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Surface Tension of Polyurethane Solution and Thermodynamic Model

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A new improved polyurethane materials was studied to improve the strength of paper, delay the aging of paper, solve the problem of poor permeability of traditional resins to paper, and meanwhile to provide basic data for industrial design and applications, the surface tension of composite solutions consisting of nano-SiO_2-based polyurethane, organo silicon-based polyurethane and epoxy cyclohexane-epichlorohydrin polyurethane dissolved in ethyl acetate had been measured at temperatures ranging from 283.15 K to 308.15 K. The surface tension was fitted with the related equation between surface tension and temperature under normal pressure. The mean relative deviations between the calculated value and the experimental value were derived. The results showed that the model estimation of the surface tension of the composite solution were in good agreement with the experimental data, the paper coated by the polyurethane materials had better mechanical property. Therefore, the prepared polyurethane material has great application prospects in the protection of paper.

Keywords: Ethyl acetate, Linear correlation, Polyurethane, Surface tension

1 Introduction

Polyurethane is a kind of polymer material polymerized by polyisocyanate and hydroxyl compound. It has good film-forming property, water resistance, colorless and transparent, and good strength of film[1,2]. Generally, a small amount of polyurethane can improve the mechanical properties of paper and the strength of fiber without affecting the appearance of paper [3]. It is an ideal reinforcement material for paper cultural relics. Surface tension is an essential fundamental property in chemical design and process optimization, and is intrinsically related to the thermodynamic properties of solutions[4, 5]. Therefore, it is necessary to determine the surface tension of polyurethane reinforcement. There are many factors that affect the surface tension, including temperature, pressure and dispersion. The intermolecular forces of different substances are different, and the surface tension is caused by the imbalance of intermolecular forces. The effect of temperature and pressure on the surface tension is complicated. It is generally believed that, as the temperature increases, the molecular volume increases, and the internal molecular force on the surface decreases, resulting in the decrease of surface tension[6]. It is found that the smaller the surface tension, the lower the surface free energy, the better the mobility, while the paper surface adhesion is better. Therefore, in order to solve the problem of poor permeability of traditional resins to paper, in this paper, the surface tension of composite reinforcement solutions was studied consisting of different mass fractions at 283.15 K, 288.15 K, 293.15 K, 298.15 K, 303.15 K and 308.15 K under normal pressure, so as to provide basic data and theoretical support for paper reinforcement.

2 Meterials and Method

2.1 Instruments and materials

Bzy-3b surface tensiometer (Shanghai Hengping instrument factory), constant temperature water bath pot (Tianjin taist Instrument Co., Ltd.), precision thermometer (Zhengzhou glass factory).

Nano-SiO_2-based polyurethane (self-made); organosilicon-based polyurethane (self-made); epoxycyclohexane-epoxychloropropane-based polyurethane (self-made); ethyl acetate (Tianjin comio Chemical Reagent Co., Ltd.).

2.2 Determination method

The surface tension of the mixture was measured according to GB/T 22237-2008. A series of composite reinforcement fluids with mass fractions of 10%, 20%, 30%, 40% and 50% were prepared. The test temperatures were controlled at 283.15 K, 288.15 K,

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293.15 K, 298.15 K, 303.15 K and 308.15 K respectively through the constant temperature tank. The surface tension value of the composite reinforcement solution was measured by surface tensiometer for three times, and the average value was obtained.

2.3 Reliability verification of experimental device

In order to verify the reliability of the experimental device, the surface tension of water at different temperatures was measured and compared with the literature value. The results are shown in Table 1, where σ_{exp} represents the experimental value of the surface tension of water, σ_{lit} represents the literature value of the surface tension of water and RD represents the relative deviation, which can be calculated from Equation (2).

Through the comparison of Table 1, it can be seen that the relative deviation between the experimental value of water surface tension and the literature value is very small, which indicates that the literature value of the experimental measured surface tension data conforms well, thus verifying the reliability of the experimental device.

3 Results and Discussion

At temperature of 283.15 K~308.15 K, the experimental surface tension of composite reinforcement solutions with mass fraction of 10%~50% was measured as shown in Table 2. Under normal pressure, the surface tension and temperature change with temperature approximately linear trend. In this work, the fitting equation of surface tension and temperature was shown as follows:

$$\sigma = a - bT \qquad \ldots(1)$$

Table 1 — Experimental value and reference value of surface tension of water

T/K	σ_{exp} (mN/m)	σ_{lit} (mN/m)	RD (%)
293.15	72.42	72.49 [7]	-0.096
298.15	71.91	71.88 [8]	0.042
303.15	71.16	71.10 [9]	0.084

Where σ is the surface tension and the unit are mN/m, a and b are the correlation coefficients, T is the thermodynamic temperature, K.

Relative deviation *RD* and mean relative deviation *RAD* are calculated as follows:

$$\mathrm{RD} = \frac{x_i - x_{ci}}{x_i} \qquad \ldots(2)$$

$$\mathrm{RAD} = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{x_i - x_{ci}}{x_i}\right| \qquad \ldots(3)$$

Where n is the number of experiments, x_{ci} and x_i are the calculated and experimental values representing the mole fraction respectively.

The linear diagram of the surface tension, temperature and concentration of the solution to be tested is shown in Fig. 1. The calculated value of the surface tension of the solution to be tested based on the correlation Equation (1) and the data of relative

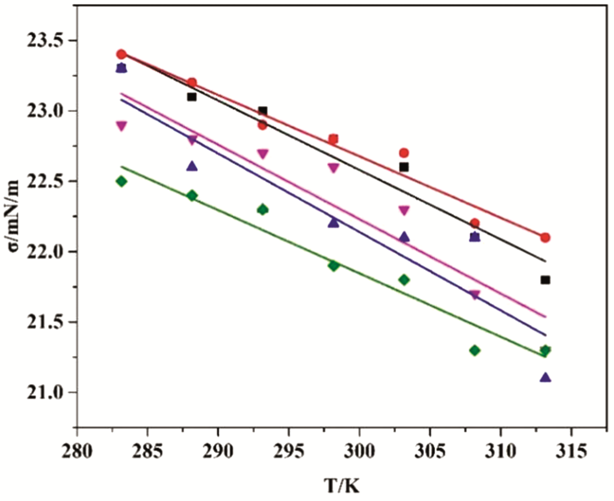

Fig. 1 — Surface tension of different mass fractions of reinforcement solution at different temperatures
■ 10% reinforcement liquid, ● 20% reinforcement liquid, ▲ 30% reinforcement liquid, ▼ 40% reinforcement liquid, ◆ 50% reinforcement liquid.

Table 2 — Experimental surface tension (σ_{exp}) values for mixtures of nano-SiO$_2$-based polyurethane, organosilicon-based polyurethane and epoxy cyclohexane-epichlorohydrin polyurethane dissolved in ethyl acetate at different temperatures

Nano-SiO$_2$-based polyurethane + Organosilicon-based polyurethane + Epoxy cyclohexane-epichlorohydrin polyurethane

Mass fraction of polyurethane/wt%	10%	20%	30%	40%	50%
T/K			σ_{exp}/mN·m^{-1}		
283.15	23.3	23.4	23.3	22.9	22.5
288.15	23.1	23.2	22.6	22.8	22.4
293.15	23.0	22.9	22.3	22.7	22.3
298.15	22.8	22.8	22.2	22.6	21.9
303.15	22.6	22.7	22.1	22.3	21.8
308.15	22.1	22.2	22.1	21.7	21.3
313.15	21.8	22.1	21.1	21.3	21.3

Table 3 — Calculated values of surface tension (σ) when applying linear correlation and relative deviation (RD)for the composite solution at different temperatures.

Nano-SiO_2-based polyurethane + Organosilicon-based polyurethane + Epoxy cyclohexane-epichlorohydrin polyurethane

Mass fraction of polyurethane/wt%	10%		20%		30%		40%		50%	
T/K	σ/mN·m^{-1}	RD (%)	σ/mN·m^{-1}	RD (%)	σ/mN·m^{-1}	RD (%)	σ/mN·m^{-1}	RD (%)	σ/mN·m^{-1}	RD (%)
283.15	23.4	-0.52	23.4	-0.05	23.1	0.95	23.1	-0.96	22.6	-0.46
288.15	23.1	-0.32	23.2	0.03	22.8	-0.89	22.8	-0.25	22.8	0.09
293.15	22.9	0.31	22.9	-0.33	22.5	-0.99	22.6	0.48	22.1	0.65
298.15	22.6	0.52	22.7	0.19	22.2	-0.19	22.3	1.21	21.9	-0.13
303.15	22.4	0.73	22.5	0.71	21.9	0.61	22.1	1.06	21.7	0.44
308.15	22.1	-0.41	22.3	-0.55	21.7	1.87	21.8	-0.46	21.5	-0.84
313.15	21.9	-0.66	22.1	-0.02	21.4	-1.46	21.5	-1.10	21.3	0.22

Table 4 — Fitting results of equation parameters

Mass fraction of composite reinforcement fluid	a	b	R^2	RAD (%)
10%	37.36	0.049	0.9371	0.49
20%	35.74	0.043	0.9579	0.26
30%	38.85	0.055	0.8039	0.99
40%	38.09	0.053	0.8599	0.78
50%	35.34	0.045	0.9383	0.40

deviation (RD) between the experimental value of the surface tension and the calculated value were shown in Table 3. Examination of the numerical entries shows that the absolute value of the relative deviation between the experimental value and the calculated value is basically below 1%, indicating that the fitting equation is applicable.

According to Equation (1), the experimental data were fitted with the least square method, and the parameters of the equation a, b and the correlation coefficient (R^2) obtained are shown in Table 4.

As can be seen from Table 2, Table 3 and Fig. 1, in the temperature range of 283.15 K~308.15 K, the surface tension of the polyurethane composite reinforcement solution increases with the increase of concentration. At a certain concentration, the surface tension of polyurethane composite solution is approximately linear with temperature, and the surface tension decreases with the increase of temperature[10]. This is because the surface tension is the result of the mutual attraction between liquid molecules rather than the molecules from the surface region. It is easy to understand that as the temperature increases, the polyurethane organic molecules gain heat energy from the thermostatic tank, and a large number of molecules with sufficient energy can overcome these attractions, weakening the cohesion between the molecules, resulting in a decrease in the surface tension of the polyurethane reinforcement solution [11, 12]. It can be seen from Table 4 that at 283.15 K~313.15 K, the average relative deviation between the calculated value and the experimental value of the surface tension of the polyurethane composite solution with the mass fraction of 10%~50% is 0.49%, 0.26%, 0.99%, 0.78%, 0.41% respectively, which showed that the calculated value is in good agreement with the experimental value, indicating that the formula is suitable for the correlation between the composite solid liquid surface tension and temperature. At the same time, the surface tension value of the composite reinforcement fluid is between 21.1 mN/m and 23.4 mN/m, with a low surface tension value, which is conducive to wetting the paper and improving the adhesion of the paper, suitable for the reinforcement of paper cultural relics.

4 Conclusion

At temperature 283.15 K~313.15 K, the surface tension of 10%~50% mass fraction composite reinforcement solution was measured, the relationship between surface tension and temperature was correlated, and the model parameters were determined. The average relative deviations of each system were 0.49%, 0.26%, 0.99%, 0.78%, and 0.41%, respectively. The surface tension value of the polyurethane composite reinforcement liquid is between 21.1 mN/m and 23.4 mN/m. The surface tension by the model equation shows good agreement with the experimental data, and we also expect that the experimental surface tension can provide basic data and theoretical support for paper reinforcement.

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