator used is fractional and ends up included in the cured product, its type and content cannot be easily analyzed using existing analytical methods. However, detection and identification of imidazol curing accelerator was enabled using dynamic head space gas chromatography (DHSGC-MS). Such advanced analytical technique can help us prove illegal patent infringements by third party marketed products, which will eventually help enhance the competitive edge of our products.



(a) Total ion chromatogram (b) Total ion chromatogram and mass chromatograms

Figure 6 DHSGC-MS Results of Copper-clad Laminate Degraded at 300 ℃/15 min

3 Biomass Resin

Finally, we would like to introduce our approach toward biomass resin.

Resins, many of which are simply called “resin”, originally came from natural resources, but many today also come from petroleum. The trend to reduce dependence on petroleum and carbon dioxide emissions is intensifying, although the urgency to conserve fossil fuels has eased, with depleting petroleum resources in mind. Consequently, research into biomass has been flourishing year after year.

Polylactic acid, the raw material of which is lactic acid produced from carbohydrate by fermentation, and bio-polyethylene, made from bio ethanol, are well-known resins of plant origin. The starting raw materials for both polymers are edible plants such as corn, a natural product significantly affected by weather conditions.

We turned our attention to lignin, which constitutes about 25% of the total wood component. Lignin can be classed as a natural polyphenolic resin, to which we considered our thermoset resin technology, the basis of our technologies, to be applicable. **Figure 7** shows the evaluation results of the property of molding resin that used lignin as a curing agent of epoxy resin; the lignin was solvent soluble and obtained from steam explosion pretreatment. By utilizing the natural network inside lignin, it is clear that

lignin-based molded products show higher flexural strength and elastic modulus than those of phenol novolac resins[8].

Previously, approaches made to enhance the performance of resins basically focused on manipulating resin composition and the molecular structure and weight. In the case of biomass resin material such as lignin, our major challenge involves finding how to use these techniques effectively. Biomass resin does not differ from petroleum-based resin, simply because its environmental impact as determined by an LCA (Life Cycle Assessment) becomes equivalent to that of usual petroleum-based resins if biomass resin is subject to multiple resin modifications, meaning such resin eventually can no longer be considered a technology to reduce carbon dioxide emissions. Currently, we are striving to carve out various applications to exploit the benefit of natural material.

Next we introduce a case example using silk fibroin. This is a protein, a major component of silk, which can also be called an animal biomass material. In other words, this protein is a natural ultrahigh-molecular-weight polymer. By exploiting its distinctive characteristics, we foresee the potential to identify unique added value, which would otherwise be unobtainable in petroleum-derived materials.

We showed an example of our development, a sponge sheet made from silk fibroin in **Figure 8**, with a soft touch, high water absorption and heat resistance. We are currently considering its applications as decorative and/or medical materials[9].

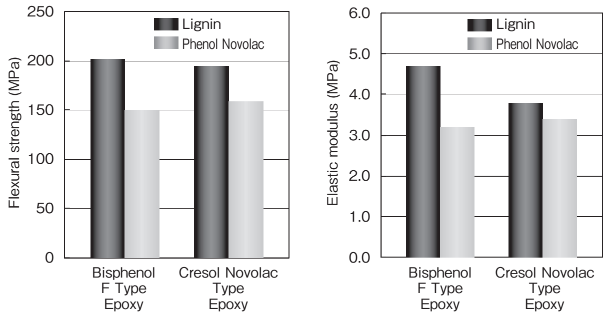


Figure 7 Flexural Strength and Elastic Modulus of Epoxy Resin Composite Using Lignin or Conventional Novolak Resin

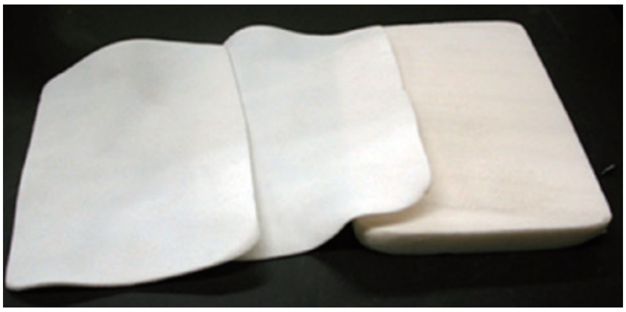


Figure 8 Example of Sponge Sheets Made from Silk Fibroin

4 Role of Resin Technology

As introduced in this report, it is now possible to obtain previously inconceivable resin properties by controlling the resin structure, further cross-linking and crystal structures. We are also striving to find a way to utilize the structure of natural products as they are. Further enhanced analytical technique not only supports the development of these resins but is also a powerful weapon to protect our proprietary technologies. Our resin technology overall is an integrated body of different technologies and by offering resin material and analytical techniques to meet contemporary needs, we are confident that we can contribute to the progress of our society and company.

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