Research on the Numerical Model of Solvent Diffusion Based on Fick's Law and Free Volume Theory

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Abstract. The release of acetone solvent from the adhesive layer is an important part of the curing of DW-1 adhesive, and this process is mainly affected by its diffusion behavior. In order to predict the volatile residual amount of acetone in the adhesive layer, the diffusion phenomenon of acetone solvent was studied. Based on Fick’s law, a numerical model of solvent diffusion is established, and a calculation method of mutual diffusion coefficient suitable for the system of acetone and DW-1 glue is proposed; a simulation model is constructed to reveal the competition mechanism of volatilization phenomenon and diffusion phenomenon, and analyzes the acetone in the diffusion process distribution status. The theoretical guidance for reducing the residual amount of acetone is provided by this research in the adhesive layer.

1. Establishment of numerical model of solvent diffusion phenomenon during coating curing

1.1. Analysis of coating diffusion

The diffusion behavior of the solvent in the coating is the result of the diffusion phenomenon and the volatilization phenomenon. The diffusion and volatilization process of the solvent is shown in Figure 1. According to Fick’s law, the concentration gradient causes the solvent molecules in the coating to spontaneously move to the coating surface with lower concentration.

Fick's first law is the key law that describes the movement of diffusion. This law can be explained as, in the diffusion phenomenon, the diffusion flux per unit time through a unit cross-sectional area perpendicular to the diffusion direction is proportional to the concentration gradient at that area[1], and the mathematical description is as follows:

\[ J = -D(\frac{dc}{dx}) \]  

(1)

In the formula: \( J \)——diffusion flux, g/cm²·s; \( D \)——diffusion coefficient, cm²/s; \( x \)——distance, cm; \( c \)——the mass concentration of the solvent, g/cm².
However, Fick’s first law describes the diffusion phenomenon under steady-state conditions, and does not apply to transient conditions where the concentration changes with time, so it is very limited when used to describe the diffusion phenomenon in practice. Fick’s second law takes into account the problem that the solvent concentration will change with time, and is more accurate in describing the diffusion phenomenon. Fick’s second law can be explained as that the rate of change of concentration with time is equal to the negative value of the rate of change of diffusion flux with distance[2], and the mathematical description is as follows:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} (D \frac{\partial c}{\partial x})$$

In the formula: \(c\)-the mass concentration of the solvent, g/cm²; \(t\)-the diffusion time, s; \(x\)-the distance, cm; \(D\)——diffusion coefficient, cm²/s.

1.2. The mass transfer equation of the coating

During the curing process of the coating, the solvent volatilizes on the contact surface of the coating and the air, causing the concentration to decrease. Therefore, the solvent molecules in the entire system will diffuse due to the concentration gradient. Fick’s second law can be used to describe the diffusion of solvents. The mass transfer equation of the solvent is obtained as[3]:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} (D(c, T) \frac{\partial c}{\partial z})$$

In the formula: \(c\)-the mass concentration of the solvent, g/cm²; \(t\)-the diffusion time, s; \(D\)——diffusion coefficient, cm²/s.

The above equation is a non-linear partial differential equation, which requires initial conditions and boundary conditions to solve.

Initial conditions:
$$\left. \frac{\partial c}{\partial z} \right|_{z=0} = 0$$

Boundary conditions:
$$\left. -D \frac{dc}{dz} \right|_{z=0} = 0$$

1.3. Coating heat transfer equation

Since the actual coating thickness is small, the temperature change inside the coating is not obvious. Therefore, when heating is not used, it can be assumed that the internal temperature of the coating system is the same, and the temperature of the coating and the substrate are the same. The heat transfer model of the coating system is described as follows:

$$\frac{dT}{dt} = \frac{h_{top} (T_{air} - T) + h_{bottom} (T_{air} - T) - \Delta H_m}{(L_{\text{substrate}} C_{\text{substrate}} \rho_{\text{substrate}} + L C_{\text{pc}} \rho_c)}$$

In the formula: \(h_{top}\) and \(h_{bottom}\)——the heat transfer coefficient of the top of the coating and the bottom of the substrate, W/(cm²·K); \(m\)——evaporation rate, J/kg; \(L, C, \rho\)——thickness (cm), specific heat (Jg⁻¹K⁻¹) and density (g/cm³), the subscripts substrate and c represent the substrate and coating respectively.

2. Calculation model of mutual diffusion coefficient

2.1. Research on calculation model of mutual diffusion coefficient in stable system

The solvent self-diffusion coefficient calculation model established based on the free volume theory can more accurately calculate the self-diffusion coefficient of small molecule solvents in the polymer coating. The theory believes that the concentration of the solvent and the temperature of the coating are the main factors affecting the self-diffusion coefficient factor.
The interdiffusion coefficient is the diffusion coefficient of a substance molecule when there is a concentration gradient, and it reflects the mass transfer process of the substance and other substances in the system\cite{4}. Vrentas and Duba found that under certain circumstances, the mutual diffusion coefficient can be expressed as \cite{5}\cite{6}:

\[
D = D_0[(1 - \phi)^2(1 - 2\chi\phi)]
\]

In the formula: \(\phi\) —— the volume fraction of the substance, \(\chi\) —— Flory-Huggins interaction parameter.

Among them \(\chi\) is the interaction parameter based on the Flory-Huggins theory\cite{7}, and its value can be obtained using the semi-empirical equation of Waston and Bristow.

\[
\chi_{ij} = 0.35 + \frac{V_i}{RT}(\delta_i - \delta_j)^2
\]

In the formula: \(V_i\) —— molar mass, \(\delta_i\) —— solubility parameter, \(\delta_j\) —— solubility parameter of other substances.

2.2. Research on Calculation Model of Mutual Diffusion Coefficient in Unstable Complex System

Although the above theory can calculate the mutual diffusion coefficient in the system very well, the mixed coating system to which the calculation model can be applied is too simple and stable. The model is only suitable for a single-component solute and solvent mixed system, that is, the A+D system, where A is the solute and D is the solvent, and no reaction occurs between the two.

The calculation model under this stable system is not suitable for the subbing system with complex composition and curing reaction.

In order to describe the inter-diffusion coefficient in this unstable and complex system, this paper improves the existing calculation model based on the numerical additivity of the solute free volume. The free volume of the solute in the unstable complex system is as follows:

\[
\frac{V_{FH}}{\gamma} = \omega_1 \frac{V_{FH1}}{\gamma_1} + \omega_2 \frac{V_{FH2}}{\gamma_2} + \cdots + \omega_n \frac{V_{FHN}}{\gamma_n}
\]

In the formula: \(n\) —— the number of material types contained in the system, \(n=4\) in the acetone and DW-1 glue system.

3. Simulation study on the diffusion of acetone solvent in DW-1 glue

3.1. Construction of simulation model of diffusion phenomenon

In order to visually observe the diffusion behavior of acetone solvent in the DW-1 adhesive layer, this paper uses COMSOL to establish a simulation model for research. The simulation model calls the material transfer interface, heat transfer interface and deformation geometry interface, and uses the diffusion parameters obtained in the previous chapter to simulate the diffusion process of acetone solvent. The composition of the simulation model is shown in Figure 2.
3.2. Analysis of Acetone Solvent Diffusion Process

The model uses the DW-1 adhesive layer with a thickness of 0.50 mm and an initial acetone mass fraction of 0.268 as the research object under a 20°C environment, and simulates the diffusion of acetone solvent inside. The distribution of acetone solvent in the adhesive layer at different times is shown in the figure 3 shown.

![Distribution of acetone during the curing and drying process of the adhesive layer](image)

Figure 3. Distribution of acetone during the curing and drying process of the adhesive layer

The results show that after the start of the diffusion movement, the acetone distribution in the lower half of the adhesive layer is relatively uniform, and the acetone solvent in the upper half diffuses and volatilizes, gradually forming a stable concentration gradient. This is due to the rapid volatilization of the acetone solvent leading to a decrease in the surface concentration of the adhesive layer, but the diffusion coefficient of the acetone solvent in the DW-1 adhesive layer is relatively small, so the acetone solvent cannot be replenished in time. With the further volatilization of the acetone solvent and the deepening of the curing reaction of DW-1 glue, the upper half of the glue layer gradually formed a stable surface crust. The extremely low interdiffusion coefficient in the surface crust will hinder the diffusion and volatilization of the acetone solvent, which will eventually lead to the residue of acetone in the lower half of the adhesive layer.
Figure 4. The change of the mass fraction of acetone solvent at different depths of the adhesive layer with time

The changes in the mass fraction of acetone solvent at different depths of the adhesive layer over time are shown in Figure 4. The results showed that the concentration of acetone within 0.20 mm of the surface of the adhesive layer decreased significantly, and the concentration near the substrate remained basically unchanged. Although the concentration of acetone at 0.30 mm and 0.40 mm decreased significantly over time, the acetone at 0.40 mm was closer to the surface of the adhesive layer, so it was more affected by volatilization and the concentration decreased faster. This shows that the solvent diffusion behavior caused by the volatilization phenomenon has a fixed radiation depth. When the thickness of the glue layer exceeds the radiation depth, the solvent diffusion behavior does not occur in the excess part.

4. Conclusion
The research in this chapter has achieved the following results:

1) In order to predict the residual amount of acetone during the curing process of the adhesive layer, this paper established a numerical model of the solvent diffusion phenomenon in the coating based on Fick’s law. This model improves the existing mutual diffusion coefficient calculation model, and the diffusion parameters of the acetone solvent and DW-1 glue system are determined by the method of theoretical calculation and gravimetric regression. The improved mutual diffusion coefficient calculation model, based on the feature of the free volume value that can be added, puts forward the concept of equivalent solute, and expands the scope of application of the calculation model by segmenting the viscosity-temperature curve of the solute.

2) In order to reveal the diffusion behavior of acetone solvent during the curing process of DW-1 glue, a simulation model is constructed in this paper. The simulation results show that the competition mechanism of volatilization phenomenon and diffusion phenomenon leads to the appearance of surface skinning on the glue layer. The low concentration of acetone solvent in the surface crust and the large concentration gradient limit the diffusion and volatilization of acetone solvent.

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