

Rheological Properties of Waterborne Polyurethane Paints^{*}

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Abstract The rheological properties of two specific waterborne polyurethane (PU) paints were studied by both macrorheological and microrheological methods. During the macrorheological measurement on a rotary rheometer, evaporation of solvent cannot be totally excluded, which has an influence on the reliability of rheological results. So, the linear oscillatory frequency sweep results (storage and loss modulus versus frequency) and steady shear results (viscosity versus shear rate) got from the rotary rheometer measurement are only used for qualitative analysis. As the evaporation of solvent can be neglected during microrheological measurements on a diffusing wave spectroscopy (DWS), the results of storage modulus (G') and loss modulus (G'') versus frequency are more credible than the results obtained from the rotary rheometer measurement. Thus, the results of G' and G'' versus frequency from DWS measurements are used for quantitative analysis in this work. The G' for both of the waterborne PU paints are larger than G'' at low frequency and that is opposite at high frequency in the experimental angular frequency range. The values of modulus at same frequency and viscosity at low shear rate for the two PU paints have apparent difference, which determines the difference of their application.

Keywords: Rheology; Waterborne polyurethane paints; Macrorheology; Microrheology; Diffusing wave spectroscopy (DWS).

INTRODUCTION

Paint or coating plays an important role in automobile industry, building industry, household industry *etc*, which provides materials with the desired properties such as color, gloss and anti-corrosion^[1–4]. However, the solventborne systems mainly used in paint industry are harmful to environment and people. Thus the paint industry is forced to develop environmentally friendly products^[5–7]. Waterborne polyurethane (PU) paint is one kind of the environmentally friendly paints, which exhibits excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance *etc*^[8, 9].

The rheological properties of PU paint are important for their application. An ideal waterborne polyurethane paint should be a soft solid at static condition, its storage modulus is bigger than loss modulus and viscosity is not too small, benefitting sagging resistance of paint. And in view of its application, the waterborne polyurethane paint should be a viscous liquid, its storage modulus is smaller than loss modulus and viscosity is not quite big, contributing to flow of paints^[10, 11]. The viscoelastic properties of waterborne PU paints dominate their application^[12–15]. However, it is difficult to get the accurate viscoelastic properties of PU paints by the traditional

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rotary rheometer, as the solvent evaporates quickly during measurements. Thus it is important and necessary to find other reliable methods to characterize the rheological properties of waterborne PU paints.

In this work, the rheological properties of two different waterborne polyurethane (PU) paints were studied by both rotary rheometer and diffusing wave spectroscopy (DWS). The relationship between rheological properties of PU paints and their application ability is also discussed.

EXPERIMENTAL

Materials

Waterborne polyurethane paint NeoReZ R-1010 was used as received from DSM NeoResins (The Netherlands). Waterborne polyurethane paint WB-107, was used as received from Shanghai Yuanhe Chemical Co., Ltd. The size of polyurethane colloidal particles for these samples was measured by Zetasizer Nano-ZS (Malvern Instruments), as shown in Table 1.

Table 1. Particles size and solid content of the samples

Samples	Average radius of particles (μm)	Polydispersity index	Solid content (%)
R-1010	0.88	0.59	25
WB-107	1.63	0.33	31

Rotary Rheometer Measurements

The macrorheology measurements were performed by an AR-2000EX rotary rheometer (TA Instruments) with 40 mm parallel plates. To prevent evaporation of water in waterborne polyurethane paint, paraffin oil was used at the edge of the samples. Strain sweep experiments were performed first to determine the region of linear response. Oscillatory frequency sweeps from 0.1 rad/s to 500 rad/s were carried out with appropriate strain in the linear region. All experiments were carried out at 25 °C.

Diffusing Wave Spectroscopy

Microrheology measurements were carried out by a diffusing wave spectroscopy Rheolab II (LS Instruments) in backscattering mode. The diffusing wave spectroscopy (DWS) was equipped with a single photon-counting avalanche photodiode (APD) with typically 65% detection efficiency and a two-channel fast multi-tau/linear correlator with the smallest sampling time of 12 ns. A two-cell echo technique that uses anergodic, turbid “reference” sample cell placed in series after the primary non-ergodic sample developed by Scheffold *et al.* was employed to deal with the non-ergodic systems^[16]. Independent speckles were introduced by a clouded glass, making sure that the efficient ensemble averaged during the dealing with the data. The coherent source was a diode laser ($\lambda = 687 \text{ nm}$; 40 mW). The Rheolab software is used to collect and analyze the data as well as the online analysis of rheology properties. The samples were put in a cell (5 mm $\times$ 10 mm) that was further sealed by tape. All experiments were carried out at 25 °C.

RESULTS AND DISCUSSION

Macrorheology Result

The linear dynamic oscillatory frequency sweep results of R-1010 and WB-107 are shown in Fig. 1. After the edge of sample is sealed by paraffin oil, the storage modulus (G') and loss modulus (G'') of samples are smaller than that without sealing. It is apparent that evaporation of solvent has an influence on the reliability of experimental results. The evaporation of solvent during the test cannot be totally eliminated by sealing the edge of the samples with paraffin oil, as the solvent can still evaporate during the process of loading samples. For above reason, the rheological results of the rotary rheometer measurement are only used for qualitative comparison in this work. In Fig. 1, it is observed that the moduli of WB-107 are larger than that of R-1010 at the same frequency. At the same time, in the experimental low frequency range, G' is smaller than G'' for R-1010, while G' is larger than G'' for WB-107. The relationship between the linear viscoelasticity and properties of the two paints will be further discussed below.

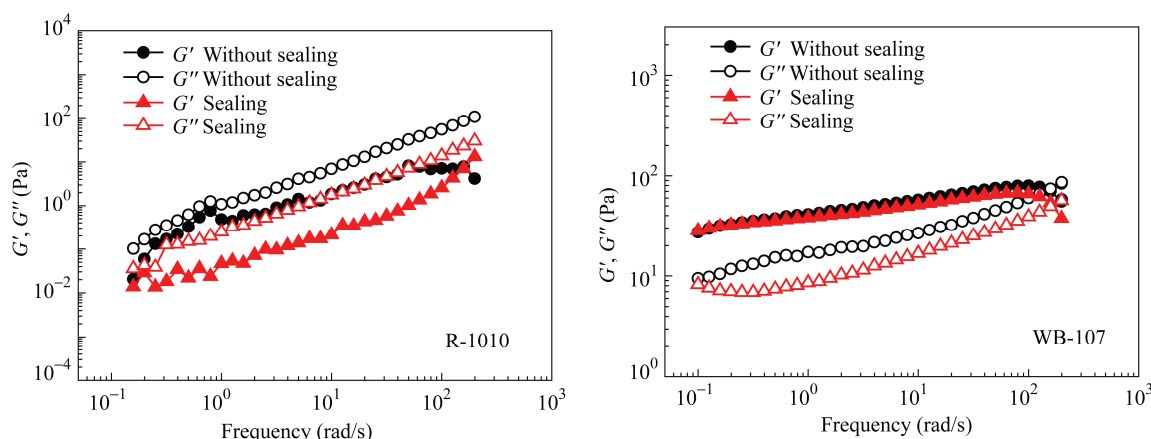


Fig. 1 Storage (G' , filled symbol) and loss (G'' , unfilled symbol) modulus versus frequency (ω) for R-1010 and WB-107 sealed by paraffin oil or without sealing during measurements on an AR-2000ex rotary rheometer

In Fig. 2, the steady shear results from the rotary rheometer measurement are also shown. The torque of R-1010 at low shear rates is close to the measurement limitation, so only the viscosity of R-1010 at relatively larger shear rates are shown. In Fig. 2, it is observed that the viscosity of WB-107 paints at low shear rate is bigger than that of R-1010. Sagging, flow and leveling of paints usually occur at low shear rates ($\sim 0.1 \text{ s}^{-1}$ to $\sim 5 \text{ s}^{-1}$). The viscosity of WB-107 at low shear rate is bigger than that of R-1010, so that the sagging resistance of WB-107 is relatively better than that of R-1010, while the flow and leveling ability of R-1010 is relatively better than that of WB-107^[10]. Brush loading, and spreading of paints usually occur at mid shear rates ($\sim 5 \text{ s}^{-1}$ to $\sim 100 \text{ s}^{-1}$), though the viscosity of two paints have some difference at this range, they both meet the requirement^[10]. At higher shear rate ($\sim 1000 \text{ s}^{-1}$), the viscosity of two PU paints are close. The application of paints in industry such as brush drag, rolling and spatter resistance *etc.* are generally occur at high shear rates ($> 1000 \text{ s}^{-1}$)^[10], this means that both PU paints have similar application properties at high shear rates.

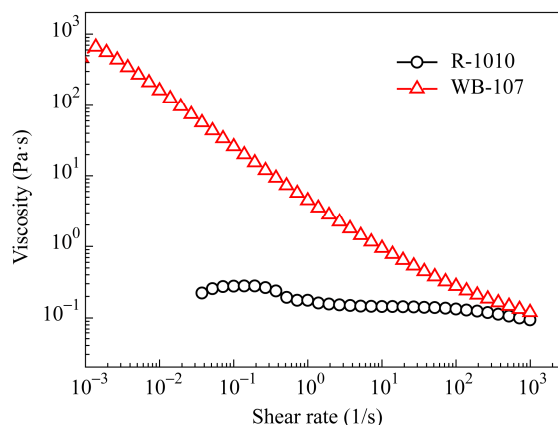


Fig. 2 Viscosity versus shear rate for R-1010 and WB-107 sealed by paraffin oil on an AR-2000ex rotary rheometer

Microrheology Result

DWS, an extension of dynamic light scattering, is one kind of microrheological methods. The viscoelastic properties of samples can be obtained by tracking the motion of colloidal particles. DWS is a powerful tool to study rheological properties of turbid materials, has an advantage of very high frequency and good spatial resolution^[17]. During the measurements of DWS, the samples are sealed in cell so that the evaporation of solvent can be avoided. Thus, DWS was also used here to characterize the rheological properties of turbid waterborne

PU paint. To get the rheological properties of the samples from the motion of colloidal particles, following steps are needed^[16, 18–31].

First, the autocorrelation function $g_2(t)$ can be given by the ensemble average intensity using the formula^[16, 18, 19]:

$$g_2(t) = \langle I(t_r + t)I(t_r) \rangle / \langle I(t_r) \rangle^2 \quad (1)$$

where $I(t)$ is the light intensity and $\langle \dots \rangle$ denotes the ensemble average. In the backscattering geometry, the autocorrelation function $g_2(t)-1$ is described by the following formula^[20–22]:

$$g_2(t)-1 = \beta \exp(-\gamma(6t/\tau_0)^{1/2}) \quad (2)$$

with a relaxation time $\tau_0 = 1/DK_0^2$, where $K_0 = 2\pi n/\lambda$ (n is the refractive index of medium, λ is the wavelength of laser in the medium). γ is a constant factor depending on the detected polarization state, and the factor β is related to the experimental setup. The mean square displacement (MSD) of a particle is defined by^[20, 23] $\langle \Delta r^2(t) \rangle = 6Dt$. Thus, the MSD ($\langle \Delta r^2(t) \rangle$) can be obtained from the autocorrelation function $g_2(t)-1$. Then the local viscoelastic modulus of a fluid is obtained by using the formula^[23–26].

$$\tilde{G}(s) = \frac{K_B T}{\pi a s \langle \Delta \tilde{r}^2(s) \rangle} \quad (3)$$

where K_B is the Boltzmann's constant, T is the temperature of the sample, a is the radius of the microsphere, s is the Laplace frequency, and $\sim$ represents the unilateral Laplace transformation. In particular, the complex modulus $G^*(\omega)$ is obtained by using $s = i\omega$ via $|G^*(\omega)| = |\tilde{G}(s = i\omega)|$ ^[23].

The storage modulus and loss modulus with respect to frequency can be obtained by^[23]

$$G'(\omega) = |G^*(\omega)| \cos(\delta(\omega)\pi/2) \quad (4)$$

$$G''(\omega) = |G^*(\omega)| \sin(\delta(\omega)\pi/2) \quad (5)$$

where $\delta(\omega)$ is dependent on the frequency and is equal to the slope m of the MSD $\langle \Delta r^2(t) \rangle$ ($m = \text{d} \lg \langle \Delta r^2(t) \rangle / \text{d} \lg t$).

The autocorrelation functions $g_2(t)-1$ of two waterborne PU paints are shown in Fig. 3. The $g_2(t)-1$ of WB-107 paint decays slower than that of R-1010 paint, as the result of the average particles size of WB-107 paint is bigger than that of R-1010 paint^[27, 28]. To get the reliable rheological properties of samples, the optimal fitting range of the autocorrelation function is restricted to the time range when the $g_2(t)-1$ decays. The time range when $g_2(t)-1$ is flat should not be included into the fit^[29].

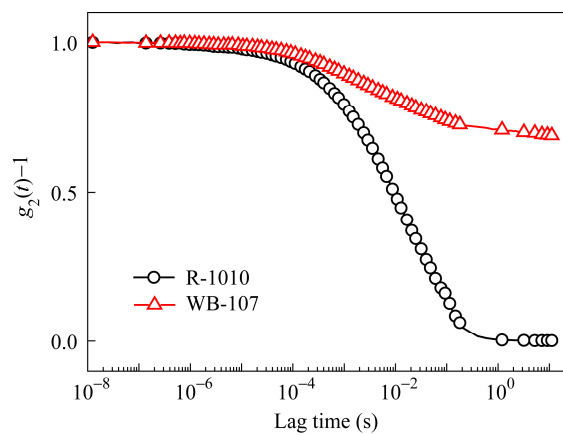


Fig. 3 Autocorrelation functions $g_2(t)-1$ of the colloidal particles imbedded in waterborne PU paints R-1010 and WB-107

The MSD ($\langle \Delta r^2(t) \rangle$) of the colloidal particles in R-1010 and WB-107 obtained by DWS is shown in Fig. 4. The $\langle \Delta r^2(t) \rangle$ varies with time as $\langle \Delta r^2(t) \rangle \propto t^m$, and the slope m is obtained by $m = \text{d} \lg \langle \Delta r^2(t) \rangle / \text{d} \lg t$. Based on the value of m , the motion of particles can be obtained. In detail, $m > 1$, the motion of the particles is superdiffusive; $m = 1$, the motion of the particle is entirely diffusive (Brownian movement) and the medium is Newtonian medium; $0 < m < 1$, the motion of the particles is subdiffusive and the medium is the viscoelastic medium; $m = 0$, the medium is elastic medium^[30, 31]. As shown in Fig. 4, the motion of the PU particles varies at different time scales as the slope of MSD changes with time. At short time scales, m is equal to 1, and the motion of PU particles is Brownian movement. At longer time scale, m becomes smaller than 1, as the motion of the PU particles is constrained by the medium^[30]. The curve of MSD versus time even reaches a plateau at longer time scale, and the value of MSD for WB-107 at the plateau is lower than that of R-1010, stating that the elasticity of WB-107 is stronger than that of R-1010^[30].

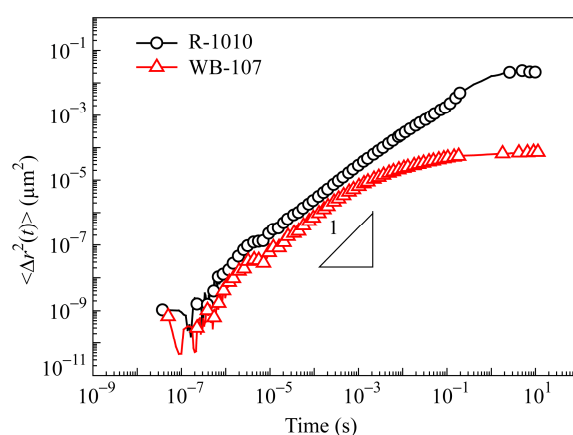


Fig. 4 Time-dependent mean square displacement $\langle \Delta r^2(t) \rangle$ of the colloidal particles in waterborne PU paints R-1010 and WB-107

The rheological results of samples measured by DWS are shown in Fig. 5. Comparing the results in Fig. 1 and Fig. 5, it is clear that the frequency range probed by DWS is wider than that of rotary rheometer. At the same frequency range, the changing trends of G' and G'' versus frequency for samples measured by DWS and rotary rheometer are similar. However, the moduli got by macrorheology are bigger than that got by microrheology due to the evaporation of solvent on rotary rheometer.

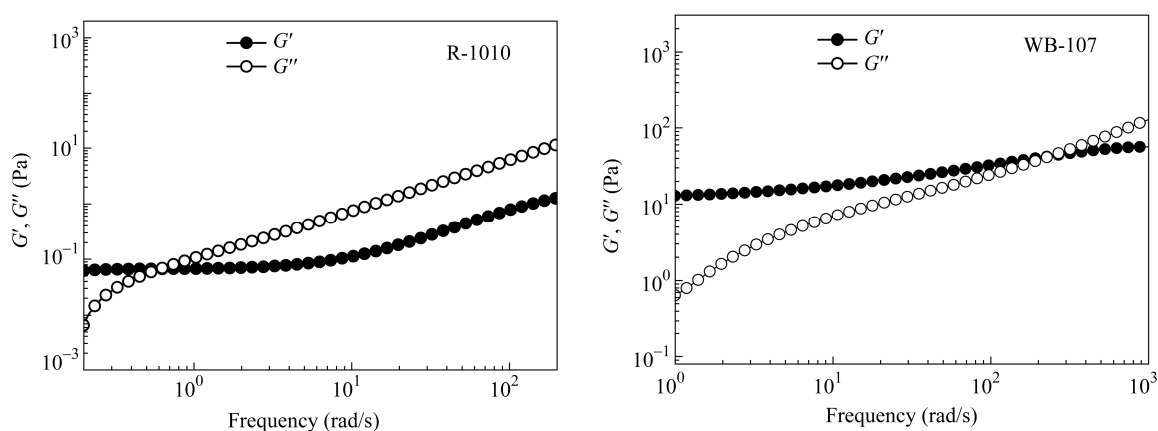


Fig. 5 Storage modulus G' and loss modulus G'' of PU paints R-1010 and WB-107 measured by DWS

In Fig. 5, at low frequency, G' is larger than G'' for both PU paints, the elasticity rather than viscous of the paint is dominant. At high frequency, G' is smaller than G'' for both PU paints, the viscous of paint dominates. It is also observed that the crossover frequency (ω_c) of G' and G'' for the two waterborne PU paints is quite different. The linear oscillatory frequency sweep results of paints can be used to evaluate the pigment suspending properties and sedimentation stability of paints^[10, 32]. When other parameters are fixed, it was reported that the PU paints whose G' is larger than G'' have better pigment suspending properties and sedimentation stability than the PU paints whose G' is smaller than G'' . Based on the above results, it is expected that WB-107 has relatively better pigment suspending properties and sedimentation stability than that of R-1010^[10].

CONCLUSIONS

The rheological properties of two specific waterborne PU paints were explored by macrorheology and microrheology method. During the macrorheological measurement on a rotary rheometer, evaporation of solvent cannot be totally excluded, which has an apparent influence on the rheological results. Using a diffusing wave spectroscopy (DWS), evaporation of solvent can be neglected, that makes DWS provide more credible linear viscoelasticity results than the rotary rheometer. Based on the rheological results of two PU paints obtained by rotary rheometer and DWS, the pigment suspending, sedimentation stability, sagging, flow, leveling and application properties of the two PU paints are qualitatively compared. It is observed that the rheological properties of two PU paints have apparent difference, which will determine the difference of their appropriate application.

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