Technical Report

Development of High-Frequency Responsive Flexible Dielectric Materials Using Materials Informatics

Tetsuya KOBAYASHI*

Abstract

In this study, we aimed to develop a novel materials development strategy utilizing materials informatics (MI), leveraging recent advancements in computational science and informatics. Using the development of high-frequency flexible dielectric materials as a model system, we employed MI technology to systematically narrow down the types of polyimide monomers of dielectric materials and to identify those exhibiting a low dielectric constant and low loss tangent. The selected monomers were synthesized into samples. By comparing the predicted dielectric constants and losses with the experimentally measured values, we validated the effectiveness of the proposed materials development approach.

1. Introduction

In the material development sector, research and development using computational science and informatics has become more active both in Japan and overseas due to the dramatic improvement of computational power. Particularly, materials informatics (MI), which combines materials science and data science, has attracted attention as a new material development methodology that does not rely on conventional empirical rules. The use of MI is expected to expand the search range for material compositions and shorten material development time. However, to introduce MI technology, it is necessary to build an MI technology scheme that combines technologies suitable for individual materials and physical properties, such as material property calculation technology, machine learning technology, and molecular structure numerical representation (descriptor design) technology for machine learning. Therefore, with the aim of building a material development scheme using MI, we verified the effectiveness of introducing MI technology by using the development of flexible high-frequency dielectric materials as a concrete model case.

In the development trends of high-frequency flexible dielectric materials, the use of high-frequency bands above gigahertz has been accelerating. In the fifth generation (5G) mobile communication system, which has been widely implemented in recent years, there is a demand for even larger capacity and faster transmission. These dielectric materials are generally laminated with copper foil and used as circuit board materials for IoT devices, etc. Since the transmission loss increases with the increase in frequency, it is important to reduce the transmission loss. The transmission loss is roughly divided into the dielectric loss and conductor loss of the circuit board material. The transmission loss increases with the increase in dielectric constant and dielectric loss tangent of dielectric materials.[1)] Therefore, in general, for flexible circuit board materials using polyimide substrates, the challenge is to reduce the dielectric constant and dielectric loss tangent of polyimide films.

Polyimide is produced by polymerization of tetracarboxylic dianhydride monomers and aromatic diamine monomers. In the molecular design of polyimide, its dielectric properties have been revealed to vary significantly depending on the monomer type. Trial and error attempts have been made to achieve the desired properties by combining monomers. On the other hand, however, the search space is wide in terms of monomer type options, monomer mixing ratios, process conditions, etc. Conditions are examined within limited ranges. Unexplored areas may remain. Against this background, this study aims to develop low-dielectric constant and low-dielectric loss tangent polyimide materials. It proposes a material development scheme that efficiently narrows down compounds by MI technology in a wide search range of polyimide monomer types. Samples of searched compounds were actually prepared and evaluated. The predicted values of the dielectric constant and dielectric loss tangent were compared with the actual values of the dielectric constant and dielectric loss tangent to verify the effectiveness of this material development scheme.

* Ph.D., Researcher, Basic Technology Integration Center, Research & Development Div., Nippon Steel Chemical & Material Co., Ltd.
1 Tsukiji, Kisarazu City, Chiba Pref. 292-0835

2. Study of Material Development Scheme Using MI

2.1 Material development scheme using MI

Figure 1 shows an outline of the material development scheme using MI as considered in this study. Low-dielectric constant and low-dielectric loss tangent materials are hypothesized. Polyimide monomers are selected on the basis of the hypotheses. Materials are then prototyped and evaluated. A scheme that utilizes machine learning and computational science at the stage of polyimide monomer selection is added to this material development flow. As a concrete material development flow, the dielectric constant and dielectric loss tangent are generally positively correlated with each other.[2] Based on this recognition, a dielectric constant regression model is built by using machine learning, and candidate materials with a low dielectric constant are selected from the search range and narrowed down. Next, detailed calculations of the dielectric constant and dielectric loss tangent are performed on the narrowed-down materials using computational science. Candidate materials expected to have low dielectric constant and low dielectric loss tangent are selected. Finally, the selected candidate materials are actually synthesized, and whether they have low dielectric constant and low dielectric loss tangent is confirmed by measurement and evaluation. Accordingly, the effectiveness of this material development scheme is verified.

The dielectric constant and dielectric loss tangent are expressed as complex dielectric functions as follows:

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \quad (1)$$

$$\tan\delta = \varepsilon''/\varepsilon' \quad (2)$$

where ω is the frequency, $\varepsilon(\omega)$ is the dielectric function, ε' is the dielectric constant, ε'' is the amount of the loss that occurs as a portion of the electrical energy becomes heat when an AC electric field is applied, $\tan\delta$ is the dielectric loss tangent, and i is the imaginary unit. When an electric field is applied to a dielectric material, various polarizations occur, including electronic polarization due to electron cloud distortion, atomic polarization due to changes in the relative positions of atoms, and orientation polarization due to the orientation of molecules by dipoles. In the high-frequency gigahertz band targeted in this study, the dielectric constant ε' is expressed as the sum of the contributions of the electronic polarization, atomic polarization, and orientation polarization as given by:

$$\varepsilon' = \varepsilon'_{ele} + \varepsilon'_{vib} + \varepsilon'_{dip} \quad (3)$$

where ε'_{ele}, ε'_{vib}, and ε'_{dip} are dielectric constants derived from electronic polarization, atomic polarization, and orientation polarization, respectively. In the gigahertz band, ε'' is dominated by the contribution of the orientation polarization due to the rotational motion of molecules. In order to calculate the dielectric constant and dielectric loss tangent by considering these polarizations, we think that first-principles calculation and molecular dynamics calculation are appropriate methods in terms of scale for the contribution of electronic polarization and the contributions of the atomic polarization and orientation polarization, respectively. However, in this study, the first-principles calculation model requires several hundred atoms. In order to calculate the dielectric properties at high frequencies such as 10 GHz, molecular dynamics calculation requires data on an extremely long timescale of several tens of nanoseconds or more. Both methods are thus expected to require a high computational load. Therefore, we investigated a workflow in which compounds with a low electronic polarization-derived dielectric constant, ε'_{ele}, exhibiting a response across the entire frequency range, are efficiently explored using machine learning, and for the selected candidate materials, detailed calculations of the remaining contributions, ε'_{vib} and ε'_{dip}, are performed using molecular dynamics simulations.

2.2 Search for low-dielectric materials

In order to construct a group of calculation data linking the structure and dielectric properties of polyimide, we calculated the dielectric constant ε'_{ele} derived from the electronic polarization by the first-principles calculation method. The calculations used the first-principles calculation program package OpenMX.[3] To create training data for machine learning, we performed calculations on 100 types of polyimides composed of 10 types of dianhydride monomers and 10 types of diamine monomers. The monomer structures of the polyimide are omitted in this report but were selected from known literature.[4, 5] The general structural formula of polyimide is shown in **Fig. 2**. As a polyimide calculation model, we created a single-chain model in which dianhydride monomers and diamine monomers were alternately bonded in tetramers and performed structural optimization calculations based on the density functional theory. The dielectric constant was calculated for the stable structure obtained. To verify the validity of the calculation results, we compared some of the calculation results with actual measurements. In **Fig. 3**, the calculation results of the dielectric constant derived from the electronic polarization for CBDA/TFMB, 10 EFDA/TFMB, 10EFDA/4FMPD, BPDA/TFMB, PMDA/ODA, and BPDA/PDA (the abbreviations before and after the slashes are the dianhydride monomers and diamine monomers, respectively) are shown in comparison with the measurement results of the dielectric constant.[6, 7] The calculated values agreed with the measured values in terms of sequence. This result indicated that the contribution of the electronic polarization may be large in the gigahertz band. **Figure 4** shows the distribution of the calculated dielectric constant ε'_{ele} due to the electronic polarization for 100 types of polyimides as a histogram. Machine learning was performed by using these calculated data as training data.

2.3 Building dielectric constant regression model by machine learning

In order to predict the dielectric constant by using machine learning, we created explanatory variables for machine learning by

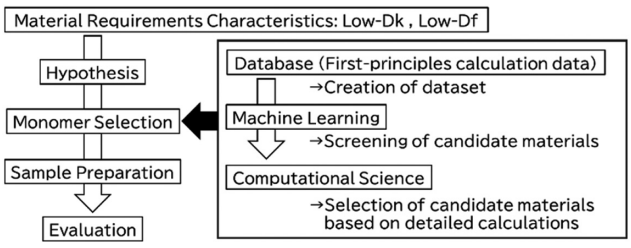

Fig. 1 Material development scheme using MI

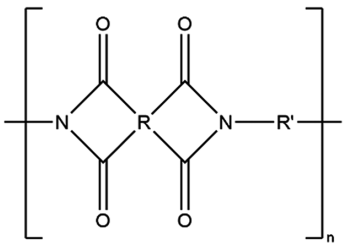

Fig. 2 General structural formula of polyimide

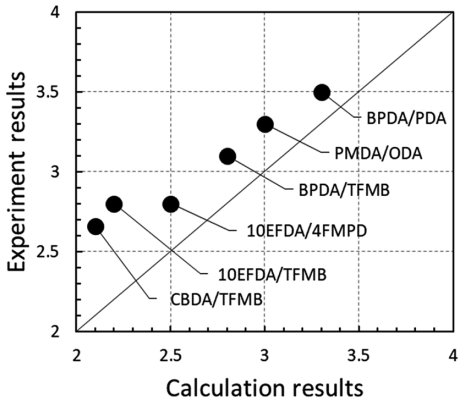

Fig. 3 Comparison of first-principles calculation results of dielectric constant derived from electronic polarization and measured dielectric constant values (literature values)

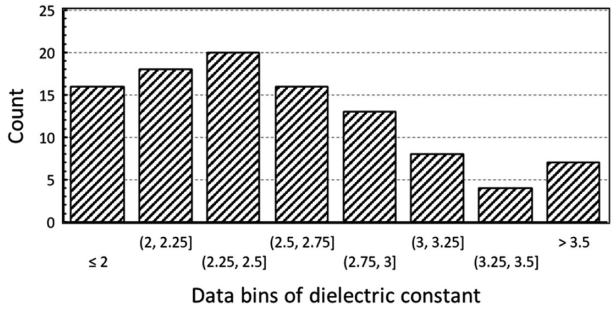

Fig. 4 Distribution of dielectric constant data derived from electronic polarization

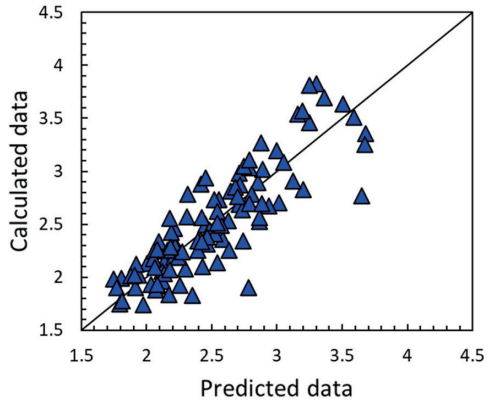

Fig. 5 Results of 10-fold cross-validation on the test data

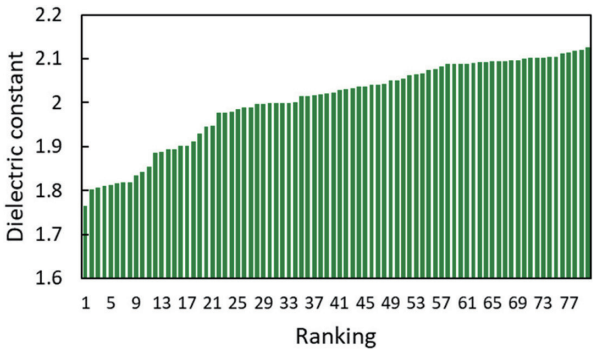

Fig. 6 Prediction results of dielectric constant using machine learning

using the number-density ECFP (extended connectivity fingerprint)[8] of the chemical structure of polyimide. This number-density ECFP is a method of quantifying the number-density of a substructure by dividing the ECFP, which is a representative molecular descriptor, by the number of constituent atoms. We used this feature quantity as the explanatory variable and the dielectric constant derived from the electronic polarization as the objective variable to build a regression model by using the Gaussian process regression, which is a machine learning method. However, since the density of ECFP generates a large number of explanatory variables compared to the number of data, there is a possibility that the reliability of the analysis may decrease. Considering this possibility, we built the regression model after deleting explanatory variables with low contributions to the objective variables by statistical processing. We performed the K-fold cross-validation to evaluate the degree to which the regression model can predict unknown materials. Specifically, K = 10. We divided 100 pieces of training data into 10 groups of 10 pieces of data each. We evaluated the accuracy rate by using one group as test data and the rest as training data. The model was trained 10 times so that all 10 groups of data were used once as test data, and the accuracy rates were averaged. **Figure 5** shows the results of 10-fold cross-validation of the test data. Here, the coefficient of determination R^2 was used as an index of the accuracy rate. The closer the coefficient of determination is to 1, the higher the predictive performance of the regression model. The coefficient of determination R^2 for the test data of the regression model was 0.73. We believe that the predictive performance of the model for unknown materials is reasonable for practical purposes.

Next, we used the constructed regression model to predict the dielectric constant ε'_{ele} of polyimide due to the electronic polarization. The polyimide to be predicted was a hypothetical polyimide structure created by combining one type of tetracarboxylic dianhydride monomer and one or two types of aromatic or alicyclic diamine monomers from among the known monomers obtained from References 4) and 5). **Figure 6** shows the predicted dielectric constants of the top 80 types (approximately 10%) of the 820 types of predicted polyimides in order of lowest to highest. By using the constructed regression model, it became possible to predict the dielectric constants of 820 types in just a few seconds. In reality, the number of combinations of tetracarboxylic dianhydride monomers and diamine monomers is so enormous that the effect of this machine learning method is expected to be very large in shortening the development period. Here, the top 80 types (approximately 10%) were selected as candidates for low dielectric constant materials. Furthermore, considering the actual polymerization process conditions, the ease of film formation, etc., we selected 8 types from these top 80 types for calculation. For these candidate materials, the dielectric constant and dielectric loss tangent derived from the atomic polarization and orientation polarization were calculated using the molecular dynamics method.

2.4 Calculation of dielectric properties due to atomic polarization and orientation polarization using molecular dynamics calculations

The frequency dependence of the dielectric properties is calculated by the following equations[9] :

$$\varepsilon(\omega) = <\Delta M_\alpha^2>/(Vk_BT)\cdot\{1-i\omega\int_0^\infty e^{-i\omega t}\,\Phi(t)dt\} + \varepsilon'_{ele} \quad (4)$$

$$\Phi(t) = \{<M_\alpha(0)\cdot M_\alpha(t)> - <M_\alpha>^2\}/<\Delta M_\alpha^2> \quad (5)$$

$$<\Delta M_\alpha^2> = <M_\alpha^2> - <M_\alpha>^2 \quad (6)$$

where M_α is the dipole moment, α is the x, y, and z coordinates, V is the volume, k_B is the Boltzmann constant, T is the temperature, t is the time, the angle brackets < > indicate the ensemble average, and $M_\alpha(0)\cdot M_\alpha(t)$ is the autocorrelation function of the dipole moment. Equation (4) is derived from the linear response theory. It means that the dielectric properties are calculated from the time change of the dipole moment M_α due to thermal fluctuations in the equilibrium state. First, the time change of the dipole moment M_α is calculated by the molecular dynamic method. However, since the charge on each atom is calculated as a point charge and does not change with time, the dipole moment M_α changes with time only depending on the distance between the point charges. LAMMPS[10] was used as the simulation software for the molecular dynamic calculations. The point charges were calculated using the density functional method at the B3LYP/6-31G(d) level. In the molecular dynamics model of polyimide, the total number of atoms was about 6 000, the number of molecules was 16, and the force field was the generalized Amber force field (GAFF). As shown in **Table 1**, structural relaxation calculations were performed by repeatedly increasing and decreasing the temperature. The change over time of the dipole moment vector M_α was obtained for the calculation model after structural relaxation. The obtained dipole moment vector M_α was used to calculate the dielectric constant and dielectric loss tangent according to Eqs. (1) to (6).

Figure 7 shows the calculation results of the loss ε'' for the eight selected polyimides. Two types of polyimides were selected for sample preparation: No. 1, which had a low ε'' in the target frequency range of 20 GHz to 60 GHz, and No. 6, which was used as a reference. Prototypes were made for these two compounds, and the dielectric constant and dielectric loss tangent were measured using a split cylinder resonator. **Figure 8** shows the predicted and measured results of the dielectric constant and dielectric loss tangent for samples No. 1 and No. 6. The calculated values of the dielectric constant and dielectric loss tangent are underestimated compared to the actual measurements, but the magnitude relationship between the two samples is captured. As mentioned above, the dielectric constant and dielectric loss tangent are generally positively correlated. So, considering that both are underestimated, we believe that there is a common factor that causes the underestimation. Focusing on the contribution of orientation polarization as a common factor, we calculate the dielectric constant and the dielectric loss tangent, both derived from the orientation polarization, from the dipole moment using Eqs. (4) to (6). In this study, the response of the orientation polarization when an AC electric field is applied to the system is approximated as an autocorrelation function of the minute fluctuation of the dipole moment of the molecule in thermal equilibrium by the linear response theory. However, since a high-frequency AC electric field of several tens of GHz is actually applied, we expect that the response of the orientation polarization will be larger than the minute fluctuation of the molecule. Due to these factors, the molecular motion may be estimated to be smaller than the actual state, and the dipole moment may be underestimated. In light of these factors, it is believed that the underestimation can be improved if the AC electric field under actual conditions can be considered in the molecular dynamic simulation. In addition, polyimide exhibits high water absorption due to the high polarity of the carbonyl group of the imide ring, and it has been reported that its dielectric loss tangent changes depending on the humidity conditions, and the dielectric loss tangent increases with the increase in water absorption.[11] This situation is also thought to be one of the factors that cause the calculated val-

Table 1 Structural relaxation procedure for molecular dynamics model of polyimide

	Ensemble	Temperature	Total time
1	NVT	300 K	100 ps
2	NPT	300 K	1 ns
3	NPT	800 K	1 ns
4	NPT	300 K	1 ns
5	NPT	800 K	1 ns
6	NPT	300 K	1 ns
7	NPT	800 K	1 ns
8	NPT	296 K	30 ns

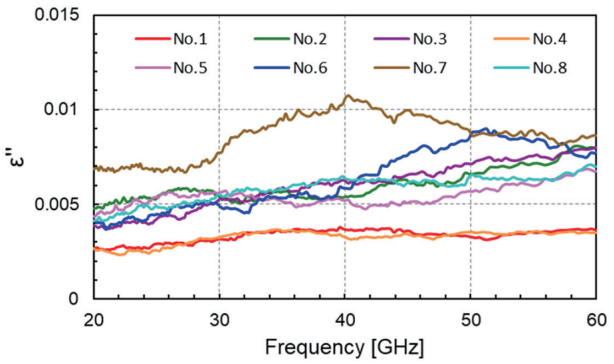

Fig. 7 Calculation results of ε″

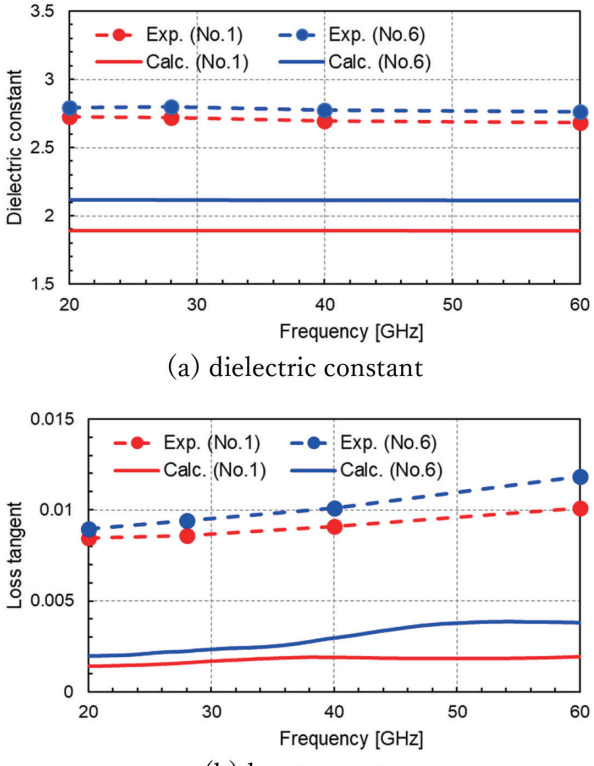

Fig. 8 Predicted results and measured results for (a) dielectric constant and (b) loss tangent

ue to be underestimated.

In the search range of this study, sample No. 1 was predicted to have the lowest dielectric constant and dielectric loss tangent. It had lower dielectric properties than the average dielectric properties of general aromatic polyimide, or a dielectric constant of 3.5 and a dielectric loss tangent of 0.01. In this way, in this model case, we were able to efficiently narrow down the compounds from a wide search range, leading to a shortened development period. We consider that we have confirmed the effectiveness of this MI scheme.

3. Conclusions

Aiming to establish a material development scheme utilizing MI, we examined the effectiveness of the material development scheme proposed in this study by using the development of a high-frequency flexible dielectric material as a concrete model case. Through this study, we found that machine learning based on a relatively small number of training data (approximately 100 data) is effective for material development and that the use of a regression model makes it possible to predict material properties in a very short time. In the future, we intend to practically deploy MI technology in the development of functional materials with excellent overall balance, combining low dielectric constant, low dielectric loss tangent, and other material properties.

Acknowledgments

The results reported here were obtained as an outcome of the Ultra High-Throughput Design and Prototyping Technology for Ultra Advanced Materials Development Project (P16010) commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

References

1) Tanaka, A.: Journal of the Japan Institute of Electronics Packaging. 8 (4), 271 (2005)
2) Kawai, A.: Journal of the Surface Finishing Society of Japan. 72 (6), 315 (2021)
3) Ozaki, T.: Physical Review B. 67, 155108 (2003)
4) Ando, S.: Recent Advances in Polyimides and Aromatic Polymers 2013. 32 (2013)
5) Ando, S.: Recent Advances in Polyimides 1995. 11 (1995)
6) Hasegawa, M.: Recent Advances in Polyimides 2001. 103 (2001)
7) Ando, S.: Materials Science and Technology of Japan. 49 (5), 194 (2012)
8) Minami, T., Okuno, Y.: MRS Advances. 3 (49), 2975 (2018)
9) Karasawa, N., Goddard, III, W.A.: Macromolecules. 28 (20), 6765 (1995)
10) Thompson, A.P., Aktulga, H.M., Berger, R. et al.: Computer Physics Communications. 271, 108171 (2022)
11) Fukunaga, K., Kurahashi, S.: IEEJ Transactions on Electrical and Electronic Engineering. 2 (6), 596 (2007)

Tetsuya KOBAYASHI
Ph.D., Researcher
Basic Technology Integration Center
Research & Development Div.
Nippon Steel Chemical & Material Co., Ltd.
1 Tsukiji, Kisarazu City, Chiba Pref. 292-0835