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Chemical Structure Evaluations of Amine Hardeners to Ensure and Predict the Performance of Wet Adhesion of Epoxies

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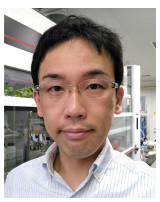

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Abstract

The relationship between the chemical structure and performance of a water-sorbed epoxy adhesive (wet adhesion) provides fundamental data for epoxy adhesives for application in wet and underwater environments. However, data on the effect of the chemical structure on wet adhesion remains insufficient. This study systematically examined the wet adhesion strengths of epoxies comprising bisphenol A diglycidyl ether and various amines. The use of numerical parameters quantifying the features of the chemical structure and physicochemical properties via theoretical calculations to analyze the correlation between wet adhesion and the chemical structure of amine yielded clear linear relationships. This enabled the extraction of the amine molecular structural features that were superior in wet adhesion, in addition to quantification of the certainties of the features contributing to the physical properties. Furthermore, a prediction model for wet adhesive strength was prepared using machine-learning least absolute shrinkage and selection operator regression analysis. The model exhibited a reasonable accuracy, even using only 14 experimental values, and its effectiveness was verified experimentally. This process facilitates the rational design and selection of amine hardeners for preparing epoxies with excellent performance in wet conditions and underwater environments.

Keywords: Epoxy | Wet adhesion | Machine-leaning prediction

1. Introduction

Epoxy adhesives are widely used for applications in wet external and underwater environments, such as construction, automobiles, aircraft, and ships. The importance is evident in the fact that they are the one of the most significant types of adhesive materials for marine applications, for example. Considering the high demand for reliability of epoxy adhesives in these applications, the adhesive performance under wet condition is critical. Compared to those of other adhesive materials, the water resistance properties of epoxies, particularly those prepared using bisphenol-type base resins and amine hardeners, distinguish them for applications under wet conditions.[1,2] However, the absorption of water by an epoxy causes detrimental effects on its properties, such as swelling,[3–5] lowering of the glass transition temperature[6,7] and modulus,[8–10] and deterioration of the adhesion performance and failure mode,[10,11] despite the epoxies often absorbing a maximum of only a few to 10 weight percent of water. The adhesive strength, in particular, is considerably affected, with a $>50\%$ reduction in performance depending on the epoxy, substrate, and conditions. Therefore, understanding the factors of adhesion strength in the water-sorbed state, that is, wet adhesion, is crucial for the development and use of epoxy adhesives.

The chemical structure of an epoxy determines the characteristics related to water in terms of the maximum water absorption content and the diffusion coefficient of water,[12–14] effects on the glass transition temperature[7,15,16] and elastic modulus,[16–18] and wet adhesion performance.[17,19–21] Wu reported the effects of the stoichiometries of oxirane (base resin) and amine compounds in the wet adhesion of an epoxy on an aluminum alloy.[19] Furthermore, the same group studied the effect of the chemical structure using combinations of 2 different oxirane and 4

different amine compounds, along with the water absorption content.[20] Nevertheless, data on the effect of the chemical structure on wet adhesion remains quite insufficient. This problem can be clarified via systematic studies of wet adhesion using various epoxies with different chemical structures and quantification of the features of the chemical structures. Epoxies prepared using bisphenol-type base resins and amine hardeners mostly contain bisphenol-A diglycidyl ether (BADGE) as the base resin. Therefore, the investigation of the structural variation of amine hardeners to clarify the relationship between the epoxy chemical structure and the wet adhesion properties is important.

The engagement of experimental data generation/collection and machine-learning prediction of polymer material properties has become promising in recent years.[22–24] Especially in material application, where experimental methods and conditions often tend to differ in each report, prediction based even a small set of methodologically unified data accelerates the development.[25,26] However, such study has never been achieved for wet adhesion of epoxies due to the lack of sufficient data. With useful experiment data, quantifying the relationship between the chemical structure of the amine and wet adhesion property enables the prediction of the performance from the chemical structure. Such prediction model accelerates the development and molecular design of novel amine hardeners with excellent performance.

In this study, the relationship of the chemical structures of diamine hardeners on the wet adhesion properties of bisphenol A-type epoxies on stainless steel was investigated. The prediction of wet adhesion by chemical structure was proposed for the first time. Fourteen amine compounds were used to prepare different epoxy adhesives, and their water absorption behaviors and wet adhesion strengths after immersion in water were examined. The use of a chemical knowledge-based list of parameters in the analysis of the correlation between wet adhesion and the chemical structure of the amine yielded clear linear relationships. These numerical parameters quantified the features of the chemical structure and physicochemical properties via theoretical calculations. The obtained linear relationships revealed the structural features that favored wet adhesion. Quantification of the effects of the features of the chemical structure via machine-learning least absolute shrinkage and selection operator (LASSO) regression analysis provided an effective model for predicting the wet adhesion strength, even based on a small set of experiments.

2. Experimental

Preparation of Epoxies. A mixture of BADGE and amines (molar ratio of 2:1) was stirred in a glass vial and then placed under vacuum at 90 °C to remove the gas within the mixture. After the gases were eliminated, the mixture was used to prepare samples for water absorption and lap-shear tests. The mixture was cured via heating for 2 h at 120 °C for 1,4-phenylenediamine (**13**) and 4,4′-diaminodiphenylmethane (**14**), or at 90 °C for others and stored in a desiccator at approximately 25 °C for 24 h. Consumption of the oxirane in BADGE was confirmed using infrared spectroscopy. Rectangular 50 × 10 × 0.5 mm (thickness is the average) samples were prepared for the water absorption tests using a bar coater. A sandwich-shaped lap-shear test sample with the dimensions as shown in Figure S1 was prepared using a silicone mold with SUS329J4L stainless steel plates, which were pretreated via sanding, washing with acetone, and drying with N_2 gas.

It is known that curing temperature affects the network structure and the properties of epoxy.[27–29] However, the difference is small (30 °C), and the effect of curing temperature difference to the properties has been estimated not as significant as that of chemical structure of hardeners.[26] Therefore, the curing temperature difference was accepted for the analysis in this study.

Water Absorption Study. The epoxy film sample was heated at 100 °C under vacuum for 2 h before testing. The initial mass and dimensions of the sample were recorded, and then it was immersed in deionized water at 40 °C under temperature control. Samples were periodically removed from the water, weighed after wiping the water off and returned to the water. Mass monitoring continued until the samples reached saturation. The increases in mass are the averages of three tests with different samples. The diffusion coefficient is determined by analyzing absorption using Fick's law according to eq 1,[30] where q_t is the absorbed water content at time t, A and V are the surface area and volume of the specimen, respectively, and D_{eff} is the diffusion coefficient.

$$\frac{q_t}{q_{max}} = \frac{2A}{V}\sqrt{\frac{D_{\text{eff}} \cdot t}{\pi}} \tag{1}$$

Lap-Shear Test. The lap-shear bonding property of the sandwich-shaped epoxy sample prepared using SUS329J4L was measured using an Autograph AG-X (Shimadzu) with a 500 N load cell in the tension mode. The crosshead speed was set at 1 mm/min, and the reported values are the medians of five measurements for each epoxy with a standard error. The nominal shear strength was determined using the following equation: $\tau_{max} = F_{max}/A$, where τ_{max} is the shear strength (MPa), F_{max} is the maximum load (N), and A is the adhesion surface area of the sample (mm^2). Prior to the lap-shear test, the sandwich-shaped epoxy samples were immersed in deionized water at 60 °C for 14 d. A sample was then removed and used in the lap-shear test after wiping the water off using flowing N_2 gas.

Definition of the Structure Feature Parameters. The number of heavy atoms (**P1**) is the sum of the number of carbon, oxygen, and nitrogen atoms. The number of single bonds yielding different conformers (**P2**) is the number of single bonds in an acyclic chain that yield a different molecular conformation upon rotation. The cyclohexane ring was counted as 1, as it adopted a chair or boat conformation, and the C–N bond of the C–NH_2 moiety was counted as 1, considering the lone pair of nitrogen atoms. The sum of nitrogen and oxygen atoms (**P3**) is as the feature name suggests, and the number of rings (**P4**) is the sum of the number of cyclohexane and benzene rings. These parameters were prepared manually.

Calculation of the Physicochemical Parameters. All computational calculations were performed using Gaussian 16 rev C.01 suite (Gaussian Inc.). Geometry optimization and frequency calculations were performed at the B3LYP/6-31G(d,p) level of theory. The molecular volume was defined as that contained within 0.001 electrons/$bohr^3$ isosurface of electron density, and calculated at the B3LYP/aug-cc-pVTZ level of

theory. Feature parameters **P5**–**P9** were obtained by calculating the amine compounds. Parameters **P10**–**P13** were obtained by calculating terminal *N*,*N*′-tetramethylated amine compounds, assuming the structure after curing.

LASSO Analysis. LASSO regression[31] was performed using the scikit-learn package. The training dataset comprised 14 samples, each with one objective variable of the experimentally measured τ_{max} of the wet adhesion sample, coupled with 13 feature parameters as standardized explanatory variables representing the chemical structure of the amine. The L1-norm regularization parameter was set as 10^{-3}, and thus, the mean-squared errors (RMSE) should be minimized in leave-one-out cross-validation (LOOCV). After confirming the validity of the model via LOOCV ($R^2 = 0.893$, RMSE = 0.48), the wet adhesive strengths of a new set of amines **15**–**22** were predicted by substituting their explanatory parameters into the model.

3. Results and Discussion

Epoxy adhesives were prepared using 14 amine compounds, including 6 aliphatic cyclic diamines (**1**–**6**), one aliphatic acyclic diamine (**7**), three aliphatic ether diamines (**8**–**10**), one aliphatic tetramine (**11**), one benzyl-type diamine (**12**), and two aromatic diamines (**13**–**14**), shown in Figure 1. BADGE was used as the oxirane compound in every epoxy because it is one of the most universally employed oxirane compounds as a base resin for various purposes.

Prior to the wet adhesion studies, the water absorption properties of the epoxy samples were examined, and the maximum absorbed water content was denoted as q_{max}. The diffusion coefficient D_{eff} is determined by analyzing absorption using Fick's law (Figure S2 and S3). The results of the water absorption studies are summarized in Figure 2a and Table S1.

A negative correlation between q_{max} and D_{eff} was observed (Figure 3). Knox *et al.*,[15] Li *et al.*,[18] and Frank and Wigging[13] studied several epoxies prepared using bisphenol-type base resins and amines and observed a positive correlation between q_{max} and D_{eff} when using structurally similar amine compounds. This discrepancy may be due to the large differences in the chemical structures of the amines used in this study, as compared to those of the amines used in previous studies. However, the positive or negative variation in the correlation between q_{max} and D_{eff} depending on the structural similarity indicates the complexity of the relationship.

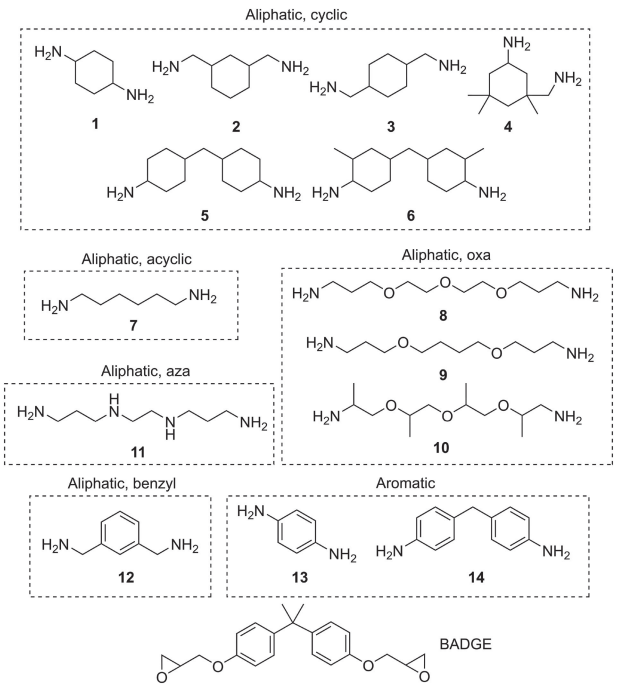

Figure 1. Chemical structures of the diamine hardeners and BADGE examined in this study.

In the lap-shear tests of the wet adhesion, a stainless-steel specimen with epoxy adhesive having a narrow adhesive face was employed to attain rapid water absorption to reach the maximum water uptake of epoxy. First, the sample was immersed in water at 60 °C, and the τ_{max} in the lap-shear test was monitored over time. When the epoxy prepared using **8** was used, an interfacial fracture mode was observed throughout the monitoring period, and the strength decreased rapidly within 1 d and remained almost constant over 8–28 d (Figure S4). Based on these results and D_{eff} of epoxies, 14 d at 60 °C was considered to be sufficient for all the specimens to reach their maximum levels of water absorption.

The resulting τ_{max} values of the water-sorbed epoxies are shown in Figure 2b and Table S1. Interfacial fractures were observed in all samples using different epoxies. The τ_{max} values of the epoxies prepared using **8**, **9**, and **11** with amines containing oxygen or nitrogen atoms in their chemical structures were high. A positive correlation was observed between q_{max} and τ_{max} (Figure 3). Wu *et al.* reported that q_{max} exhibits little correlation with wet adhesion in studies using epoxies prepared using a bisphenol-A type base resin and oligo(propylene glycol)diamine in different stoichiometries.[19] On the other

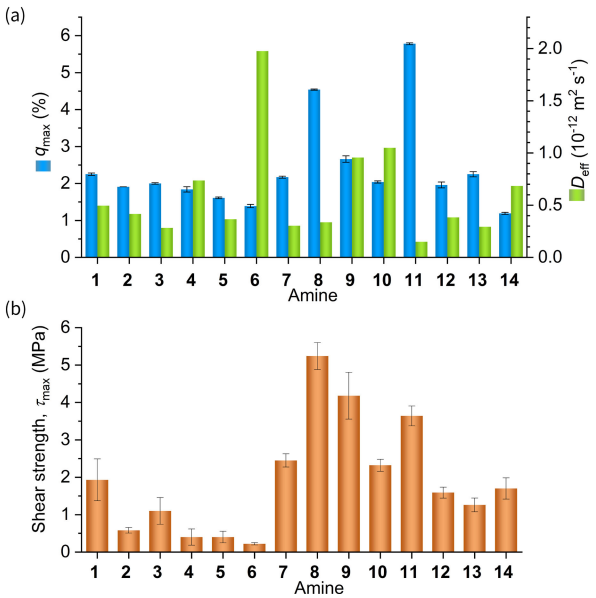

Figure 2. Summary of the water absorption studies and lap-shear tests of the epoxy samples. (a) Maximum absorbed water content (q_{max}) and diffusion coefficients (D_{eff}) of epoxies prepared using different diamines. Standard errors are shown on the blue bars representing q_{max}. (b) Shear strength (τ_{max}) in the lap-shear tests of water-sorbed epoxy adhesives prepared using different amines. The standard errors are shown on the bars.

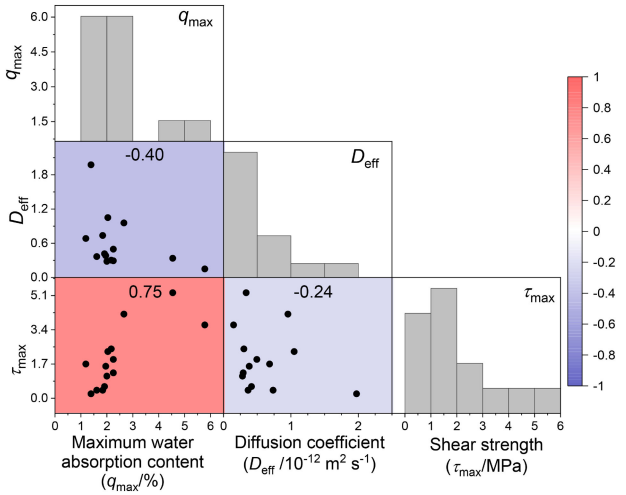

Figure 3. Scatter plot matrix showing the correlation between the experimental values obtained via the water absorption studies and lap-shear tests. The Pearson coefficient is shown in each diagram in terms of number and color.

Table 1. Feature parameters of the amines used in the correlation analysis.[a]

Index	Feature
P1	Number of heavy atoms
P2	Number of single bonds yielding different conformers
P3	Sum of the number of nitrogen and oxygen atoms
P4	Number of rings
P5	Highest occupied molecular orbital energy
P6	Lowest unoccupied molecular orbital energy
P7	Distance between the terminal nitrogen atoms
P8	Molecular volume
P9	Aspect ratio of the molecular shape
P10	Dipole moment
P11	Polarizability
P12	Sum of the Mulliken charges on the nitrogen atoms
P13	Sum of the Mulliken charges on the oxygen atoms

[a]Definitions and calculation methods of the feature parameters are described in the Experimental section.

hand, when the chemical structure of the amine hardener was varied, the discernible pattern observed in our results suggests that epoxies with high absorbed water contents exhibit superior levels of wet adhesion.

To investigate the correlation between the τ_{max} and the chemical structure of the amine, the feature parameters describing the molecular structure were prepared. These parameters were based on chemical knowledge of the structure factors which possibly related to the interaction with water and the polymer network dynamics. In addition, physicochemical properties were calculated as parameters by density functional theory calculations of amine compounds. Initially 44 broad potential parameters were prepared as summarized in Table 1 and Table S2, and then, they were reduced to 13 parameters, **P1**–**P13** in Table 1, through the refinement by knowledge-based and statistical criteria as the following (see Supporting Information for the detail). (A) Excluding parameters which are derived from the same chemical or physical mechanisms, (B) which are chemically or physically related and show linear correlation with each other, and (C) which are calculated by the combination of other parameters. And (D) choosing between parameters of absolute and relative value or meaning.

Figure 4 shows the correlations between feature parameters **P1**–**P13** and the experimentally obtained q_{max}, D_{eff}, and τ_{max} of wet adhesion. Linear or almost-linear relationships were observed between the wet adhesion strength and several parameters, and the degrees of linearity were evaluated using the Pearson coefficient. **P2**, **P3**, **P4**, **P7**, and **P9** exhibited clear positive or negative effects. Therefore, these results provide an estimation of the preferable chemical structure of the amine to yield strong adhesive properties in water, namely, (a) amine molecules with highly conformationally flexible structures without rings (**P2**, **P4**), (b) with numerous oxygen and nitrogen atoms (**P3**), and (c) with elongated shapes with long distances between the terminal NH_2 groups (**P7**, **P9**, Figure 5). As wet adhesion correlates positively with q_{max}, these structural features should also result in a high absorbed water content.

Although understanding the mechanism of interfacial adhesion in wet conditions is challenging,[32–35] these molecular structural features suggest that the chemical structure possibly affects the wet adhesion performance. Epoxy structures with numerous oxygen and nitrogen atoms enable active interactions between the epoxy network and water molecules via hydrogen bonds,[33,36,37] which may support interfacial adhesion.[38] The significance of conformational flexibility indicates that the transition of the network structure to an energetically stable structure in the presence of water within the network favors adhesion. The long distance between the terminal nitrogen atoms also contributes to the structural flexibility. Additionally, a higher absorbed water content generally results in a superior adhesion strength in the water-sorbed state, and thus, amines with these large positive effects induced by water are superior amine hardeners.

Based on the wet adhesion experimental results, a correlation analysis between the wet τ_{max} and feature parameters was conducted using machine-learning LASSO regression to quantitatively estimate the adhesion performance.[31] A coefficient of determination $R^2 = 0.893$ was obtained, indicating a reasonably strong relationship between the predictor parameters and adhesion strength (Figure 6). Because a prediction model was prepared using the refined parameters, a few features exhibited zero feature coefficients in the LASSO analysis (Figure S6). The LASSO analysis revealed the following implications: 1) the parameters with larger feature coefficients are often consistent with the features of the chemical structure of the amine, which is qualitatively suggested by the linear correlation analysis shown in Figure 4. Meanwhile, 2) the signs of the feature and Pearson coefficients in these two analyses were not perfectly consistent. This discrepancy might indicate the **P2** compensates for the positive influence of other features in LASSO algorithm, or the non-linearity of the relationship between **P2** and τ_{max}. On the other hand, the analysis using all the parameters (Table 1, Table S2, and Figure S7) resulted in the prediction model with $R^2 = 0.774$, which were inferior to those using **P1**–**P13** (Figure S7). This result indicated that too many parameters are inappropriate for this LASSO regression analy-

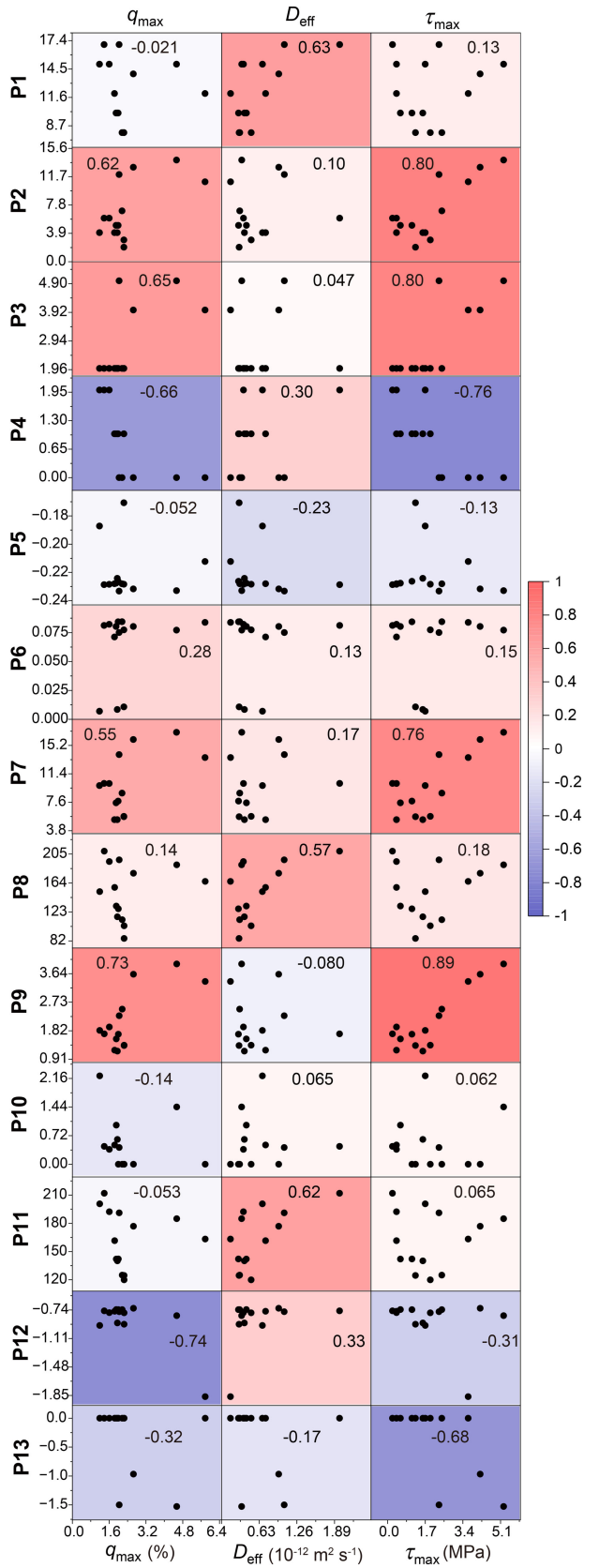

Figure 4. Scatter plot matrix showing the correlations between the experimental values and structure feature parameters. The Pearson coefficient is shown in each diagram in terms of number and color.

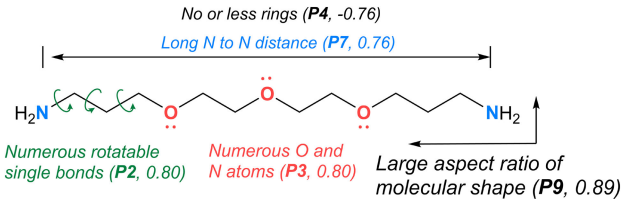

Figure 5. Chemical structure features that contribute to the wet adhesion strength, exemplified by the optimal amine used in this study (**8**). Features with an absolute value of Pearson correlation coefficient more than 0.75 (**P2**, **P3**, **P4**, **P7**, and **P9**) are shown, and the font size expresses the value.

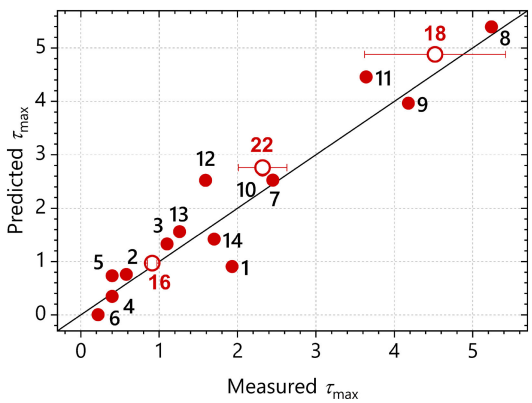

Figure 6. LASSO regression analysis of the shear strengths (τ_{max}) of wet adhesion of the epoxy specimens. The number in the plot indicates the amine compound used for preparing the epoxy. The filled circles represent the data used for constructing the model, and the open circle represents the verification (standard error is shown for **16**, **18**, and **22**). The data plots of **10** and **22** are overlapped.

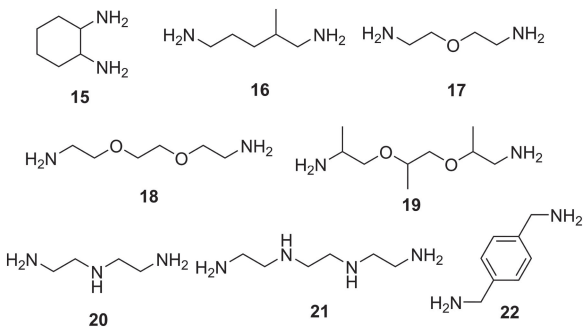

Figure 7. Diamines used for the validation of the prediction model. The τ_{max} of **15**–**22** were predicted using the model, and lap-shear tests using **16**, **18**, and **22** were conducted for the experimental verifications in low to high strength range.

sis, which is possibly related to the existence of parameters with close feature.

The prediction model enables estimation of the wet adhesive strength of the epoxy based on the chemical structure of the amine. The predictions of τ_{max} for additional diamines were carried out to validate the prediction model (Figure 7, Table S3), and experimental verification was conducted using an amine (**18**) that was predicted to be the optimal candidate

among these amines. The experimental results were consistent with the expected excellent epoxy (predicted τ_{max}: 4.88, measured τ_{max}: 4.52 ± 0.90), confirming the effectiveness of the prediction. Furthermore, experimental verifications were also conducted using **16** and **22** with low and moderate predicted strength. The measured values were well matched with the predicted strength (Figure 6). These verifications indicated the prediction is sufficient to select amines for generating epoxies showing superior wet adhesion from a wide range of candidates, and also acceptable for the numerical evaluation in the design of amine compounds.

Finally, the limitations and scope of this study were considered. Based on a limited number of experiments, a reasonable interpretation and an effective prediction model were successfully obtained. These results could be attributed to the use of chemically meaningful numerical feature parameters based on chemical and physical knowledge, rather than molecular fingerprints which are widely used in quantitative structure-property relationship modeling.[39,40] This study focused on the use of low-molecular-weight amines. Therefore, the structural interpretation and prediction of strong wet adhesion may be difficult to apply to polymeric amines, such as amine-terminated polypropylene glycol. The use of other oxirane compounds that are not BADGE or the use of branched polyamines may also exhibit a different trend of wet adhesion strength. However, the chemical structure factors contributing the wet adhesion found in the present study should be widely applicable because the parameters are based on the structure between amine (NH_2) groups of hardeners, which corresponds to the epoxy chain structure. This study did not analyze the adhesive strength in the dry state. Preliminary analysis implied that further studies are necessary to analyze the relationships between the adhesive strengths in the dry and wet states, chemical structure, and other material properties.

The advantage of machine learning is that it does not only predict material properties, but also aids design of chemical compounds with superior properties through inverse problem analysis. Recently, research and applications of machine learning molecule generators for the development of organic and polymer materials has been growing.[41–44] By combining these with the wet-adhesion prediction model obtained in this study, the creation of amine compounds with excellent wet-adhesion property is expected.

4. Conclusion

The wet adhesion strengths of epoxies synthesized using various amine hardeners with different chemical structures was investigated in this study. The quantification of their structural features revealed those that certainly contribute to the wet adhesion strength. An elongated, flexible amine molecular structure with oxygen and nitrogen atoms clearly resulted in a superior wet adhesion performance. Furthermore, regression analysis provided a prediction model for the levels of the wet adhesion of epoxies. These results enhance our understanding of the relationship between the epoxy chemical structure and wet adhesion performance, thereby facilitating the rational design and selection of amine hardeners for preparing epoxies with enhanced performance in wet conditions and underwater environments.

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Supporting Information

Describe concisely what is in the material. This material is available on https://doi.org/10.1246/bcsj.20230218.

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