Technical Report

Development of Low Dielectric Vinyl Resin for Next-generation High-speed Communication Circuit Boards

Shinichi IWASHITA*

Abstract

In response to the increasing demand for high frequency, high speed, and large capacity in 5th generation communication systems (5G), materials for rigid copper clad laminate used in high-speed communication devices are required to have low dielectric loss, moldability for multi-layer boards, and heat resistance. There is a high demand for low dielectric loss, and 5G circuit boards must have a dielectric tangent of 0.0015 or less. In response to these requirements, a polydivinylbenzene resin (PDVB) was developed as a soluble low-dielectric vinyl resin that is considered to be suitable, and its dielectric properties and thermal melting properties were evaluated. Furthermore, we blended PDVB with other board resins to create copper-clad laminates and evaluated their physical properties.

1. Introduction

Driven by humanity's pursuit of convenience and comfort, information and communication technology has made great progress. A ubiquitous network society in which we can obtain the information we want anytime and anywhere has become a reality. A society in which large volumes of information are exchanged at high speed via the Internet has arrived. In addition to the fourth-generation (4G) communication system (communication speed of up to 1 Gbps when moving at low speed) that started around 2010, the fifth-generation (5G) communication system became fully operational in around 2022. Ultra-high speeds of up to 20 Gbps have been realized to meet the IoT era. The transmission of information signals is increasing in frequency, speed, and capacity.[1–3)]

To meet the demand for larger capacity, faster transmission, and faster processing of the above-mentioned information and communication equipment, the signal frequency is becoming higher as communication standards progress. Various problems occur in printed wiring boards through which these high-frequency signals flow. Specifically, the increase in transmission loss increases the heat generated in the printed wiring boards and exacerbates the attenuation and delay of signals through the printed wiring boards. Transmission loss includes conductor loss caused by the conductors that form the transmission circuit and dielectric loss caused by the consumption of the electric field energy of the signal by insulators. Information and communication equipment and infrastructure for 5G communication system are required to reduce transmission loss in the GHz range used. The contribution of dielectric loss is particularly large in this frequency range. The printed wiring boards used in 5G communication system equipment and infrastructure require materials with low dielectric loss as insulators.[3–6)]

In this report, we describe low-dielectric vinyl resins that are suitable as materials for rigid circuit boards for 5G communication.

2. Main Body

2.1 Structure of rigid copper clad laminates and manufacturing method for multilayer circuit boards

Rigid circuit boards used as printed wiring boards are fabricated by processing copper-clad laminates (hereafter abbreviated as CCLs) into circuits. The general structure of rigid CCLs and the process for fabricating multilayer boards are shown in **Fig. 1**.[7, 8)]

First, a glass cloth is impregnated with a diluted organic solvent solution of resins, flame retardants, and fillers. The solvent is then dried to create a prepreg. A copper foil is attached to one or both sides of the prepreg, and the prepreg is then hot press cured to produce a rigid CCL. The heat-cured organic-inorganic composite material portion is the dielectric part, and the copper foil portion is the conductor part. The soluble polydivinylbenzene resin described in this report is the organic material used as the dielectric.

The rigid CCLs obtained in this way are processed into circuits, alternately laminated with prepregs, and hot press cured under reduced pressure to produce a multilayer board. At this time, the prepregs are hot press cured into a molten state and are required to flow

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* Ph.D., Senior Researcher, Functional Resin Materials Development Center, Research & Development Div., Nippon Steel Chemical & Material Co., Ltd.
11-5 Kitasode, Sodegaura City, Chiba Pref. 299-0266

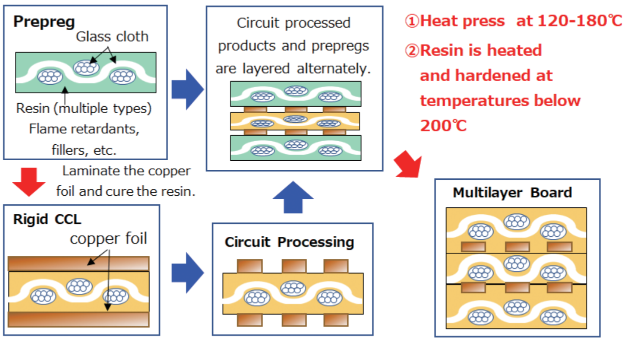


Fig. 1 Rigid CCL structure and multi-layer board processing

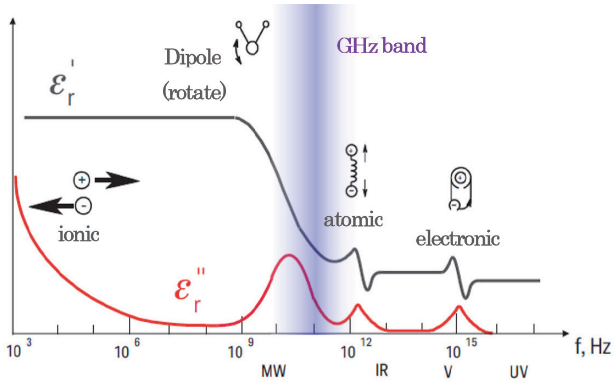


Fig. 2 Frequency dependence of complex permittivity[14)]

sufficiently to fill the steps in the circuit.

2.2 Performance required of materials for rigid circuit boards for high-speed communication

The main properties required of high-speed communication CCLs for 5G communication are 1) low dielectric loss, 2) moldability, i.e., the ability to melt at 120 to 180°C and then heat cured at temperatures below 200°C, 3) adhesion to the copper wiring layers, 4) low linear expansion, especially in the Z direction (thickness direction of the board), and 5) flame retardancy. It is difficult to satisfy all of these performance requirements with one type of material alone. In most cases, therefore, a combination of multiple materials is designed as a blend. Concerning the required properties described above, the functions particularly strongly required of the base resin that accounts for a large proportion of organic materials are 1) low dielectric loss and 2) moldability. The demand for the low dielectric loss is particularly strong.[4–6)] To achieve the Ethernet communication speed of 800 GbE or more as required for 5G communication, the dielectric dissipation factor (herein abbreviated to Df) of the rigid circuit boards must be 0.0015 or less. The base resin, which is a component of the board, must also have a similarly low Df.[3, 4)]

2.3 Soluble polydivinylbenzene resin

Nippon Steel Chemical & Material Co., Ltd. has developed a soluble polydivinylbenzene resin (PDVB) that is particularly excellent in the performance requirements mentioned above, especially in 1) and 2).[9–11)] This resin uses divinylbenzene (DVB) as the raw monomer. Its characteristics include: 1) extremely low dielectric loss because its skeletons are composed only of hydrocarbons, 2) compatibility with organic materials used in rigid CCLs because the skeletons are aromatic, 3) heat resistance because it is mostly composed of aromatic skeletons, 4) thermosetting possibility because it retains vinyl groups as reactive sites even after polymerization, and 5) low melt viscosity enabled by low molecular weight oligomers. The design and performance of the PDVB are described in detail below.

2.3.1 Resin design for dielectric loss reduction

First, the basic concept of dielectric loss reduction is presented. When a dielectric is exposed to a high-frequency electric field, the electric charges inside the dielectric are displaced and biased by the external electric field. This is called dielectric polarization of which there are four types: electronic polarization, atomic polarization, dipole polarization (orientation polarization), and interface polarization.[12)] Dielectric loss refers to the above-mentioned dielectric polarization that occurs when the dielectric is exposed to an electric field, resulting in the energy loss of electromagnetic waves. This loss is given by Eq. (1).[13)]

$$\text{Dielectric loss} = f \times K_2 \times \sqrt{\text{Dk}} \times \tan\delta \qquad (1)$$

where f is frequency, K_2 is a constant, Dk is dielectric constant, and tan δ is dielectric loss tangent. This equation shows that the dielectric loss depends on the relative dielectric constant and dielectric loss tangent and that the dielectric loss tangent has a particularly large effect. **Figure 2** schematically illustrates the frequency dependence of the real part (relative dielectric constant ε') and the imaginary part (dielectric loss factor ε'') of the complex dielectric constant.[12, 14)]

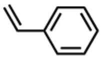
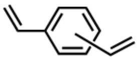
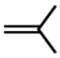
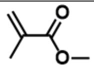
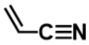
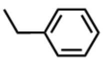
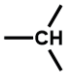
When we look at Fig. 2, we see that the dependence of both the relative dielectric constant and the dielectric loss factor varies with frequency. This is because the polarized structural types that easily absorb electromagnetic waves differ for each frequency band. In the electrical signal frequency range (1 to several tens of GHz) used in 5G communication, the contribution of electronic polarization and atomic polarization is small, and the contribution of dipole polarization is dominant. In order to reduce the dielectric loss in this frequency band, it is effective in reducing the contribution of dipole polarization.

Dipole polarization occurs when permanent dipoles change their direction in the electric field direction. Their moment depends on the moment of the permanent dipoles in the material. A permanent dipole is a dipole that exists regardless of an external electric field or magnetic field and occurs because an electrical bias is inherently present in the structure of the material. Therefore, reducing the electrical bias in the molecular structure is effective in reducing the permanent dipoles.

The structures and dipole moments of several polymerizable monomers are shown in **Table 1**.[15)] Looking at Table 1, we can see that compared to methyl methacrylate and acrylonitrile, which have atoms with high electronegativity in their molecules, hydrocarbon compounds that do not contain atoms with greatly different electronegativity, such as styrene, DVB, and isobutylene, have dipole moments that are about one order of magnitude smaller. This means that hydrocarbon monomers are suitable for designing polymer materials with low dielectric loss.

When these monomers are polymerized, the vinyl functional groups are lost and converted into saturated hydrocarbons. When ethylbenzene and isobutane with similar skeletons after polymerization of styrene and isobutylene are compared, the magnitude relationship of the dipole moments is reversed, depending on the presence or absence of the vinyl groups. This indicates that aliphatic hydrocarbon vinyl monomers can have lower dielectric loss. However,

Table 1 Chemical structure and dipole moment of vinyl monomers[15)]

Monomer	Chemical Structure	Dipole Moments(D)
Styrene		0.123±0.003
Divinylbenzene		0.09
Isobutylene		0.503±0.010
Methyl methacrylate		1.67
Acrylonitrile		3.92±0.07
Ethylbenzene		0.59
Isobutane		0.132

aliphatic compounds generally have lower glass transition temperature (Tg) than aromatic compounds, and the reactivity of the vinyl groups is lower than that of aromatic vinyl monomers. Aromatic vinyl monomers are thus considered to be more suitable for rigid circuit boards for high-speed communication.

In addition, monofunctional vinyl monomers lose their vinyl groups during polymerization, leaving no reactive functional groups in the resulting polymers, and the polymers have no thermosetting capability. As mentioned before, thermal curing is essential for this application, so bifunctional monomers must be used. For these reasons, if a polymer that retains its vinyl functional groups after polymerization can be obtained using DVB, which is a bifunctional aromatic vinyl monomer, it is believed that a resin suitable as the base resin for low-dielectric substrates for high-speed communication can be obtained.

2.3.2 PDVB synthesis examples

Various methods have been studied for the synthesis of PDVB. It is difficult to control the polymerization of PDVB. Although there have been several successful reports of soluble PDVB on a laboratory scale,[16–21)] Nippon Steel Chemical & Material is the first to achieve industrial-scale production of PDVB. Some prior examples and the technical challenges of this polymerization are described below.

When radical polymerization or anionic polymerization is performed using DVB as a monomer, intermolecular reactions at side chain double bonds (pendant vinyl groups) proceed in the early stage of the polymerization reaction, forming a three-dimensional crosslinked polymer, and ultimately yielding highly crosslinked insoluble materials.[22–27)] The key to designing soluble PDVB is how to suppress this three-dimensional crosslinking during polymerization. Two examples of the synthesis of soluble PDVB have been reported. One is the achievement of anionic polymerization by Tsuruta et al.[16, 17)] and Goseki et al.[21)] In this method, linear PDVB is obtained without the reaction of pendant vinyl groups by utilizing the fact that the reactivity of vinyl groups with one functional group consumed by polymerization, or pendant vinyl groups, is more than 100 times lower than that of vinyl groups with two functional groups. Gelation is consequently prevented (**Fig. 3**(a)).

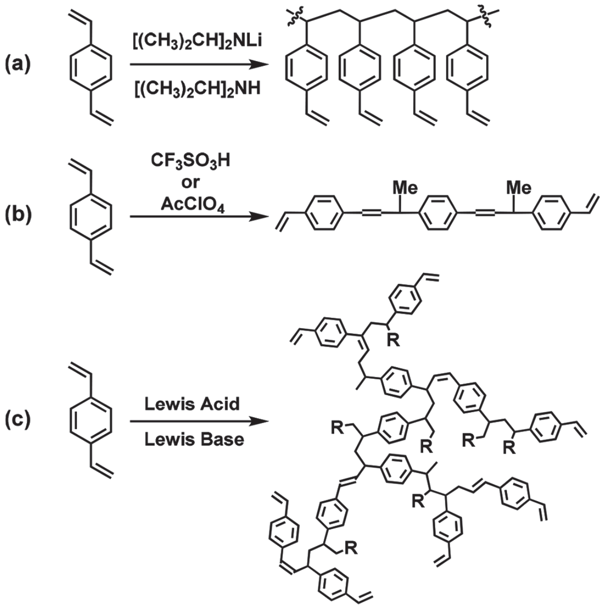


Fig. 3 Schematic diagram of previously reported soluble PDVB

However, it has been reported that the PDVB prepared by this method has low storage stability and that its pot life is only about 2 to 3 months when it is stored at extremely low temperatures.[21)] In general, the polymerization rate of vinyl groups is proportional to the concentration of functional groups. Since the reported PDVB is composed only of DVB, the vinyl functional group concentration is extremely high and excessive. This is presumably the cause of this phenomenon. In addition, the number-average molecular weight Mn of the PDVB synthesized by this method is about tens of thousands. This value is too large from the viewpoint of moldability.

The other example is cationic polymerization using an oxoacid catalyst (Fig. 3(b)).[19, 20)] In this method, the oxoacid not only acts as an initiator but also abstracts β protons near active ends faster than the propagation reaction, resulting in the synthesis of linear soluble PDVB with many multi-substituted olefins inside main chains. Generally, multi-substituted olefins have poor reactivity. In the reported structure, only the pendant vinyl groups at both ends function as reactive functional groups.

In contrast, Nippon Steel Chemical & Material reported that by carefully controlling the reactivity of DVB and pendant vinyl groups, the growth of branched chains from the pendant vinyl groups can be partially promoted. This approach enables the synthesis of oligomer-type hyperbranched PDVB while maintaining a moderate level of pendant vinyl groups, as illustrated in (Fig. 3(c)).[9–11)] This behavior is believed to be realized because of the simultaneous occurrence of two things: 1) moderate selectivity is achieved in the reactivity of pendant vinyl groups in DVB and PDVB in a particular combination of particular Lewis acid catalyst and solvent and 2) the Lewis base compound added as a third component causes β-deprotonation near the active site, suppressing the increase in molecular weight.

2.3.3 Synthesis and polymerization behavior of hyperbranched soluble PDVB

Next, based on the concept described in the previous section, a polymerization reaction was performed by using DVB, ethyl vinylbenzene, and styrene as monomers, as shown in **Fig. 4**. The results are described below.

In the combination of a Lewis acid catalyst and a solvent, a polymer with Mn exceeding tens of thousands was formed about 10 min after the start of polymerization, and some insoluble gels were observed. On the other hand, when a weak Lewis base compound was added in large excess to the catalyst in the same combination as that of the Lewis acid catalyst and solvent, polymerization proceeded without the addition of a gelled compound. **Figure 5** shows a chart of the change in molecular weight during polymerization as tracked by gel permeation chromatography.

From this chart, we can see that there is a single peak near the molecular weight of 2000 from the beginning of the polymerization. The position of the peak top changes little until the end of the polymerization. The molecular weight of PDVB formed through the propagation reaction until the chain transfer or reaction termination has a nearly constant distribution. On the other hand, with time, polymer components are formed at the peaks mentioned above. This indicates that the monomer or PDVB molecules are polymerized starting from the pendant vinyl groups of the formed PDVB and that their branching proceeds. The increase in molecular weight accelerates at the end of the polymerization because the concentration of PDVB molecules in the system increases at the end of the polymerization. In contrast, the monomer concentration decreases, resulting in a relatively high polymerization rate between PDVB molecules.

2.3.4 Properties of hyperbranched soluble PDVB

The obtained polymer solution was reprecipitated in methanol, and a white soluble solid material was obtained. The obtained solid material at a conversion ratio of 50% had a number-average molecular weight Mn of 2570 and a weight-average molecular weight Mw of 34000. The molecular weight distribution was relatively narrow. When the vinyl equivalent in the molecules was determined by iodine value measurement, it was 390 g/eq., confirming the presence of 6.6 vinyl groups per molecule. Proton NMR analysis showed peaks attributable to pendant vinyls at 5.0 to 5.3 ppm and 5.5 to 5.8 ppm and confirmed the presence of reactive functional groups. The obtained PDVB was pressure molded into sheets under reduced pressure at 200°C for 120 min by adding 1.0 part of the peroxidic initiator α,α'-Di(t-butylperoxy)-diisopropylbenzene to 100 parts of PDVB, and a white molded sheet was obtained. When the dielectric properties of the molded sheet were measured by the cavity resonance method at 18 GHz, the dielectric constant Dk was 2.38, and the dielectric loss tangent Df was 0.00128. The dielectric loss tangent Df of 0.00128 is extremely small compared to the Df of 0.003 for thermosetting polyphenylene ether (PPE), which is reported to have been adopted in 4G communication circuit boards. The hyperbranched soluble PDVB was thus found to exhibit excellent dielectric properties as designed.

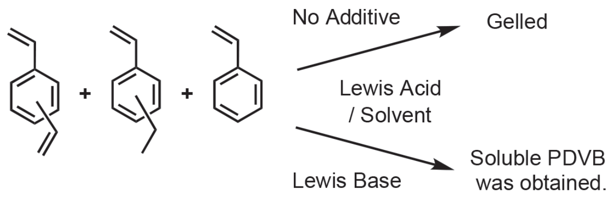


Fig. 4 Differences in polymerization behavior depending on the presence or absence of Lewis base compounds

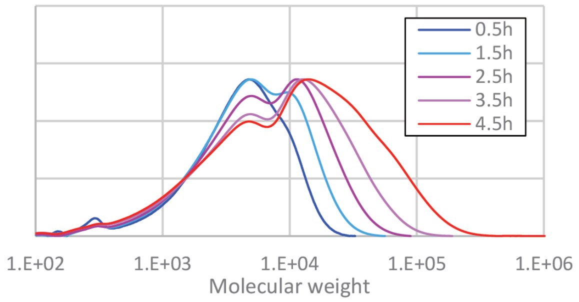


Fig. 5 Changes in molecular weight distribution during PDVB polymerization

2.3.5 Temperature-viscosity behavior of hyperbranched soluble PDVB

Figure 6 shows the temperature-viscosity curve of PDVB measured at a heating rate of 3°C/min by using a rheometer with a parallel plate. As a reference material, data for thermosetting PPE is also shown. Thermosetting PPE has both phenolic terminal groups functionalized with vinyl groups (Mn: 2400). There is no data below 120°C for thermosetting PPE because it did not liquefy below 120°C and could not be measured. This figure shows that the viscosity of PDVB decreases by more than two orders of magnitude as the temperature increases and then increases sharply from 140°C. This increase in viscosity is ascribed to the self-polymerization of the pendant vinyl groups in PDVB at high temperatures and the progress of gelation.

On the other hand, in thermosetting PPE, the main chains are linear, and the Tg of the main chains themselves is high, so the drop in viscosity near the temperature at which curing begins is smaller than that of PDVB. As the curing temperature increases further, the curing reaction begins at 140°C, and the viscosity increases slowly. The difference in the viscosity increase between the two at 140°C and above is thought to be due to the difference in functional group density. PDVB has six or more pendant vinyl groups in one molecule, while thermosetting PPE has vinyl groups only at both ends, so its gelation rate is slow. The above data suggests that PDVB is more advantageous in ensuring fluidity during molding. Still, the curing rate of PDVB is so fast that detailed consideration is required to control the press pressure and press timing when creating laminates.

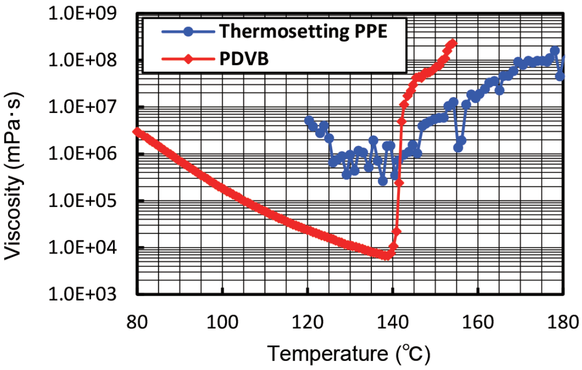


Fig. 6 Relationship between temperature and viscosity of PDVB and thermosetting PPE resin

2.4 PDVB laminate evaluation

2.4.1 PDVB laminate preparation conditions

Next, copper-clad laminates were fabricated using the PDVB obtained as described above, and their physical properties were evaluated. The physical properties of laminates produced by blending PDVB with other resins are also described.

As described before, PDVB exhibits good compatibility with various polymers due to its multi-branched structure and aromatic main chain structure. For example, it is very compatible with the aforementioned vinyl-functionalized thermosetting PPE, and it also exhibits a certain degree of compatibility with high molecular weight resins such as hydrogenated styrene-butadiene rubber (HSBR), which is sometimes used to impart ductility to laminates. In particular, it exhibits good compatibility with HSBR, which has a high styrene content. This good compatibility means that there is a high degree of freedom in blend design when we try to meet the required properties of multilayer boards for high-speed communication.

According to the conditions in **Table 2**, rigid CCLs were prepared using compounds consisting of PDVB, thermosetting PPE, and HSBR. The physical properties of the obtained rigid CCLs were measured. The compound compositions and the measurement results of the physical properties are summarized in **Table 3**. The HSBR in the table has a styrene content of approximately 60%. The copper foils used in the CCLs are based on low-roughening foils (VSP foils). The roughened surface is prepared with a type of treatment that is compatible with vinyl groups. In order to clarify the effect of the resin compound composition, silica filler, and flame retardant were not added. A peroxide-type radical initiator was added as a curing catalyst, and the CCLs were prepared under the conditions listed in Table 2.

Table 2 Processing conditions for manufacturing the prepreg and laminate

Prepreg	Glass cloth	NE-Glass #2116
	Drying conditions	130°C × 5 min
	Resin content (%)	49–51
Laminate	Number of ply	8
	Copper foil	VSP, 35 um
	Press conditions	130°C × 15 min. ⇒ 210°C × 80 min. × 2.0 MPa (Under vacuum)

2.4.2 Evaluation results of laminates using PDVB

For laminates composed only of PDVB, the Df value measured by the SPDR method at 10 GHz was 0.0018. This value is higher than the Df value for PDVB alone. This situation is due to compounding with glass cloth. (The dielectric property of NE Glass (low dielectric glass fiber cloth manufactured by Nitto Boseki Co., Ltd.) has a dielectric property of about 0.003 at 10 GHz). In actual 5G CCLs, glass cloths with a lower Df are used.3) In addition, the copper foil peel strength and interlayer peel strength (IL Peel in Table 3, that is, the interlaminar adhesion strength of the prepreg.) of PDVB alone are 0.46 kN/m. This value is about 60% of the 0.8 kN/m of laminates produced by using thermosetting PPE for 4G communication. On the other hand, blending of thermosetting PPE can improve the peel strength and Tg at some sacrifice of the dielectric property. Observation of the copper foil interface after peeling showed that cohesive failure occurred at the interface in all experimental levels. It is thought that the addition of thermosetting PPE improved the toughness of the resin compound, resulting in improved peel strength. By further adding HSBR, which is a rubber-like thermoplastic resin consisting only of hydrocarbons, to these two components, it is possible to improve the peel strength while maintaining the dielectric tangent. As described above, compounding PDVB with multiple resins can control its physical properties to suit its application in 5G communication.

2.4.3 Viscoelastic behavior of laminates using PDVB

In order to investigate how the mixed and cured PDVB and thermosetting PPE undergo three-dimensional crosslinking, we measured the viscoelastic behavior of laminates by dynamic mechanical analysis (DMA). The results are shown in **Fig. 7** (measurement frequency of 10 Hz). The storage modulus E' and loss modulus E'' of PDVB alone do not show any clear Tg and do not appreciably decrease either, and tan δ exhibits broad peaks over a wide temperature range.

This finding suggests that there are variations in the crosslink density in the cured material. The following two factors are thought to be responsible for this uneven crosslink density: 1) the wide molecular weight distribution of PDVB causes variations in the number of reactive functional groups per molecular chain, and 2) the composition of each molecular chain varies as the polymerization pro-

Table 3 Properties of laminates made from PDVB and its compounds

Property[*1]	Run-4	Run-5	Run-6	Run-7	Run-8	Run-9
PDVB	100	70	50	30	63	56
Thermosetting -PPE	0	30	50	70	27	24
HSBR	0	0	0	0	10	20
Dk(-), 10GHz[*2]	3.12	3.14	3.16	3.17	3.15	3.05
Df(-), 10GHz*[2]	0.0018	0.0023	0.0025	0.0026	0.0023	0.0022
Tg (°C), tan δ, DMA, Three-Point Bend	171	186	185	175	184	181
CTE (ppm/°C) 70–100°C	79	56	56	75	108	145
CTE (ppm/°C) 200–230°C	278	326	361	422	359	400
Cu Peel Strength (kN/m)	0.46	0.66	0.79	0.87	0.77	0.91
IL Peel Strength (kN/m)	0.46	0.74	0.91	1.08	0.89	1.39

*1 Initiator: *α*, *α*’-Di(*t*-butylperoxy)- diisopropylbenzene

*2 Split post dielectric resonator (SPDR) measurement

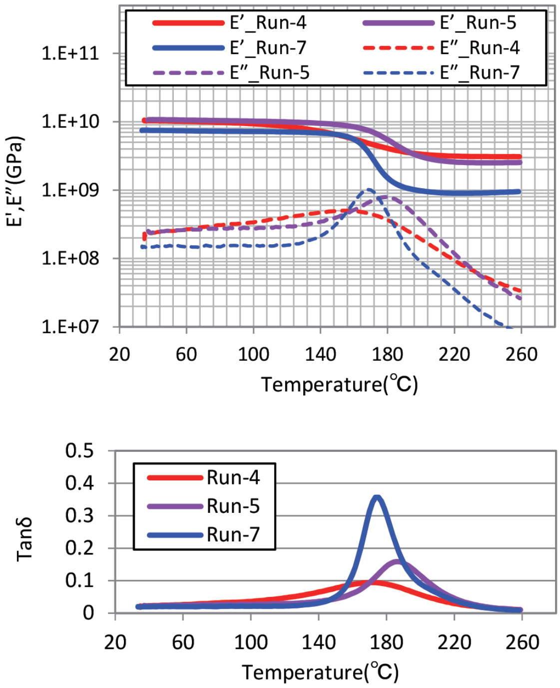


Fig. 7 DMA Thermogram for PDVB and thermosetting PPE blends (upper chart: storage modulus E′ and loss modulus E″, lower chart: loss tangent tan δ)

gresses. Regarding factor 2), the reaction rate constants differ between the DVB and styrene used in the polymerization, resulting in differences in the consumption rate of the monomers. As a result, it is speculated that the monomer composition in the reaction system changes between the start and end of the polymerization, causing variations in the concentration of pendant vinyl groups.

On the other hand, the blend of PDVB and thermosetting PPE gave a clear single-peak Tg, and the peak of tan δ became sharper as the content of thermosetting PPE increased. This situation is presumably because the number of vinyl functional groups per molecule of thermosetting PPE is smaller than that of PDVB (vinyl group equivalent of thermosetting PPE is 1200 g/eq.), the distance between crosslinking points increases when thermosetting PPE is copolymerized with PDVB, and the influence of polyphenylene ether chains in the crosslinking chain becomes stronger. These results suggest that PDVB and thermosetting PPE are copolymerized well and uniform during the curing process, making it possible to obtain laminates without variations in properties such as strength.

3. Conclusions

We developed a soluble PDVB suitable as a base resin for rigid circuits for 5G high-speed communication and described its design, polymerization behavior, and dielectric properties. We also prepared and evaluated laminates using the soluble PDVB and its blends with other resins and described the characteristics of the laminates. At present, the soluble PDVB produced by applying the technology described in this report has already been adopted by some customers and is now being mass-produced.

Currently, material development for next-generation 6G communication is already in full swing. 6G communication demands that the dielectric tangent must be nearly halved. In addition, optical communication is beginning to be targeted as a means of communication after 6G. We must endeavor to perform our development work while focusing on these wide-ranging technical fields.

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Shinichi IWASHITA
Ph.D., Senior Researcher
Functional Resin Materials Development Center
Research & Development Div.
Nippon Steel Chemical & Material Co., Ltd.
11-5 Kitasode, Sodegaura City, Chiba Pref. 299-0266