OPTIMIZATION OF HEAT FUSION OF THERMOPLASTIC RESIN BY MOLECULAR DYNAMICS AND A RESPONSE SURFACE METHOD

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Abstract

Heat fusion is used to bond structural components made of thermoplastic resins. These reactions have garnered much interest in bolstering the strength of polymer–polymer interfaces; however, the pressure and temperature used for heat fusion and its effects on the polymer structure and molecular-scale tensile strength are unknown. Thus, the present study investigates efficient heat fusion optimization conditions between thermoplastics using molecular dynamics (MD) and a response surface method. The heat fusion between polypropylene (PP) and polyethylene (PE) and the uniaxial elongation for evaluating the interfacial bonding strength were modeled by coarse-grained MD simulation. To determine the optimal heat fusion conditions, experimental points were selected based on a central composite design which is the experimental design, and a second-order polynomial response surface was created by setting the temperature, pressure, and polymerization degree as explanatory variables and the strength of the fused interface as the response. The obtained optimal solution under constrained conditions yielded the highest strength when compared with other experimental points.

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1. Introduction

Thermoplastic resins are more reprocessable, reparable, and reformable than thermoset resins because thermoplastic resins can be melted by heating and can then be solidified by cooling in short spans of time. Hence, the application of thermoplastic composite materials to automotive and secondary aircraft structures is under consideration recently[1, 2]. Further, thermoplastic resins can be joined by heat fusion because of their ability to melt. Integration by heat fusion occurs by entanglement[3, 4] during the movement and diffusion of molecular chains under high temperature. Heat fusion is a common method of joining thermoplastic resin structures because a clear interface is absent and the method can easily be used to obtain high interfacial strengths[5] in comparison to conventional bonding methods using adhesives.

Entanglement of the molecular chains in thermoplastic resins is an interesting area and has been studied widely. Many experimental investigations on the relationship between molecular chain entanglement and macroscopic properties, such as material strength and fracture behavior have been carried out; however, gaining understanding about entanglement, which is an atomic and molecular scale phenomenon, is difficult through macroscopic experiments. To understand entanglement in atomic and molecular scales, recently, functions representing the entanglement mechanism have been proposed using molecular dynamics (MD) simulations, which calculate the physical motion of atoms and molecules by numerical calculations. Using MD simulations, the entanglement length and polymerization degree and their effects on material properties can be evaluated. Further, since the entanglement density and behavior of molecular chains can be observed on a computer, it is possible to predict the effects of specific molecule chain arrangements on mechanical strength (and other properties) by numerical calculations.

However, factors affecting interfacial strength, such as polymerization degree (*N)*, temperature (*T*), and pressure (*P*) at fusion mutually affect each other. Therefore, considerable trial and error is involved to optimize the heat fusion. The heat fusion may be optimized by taking into account the molecular chain characteristics using MD simulations; however, this requires calculating models, which include many molecular chains to represent the entanglement. This requires tremendously large calculation capabilities and exploring the entire design area is challenging. Therefore, there is a high demand for the efficient optimization of heat fusion.

In this study, to optimize heat fusion efficiently, we use MD simulations based on the experimental design and response surface method. First, we construct a MD model to replicate the heat fusion process and test the interfacial strength. We then evaluate the effect of heat fusion conditions, such as *N*, *P*, and *T* on the interfacial strength based on experimental design. Subsequently, we create a response surface method, calculate the optimal conditions from the regression equation, and verify the interfacial strength of the optimum model. Fig. 1 shows the schematic diagram of the optimization process used in this study.

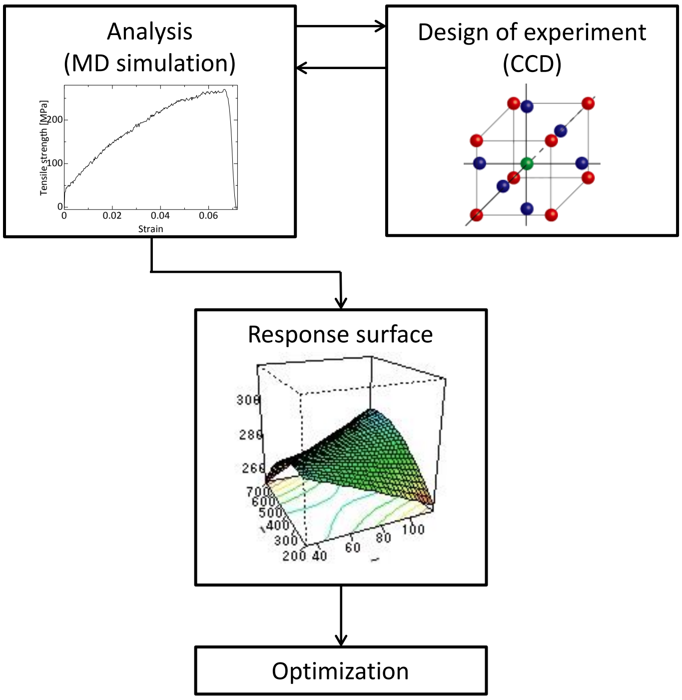

Figure 1. Schematic of the optimization of the heat fusion process by a response surface method and MD simulations.

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2. Modeling heat fusion and evaluating interfacial strength by MD

2.1. MD simulation

To evaluate the interfacial strength after heat fusion, we prepare two types of polymers, model the heat fusion, and test the tensile strength. However, this requires a large amount of calculation to simulate the heat fusion by modeling each atom. Hence, we simplified the model using a coarse-grained model in which the polymer is approximated as a string of beads (each with mass m) connected by springs. The bond stretching potential is represented by a harmonic. A theta harmonic represents the angle bending potential and a cosine polynomial represents the torsion angle potential. We use the Dreiding[6] force field and the potential used has a shape similar to the Lennard Jones (LJ) non-bonding pair potential (Eq. 1).

$$U_{nonbond}(r_{ij}) = 4\varepsilon\left\{\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right\} \tag{1}$$

r_{ij} is the distance between the molecule i and j, σ is a parameter related to the distance, ε is a parameter representing the depth of the potential.

We use time evaluation operations[7] to typify the time evolution of the molecular population as the equation of motion. The time evaluation of position and velocity in the time span 0–t can be expressed by the following equation.

$$\mathbf{\Gamma}(t) = \exp(iLt)\mathbf{\Gamma}(0) \tag{2}$$

iL is the Liouville operator, $\mathbf{\Gamma}$ is the multi-dimensional vector of independent variables (position and velocity). J-OCTA[8], a commercial version of the software open computational tool for advanced material technology (OCTA), is used for the MD simulations.

2.2. Heat fusion and evaluation of interfacial strength

For the heat fusion, the two types of the polymers are placed apart in the z direction. Then, the polymers are heated to enable diffusion across each other and cooled. The cell lengths in the x and y directions of the NPT ensemble are fixed. Then, the uniaxial elongation is calculated by fixing the molecules at the ends of the cell and moving the ones in the positive z-axis direction (the tensile direction) of the NVT ensemble to evaluate the interfacial strength. Fig. 2 shows the schematic of the fixing and uniaxial elongation processes.

The stress is calculated from the pressure tensor **P** consisting of the interaction and kinetic energies based on virial theory.

$$\mathbf{P} = \frac{1}{V}\left(\sum_{i=0}^{N}\frac{\mathbf{p}_i^2}{m_i} + \sum_{i=0}^{N-1}\sum_{j>i}^{N}\mathbf{r}_{ij}\mathbf{f}_{ij}\right) \tag{3}$$

V is the volume of the system, $\mathbf{p}_i$ is the momentum of the atom i, m_i is the mass of the atom, $\mathbf{f}_{ij}$ is the interatomic force between atom i and j. In this study, we calculate the heat fusion between polypropylene (PP) and polyethylene (PE).

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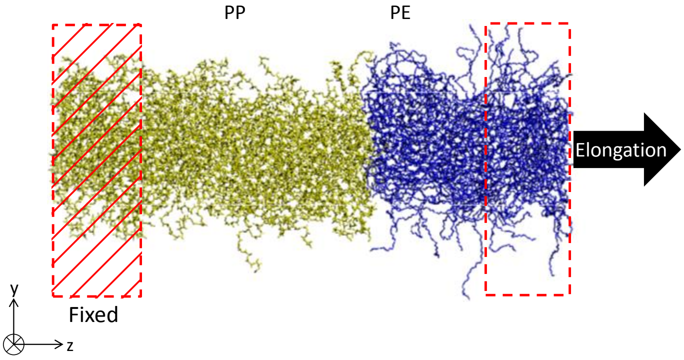

Figure 2. Schematic of the unidirectional elongation of heat-fused polymers by MD simulation.

3. Design of experiment

In this study, we define three explanatory variables, i.e., *T*, *P*, and *N*. We use a central composite design (CCD)[9, 10] to determine the model parameters. CCD is organized as follows.

- The two-level full implementation design for each factor. (point 1)
- $2k$ number of experimental points on the axis. (point 2)
- n number of center conditions. This point is calculated thrice to estimate the error. (point 3)

k is the number of design variables. At point 1, N is 50 and 100, T is 600 K and 800 K, P is 300 kPa and 600 kPa. Fig. 3 shows a combination of levels for the three factors. Table 1 shows the combinations of N, P, and T based on CCD.

To determine the optimum design parameters N, P, and T, we determine the relationship between the design parameters and interfacial strength as a regression equation using the response surface method. In the response surface method, the relationship between p number of explanatory variables x_1, x_2, …, x_p and the response variable y is modeled by the following equation.

$$y = f(x_1, x_2, \ldots, x_p) + b \tag{4}$$

b is the error. The relationship approaches to a second-order polynomial by least squares method as shown in the following equation and a response surface is obtained.

$$y = \beta_0 + \sum_{i=0}^{n} \beta_i x_i + \sum_{i=0}^{n} \beta_{ii} x_i^2 + \sum_{i<j}^{n} \beta_{ij} x_i x_j \tag{5}$$

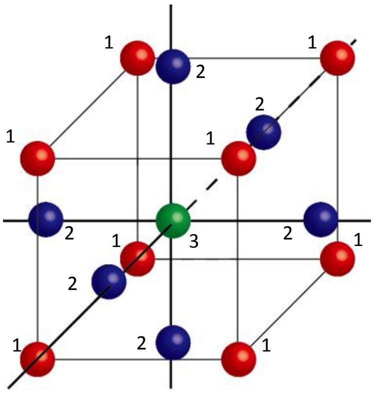

Figure 3. Schematic of the CCD constituted by a two-level experimental design of each factor (1), axial points (2), and central point (3).

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Table 1. Parameters and fused interface strength of each experimental point determined by a CCD.

Model	Polymerization degree N	Heat fusion temperature T [K]	Heat fusion pressure P [kPa]	Tensile Strength [MPa]
1	100	800	600	270.5
2	100	600	300	288.6
3	75	700	450	277.0
4	50	800	600	272.4
5	100	800	300	252.7
6	75	700	450	279.2
7	50	600	300	286.7
8	50	800	300	298.3
9	100	600	600	276.5
10	50	600	600	273.3
11	75	700	450	283.7
12	75	868	450	296.1
13	75	532	450	301.3
14	33	700	450	268.1
15	75	700	702	285.7
16	117	700	450	302.5
17	75	700	198	265.7

* According to Fig.3, models 1-2, 4-5, and 7-10 correspond to point 1, models 12-17 correspond to point 2, and models 3, 6, and 11 correspond to point 3.

4. Results

The interfacial strength after heat fusion of each model with parameters determined by CCD are shown in Table 1. Based on these results, we obtained the second-order polynomial response surface in which N, P, and T are the design variables and the interfacial strength is the response variable (Eq. 6).

$$\begin{aligned} y = 441.78 + 1.268N - 0.528T - 0.069P \\ + 0.00014TP - 0.0026TN + 0.0015NP \\ - 0.00039N^2 + 0.00045T^2 - 0.00016P^2 \end{aligned} \tag{6}$$

Since it is not possible to illustrate the response surface consisting of three variables, Fig. 4 shows the response consisting of two variables by fixing the third variable at a central value. Fig. 4 (a) shows that the strength is maximized at high N and low T values or when N is low and T is high, which indicates an effect of the interaction. Fig. 4 (b) indicates that the response consisting of P and T is smoother in shape than the other plots. Fig. 4 (c) shows a convex response with P; hence, the maximum value is contained within the surface.

Using the response surface shown in Eq. 6, we optimize by generalized reduced gradient (GRG) method[11]. In this case, we set the constraint conditions considering the melting points of PP and PE (PP: 441 K, PE: 368-413 K) and the computational costs.

- $33 \le N \le 130$

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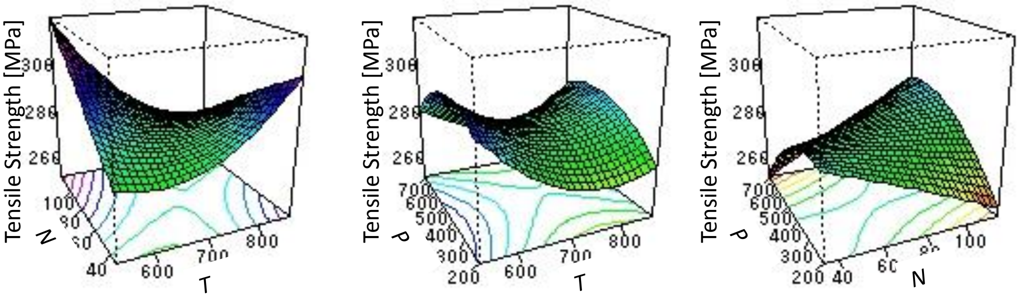
- $450 \leq T \leq 1000$
- $100 \leq P \leq 900$

The optimized values are N = 130, T = 450 [K]. P = 594 [kPa]. T is the minimum and N is the maximum values in the constraint levels. This trend can be read from the response surface.

Subsequently, we calculate this optimum model many times and compare the strength of each model, as shown in Table 1. The mean and standard deviation of the optimum model is 315.4 (± 4.1) MPa. We verify the optimum model by comparing with other models determined by CCD. We conclude that the interfacial strength of our optimum model is higher than models listed in Table 1 and shows a 4.26% increase from the highest strength recorded by CCD. This indicates the practicability of the proposed optimization method.



P = 450 [kPa] N = 75 T = 700 [K]

(a) (b) (c)

Figure 4 Response surfaces of the fused interface strength when one variable is fixed. N is the polymerization degree, T is the temperature at heat fusion, and P is the pressure at heat fusion.

5. Conclusion

To maximize the fused interfacial strength of thermoplastic composite materials, we calculated heat fusion conditions and uniaxial elongation using MD simulations based on the design of experiment and response surface method. First, we constructed MD simulation models of the heat fusion and tested the uniaxial elongation of PP and PE using a coarse-grained model. Based on CCD, we performed MD simulations by changing N, P, and T to create a response surface in which the heat fusion conditions are explanatory variables and interfacial strength is the response. Further, we calculated the optimal conditions from the response surface. The interfacial strength of the optimum model is higher than the models in which the parameters are determined by CCD. Hence, we have demonstrated the effectiveness of the optimization method proposed.

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