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Rheological behavior of waterborne polyurethane/starch aqueous dispersions during cure

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ABSTRACT

Isothermal rheological behaviors of waterborne polyurethane (WPU)/starch aqueous dispersions during cure were investigated with a small-amplitude oscillatory shear flow experiment to evaluate their crosslinked structure and to predict their mechanical properties, for the first time. An abrupt increase in the elastic storage modulus (G'), the viscous loss modulus (G''), the complex dynamic viscosity (η^*) and the loss tangent ($\tan\delta$) was observed during the curing process of the dispersions, as a result of the formation of a fractal polymer gel. The gel point (t_{gel}) was determined from the intersection in $\tan\delta$ vs curing time for different constant shear frequencies, where $\tan\delta$ was frequency independent and all curves crossed over, indicating the validity of the Winter–Chambon criterion for the complex system. The values of the power law exponent (n) and the gel strength (S_g) at the gel point indicated that with an increase of starch content the crosslinked WPU/starch gels underwent a transition from weak fractal to strong elastic ones. Moreover, the WPU/starch composite sheets, obtained from the aqueous dispersions with relatively high S_g values, also exhibited the increased tensile strength (σ_b) and Young's modulus (E). Their structure–mechanical properties relationship and the phase transitions of dispersed starch–dual-phase continuity–starch matrix were revealed. This work confirmed that the rheological characters could be used to predict the mechanical properties of the WPU materials blended with natural polymer.

1. Introduction

Worldwide potential demands for replacing petroleum-derived raw materials by renewable resources in the production of valuable biodegradable materials are significant from the social and environmental standpoints [1,2]. Natural polymers are the most promising candidates; however their poor mechanical properties limit further applications. Polyurethane (PU) products have found extensive application in producing elastomers, coatings and foams [3]. By blending PU with natural polymers, the new materials with improved properties and kept biodegradability have been obtained [4–7]. There is a good miscibility between PU and natural polymers in their blends due to the hydrogen bonding interaction between urethane groups and hydroxyl groups. It is noted that waterborne polyurethane (WPU) has now emerged as an important alternative due to its extensive applications, tunable physical properties, good biocompatibility, and biodegradability [8]. It is very useful in many applications, and is gradually replacing the conventional organic solvent-borne PU products [9,10]. In recent years, a series of composite materials have been prepared via casting and evaporating processes from natural polymers and WPU with the aim of improving the properties of both components [11–16]. Some crosslinking reagents were also added to form interpenetrating network, leading to the improvements of the mechanical properties and water resistivity of these materials [17,18]. In the mean time, fundamental investigations of the cure behavior and the mechanism of macroscopic gelation in the composite materials have attracted more and more attention [19–21]. It is critical for controlling the production process and the final performance of the systems [22].

The viscoelastic properties of hydrogels correlate strongly with their microstructures, and can provide useful information for modulating their performance characteristics [23,24]. Rheological measurements can be used as a powerful experimental tool to monitor the polymer phase transition behavior [25–28], because it allows properties to be probed under at-rest conditions without disruption of the microstructure [29]. Moreover, this is quite an effective method for studying the curing process of thermosetting polymers and for the examination of the viscoelastic properties and the transition temperatures and gelation times of the cured products [30,31]. A transition of liquid to solid structure, as a result of gelation, is a phenomenon in which a polymeric liquid dramatically

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becomes solid-like at a critical point in polymer concentration, temperature, storage time, etc [32]. The dynamic viscoelastic parameters are important for the understanding and control of the liquid–solid transition process and to clarify the effects of the different interactions between the particles on the cure mechanisms in colloidal dispersions [31,33,34]. However, investigation on the viscoelastic behaviors of materials blended with aqueous dispersions containing natural polymers during the curing process has been scarcely reported.

An understanding of the relationship between the rheological behaviors and the mechanical properties is beneficial to the development and application of natural polymer-based composite materials. In the present work, we chose the system of glutaraldehyde crosslinked WPU/starch aqueous dispersions as the model. The isothermal rheological behavior of this system was investigated with small-amplitude oscillatory shear flow experiments as a function of starch concentration. Their morphology, structure and mechanical properties were characterized by scanning electron microscopy, dynamic mechanical thermal analysis and tensile testing to evaluate the relationship between the microstructure and properties of the materials. Furthermore, our findings are expected to provide useful information for the preparation of the composite materials based on natural polymers via casting and evaporating.

2. Experimental section

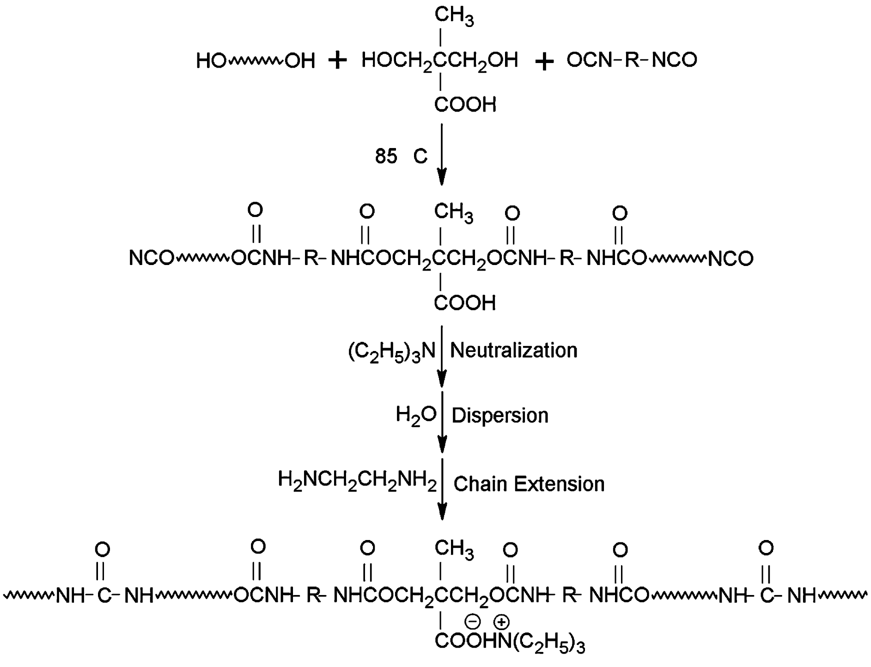
2.1. Materials

All the chemical reagents used in this work were of analytically grade, and were obtained from commercial sources in China. Commercial waxy maize starch containing 0.5 wt% protein, 0.15 wt% fat and 0.15 wt% ash was a gift of Gansu Xue Jing Biochemical Co., Ltd. (China). 2, 4-Toluene diisocyanate (TDI) was purchased from Jiangbei Chemical Reagents Factory (Wuhan, China). TDI was redistilled before use. Polypropylene glycol (PPG) having weight-average molecular weight (M_w) of 2000 was supplied by Sinopharm Chemical Reagent Co., Ltd., and vacuum dried at 120 °C for 1 h before use. Dimethylol propionic acid (DMPA) was obtained from Chengdu Polyurethane Co. in China. Aqueous solution of glutaraldehyde (25 wt%), supplied by Shanghai Chemical Reagent Plant, was diluted to 10 wt% aqueous solution before use. Triethylamine (TEA), ethylenediamine, and acetone were purchased from Shanghai Chemical Co. in China. TEA and acetone were treated with 3 Å molecular sieves to dehydrate. Starch was vacuum-dried at 105 °C for 5 h before use.

2.2. Preparation of blends

PPG2000 (116 g, 0.058 mol) and TDI (20 g, 0.111 mol) were introduced by pouring the reagents into a four-neck flask equipped with a thermometer, mechanical stirrer, dropping funnel, and a condenser tube. The resulting mixture was stirred and heated to 80 °C for 60 min, and then DMPA (2.68 g, 0.02 mol) was added. The reaction occurred at 85 °C for 2–3 h until the –NCO content reached a desired value, which was determined by using the standard dibutylamine titration method. After cooling the reaction mixture to 40–50 °C, 30 g acetone was added to reduce the viscosity of the prepolymer, and the carboxylic groups of DMPA were neutralized with TEA (2.1 g, 0.02 mol). Finally, 710 g deionized water was added to emulsify, and then 10 wt% ethylenediamine aqueous solution (12 g, 0.02 mol) was added to extend the chain at room temperature. The excessive –NCO groups reacted with H_2O to produce $–NH_2$ groups and CO_2 slowly. Thus some WPU molecules contained the $–NH_2$ group as the end group. The reaction steps of prepolymer preparation and chain extension are presented in Scheme 1.

The starch–water mixture was heated slowly up to 80 °C with vigorous stirring for 1 h to obtain a translucent paste of starch. After cooling the paste to room temperature, the WPU solution was added and the mixture was stirred for 12 h. Subsequently, the dispersions were degassed and coded as US10-l–US70-l, corresponding to a starch content of 10, 20, 30, 40, 50, 60, and 70 wt%, respectively. In addition, the total solid content of each of these dispersions was 13 wt%. These dispersions were used immediately



Scheme 1. Elementary steps for the synthesis of WPU.

for viscoelastic tests without delay. The same dispersions were prepared and then a desired amount of 10 wt% aqueous glutaraldehyde was added to crosslinking WPU molecules. The glutaraldehyde content in WPU was 2 wt%. The resulting mixture and the pure WPU solution were degassed and cast onto the Teflon mold. The casting solutions were heated at 65 °C for 24 h to obtain the transparent sheets with thickness of 0.2 ± 0.04 mm. The thickness was measured by ProMax Electronic Caliper (Fowler Company, U.S.A.). These sheets were coded as WPU and US10-s–US70-s, corresponding to a starch content of 0, 10, 20, 30, 40, 50, 60, and 70 wt%, respectively. Before characterizations, the sheets were conditioned at room temperature in a desiccator containing P_2O_5 with 0% relative humidity (RH).

2.3. Characterization

The dynamic rheology measurements were carried out on an ARES-RFS III rheometer (TA Instruments, U.S.A.). Double-concentric cylinder geometry with diameters of 32 and 34 mm, and a gap of 2 mm was used to measure the dynamic viscoelastic parameters such as the elastic storage modulus (G'), the viscous loss modulus (G''), the complex dynamic viscosity (η^*) and the loss tangent ($\tan \delta$) as a function of time at 65 °C and constant frequency (0.4, 1, and 4 Hz). The rheometer was equipped with two force transducers, allowing the torque measurement in the range from 0.004 to 1000 g cm. The existence and extent of the linear viscoelastic regime were determined by G' and G'' as a function of strain (0.1%–100%) at an angular frequency of 1 rad/s. The values of the strain amplitude were checked to ensure that all measurements were set as 10%, which is within a linear viscoelastic regime. These testing conditions were chosen to simulate the casting and evaporating process. A desired amount of 10 wt% aqueous glutaraldehyde was added into the dispersions (time $t = 0$) and the mixtures were poured into the couette geometry instrument immediately after fully mixing. Temperature control was established by connecting instrument (or couette) to a Julabo FS18 cooling/heating bath kept 65 ± 0.2 °C over an extended period of time. In order to reduce the experimental errors, we repeated each test two times, and the differences were all very small and within experimental errors.

Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical analyzer (DMAQ800, TA Instruments, U.S.A.) in tensile mode at a frequency of 1 Hz. The sheets were 10 × 10 mm (length × width) in dimension, and the test temperature ranged from −70 to 80 °C, with a heating rate of 5 °C per min. The α-relaxation temperature, T_α, was determined as the peak value of the loss angle tangent ($\tan \delta$). The sheets were frozen in liquid nitrogen, snapped immediately, and then vacuum-dried. The fracture surfaces (the cross-sections) of the samples were sputtered with gold, and then observed and photographed with scanning electron microscopy (SEM, S-570, Hitachi, Japan) at 20 kV. The tensile strength (σ_b), elongation at break (ε_b), and the Young's modulus (E) of the sheets were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) with a tensile rate of 50 mm per min at 25 ± 2 °C according to ISO527-3: 1995(E). Before testing, the sheets were allowed to rest for one week in 0% RH. Five parallel measurements were carried out for each sample.

3. Results and discussion

3.1. Rheological behaviors of WPU/starch aqueous dispersions

The isothermal time dependence of G' and G'' for the samples with different starch contents at constant shear frequency ($\omega = 1$ rad s^{-1}) and 65 °C is shown in Fig. 1. A dramatic increase in G' of all samples was clearly observed as a result of the gelation. For US10-l, US50-l, US60-l and US70-l, the G' values leveled off and became time independent at long times. The plateau values of G' were found to be the same when the starch content was more than 40 wt%, and were much bigger than that of US10-l. The experimental result indicated the formation of a starch matrix which made a great contribution to G'. G' reached a plateau value at long times as a result of the creation of an equilibrium modulus (G_{eq}), which is a typical criterion for the formation of an elastic, fractal gel. Interestingly, there was no G_{eq} in US20-l, US30-l and US40-l. The changes of G' in these samples could be divided into two regions, namely the G' values increased and leveled off, and subsequently another sharp increase in G' occurred at 1716 s, 1734 s and 1600 s, respectively. The results revealed that these samples formed the fractal gel firstly, but the systems were not stable. It could be explained that the presence of starch prevented the formation of a tight WPU network, when the starch content was lower than 50 wt%. However, the crosslinking structure of WPU was stable when the starch content was very low (10 wt%), in which the starch exhibited a good dispersion in the WPU matrix.

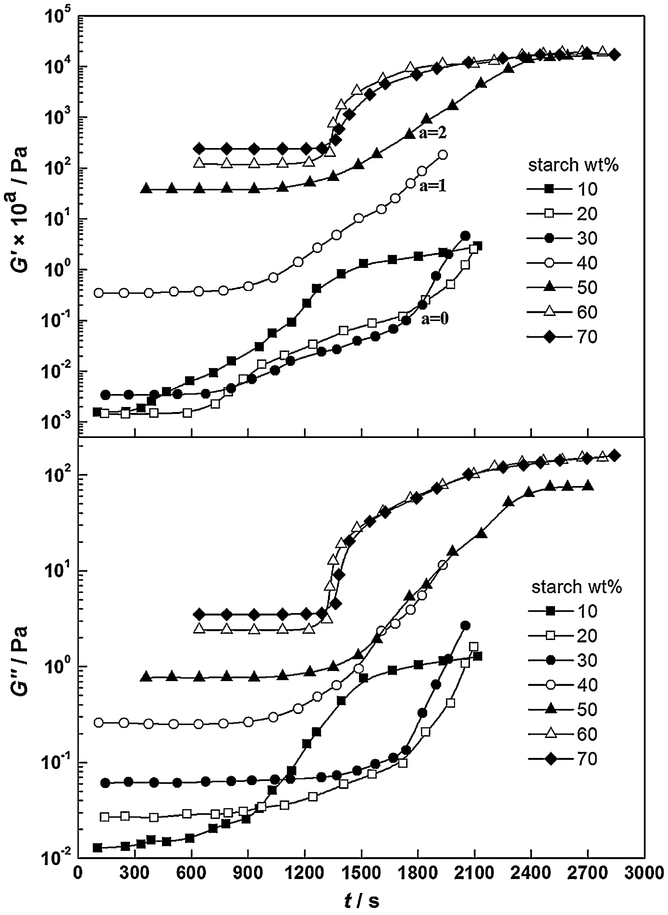


Fig. 1. Time dependence of the dynamic storage modulus (G') and dynamic loss modulus (G'') of crosslinked WPU/starch aqueous dispersions with different starch contents at constant shear frequency and temperature ($\omega = 1$ rad s^{-1}, 65 °C). The data are shifted along the vertical axes by 10^a-fold (a value given) to alleviate the overlapping of the curves.

The time dependence of G'' and η^* for the samples at $\omega = 1$ rad s^{-1} and 65 °C is shown in Figs. 1 and 2. With an increase of the gelation time, G'' and η^* increased and reached equilibrium values, namely time-independent, at long time (1500 s) for US10-l, US50-l, US60-l and US70-l. Interestingly, both G'' and η^* reached a plateau almost at the same gelation time, indicating that an elastic

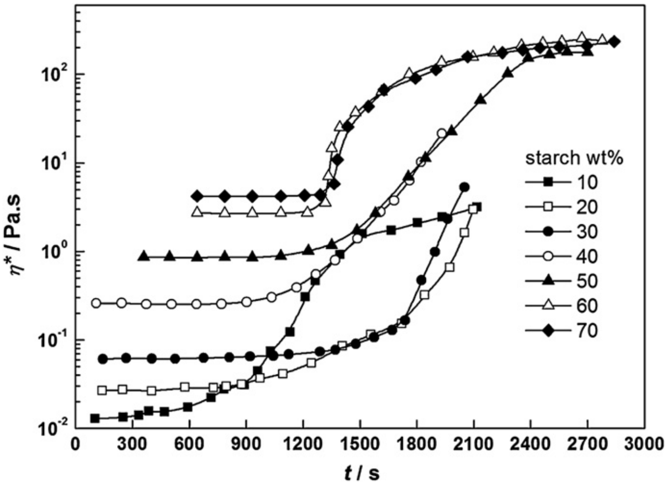


Fig. 2. Time dependence of the dynamic complex viscosity (η^*) of crosslinked WPU/starch aqueous dispersions with different starch contents at constant shear frequency and temperature ($\omega = 1$ rad s^{-1}, 65 °C).

fractal gel formed when the starch content was very low (10 wt%) or more than 40 wt%. Furthermore, the changes of G'' and η^* were also composed of two steps for US20-l, US30-l and US40-l. It is worth noting that, their variations of G'' and η^* were the same as those of G', which could not reach a plateau value during the testing process. This could be attributed to the formation of weak fractal gel and the existence of obvious phase separation in the systems. It could be expected that relatively weaker mechanical properties would appear in US20-s, US30-s and US40-s.

The effect of starch content on the gelation kinetics can be quantified by calculating the average rate of change, $(\mathrm{d}f/\mathrm{d}t)_{\mathrm{av}}$ of the viscoelastic material functions (G', G'', and η^*) with time by:

$$\left(\frac{\mathrm{d}f}{\mathrm{d}t}\right)_{\mathrm{av}} = \frac{1}{t_2 - t_1}\int_{t_1}^{t_2}\frac{\mathrm{d}f}{\mathrm{d}t} \qquad (1)$$

where f is the viscoelastic material function (G' or G'' or η^*) and t_1 and t_2 are the times at the beginning and ending of gelation process, respectively [35]. Fig. 3 shows the change of $(\mathrm{d}f/\mathrm{d}t)_{\mathrm{av}}$ as a function of starch content. The f values for US20-l, US30-l and US40-l were calculated within the first transition part. $(\mathrm{d}f/\mathrm{d}t)_{\mathrm{av}}$ decreased with an increase of the starch content to 30 wt%, and then increased exponentially with a further addition of starch. It indicated that the formation of fractal gel in WPU matrix was prevented when the starch content was low, and then the starch domain extended, leading to the continuous phase of starch which made a contribution for the gel formation. These results are in good agreement with those in Figs. 1 and 2, revealing that the variation of starch content affected the gelation of the composite systems. Interestingly, the $(\mathrm{d}f/\mathrm{d}t)_{\mathrm{av}}$ value of η^* was higher than that of G', and much higher than the corresponding G'' value. This behavior reflected a high sensitivity of η^*, and was different from that in pure polyurethane system, in which G' had the highest sensitivity to the structural change occurring in the gelation process, compared to the other viscoelastic material functions [22]. Furthermore, the low sensitivity of G'' to structural change of a material has also been previously observed in some polymer blends near the phase separation temperature [36]. The unusual rheological behaviors of the composite systems were as a result of the addition of natural polymer, which was quite different from synthesized polymers.

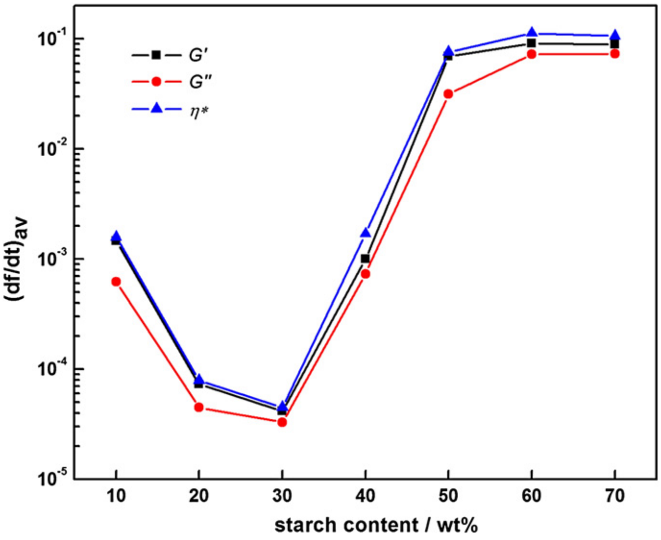


Fig. 3. Average rate change of G', G'', and η^* of crosslinked WPU/starch aqueous dispersions with different starch contents.

According to the Winter–Chambon criterion, the following power law behavior exists at the gel point:

$$G'(\omega) = G''(\omega) \sim \omega^n \quad 0 < n < 1 \qquad (2)$$

and

$$G''(\omega)/G'(\omega) = \tan\delta = \tan(n\pi/2) \qquad (3)$$

where $\tan\delta$ is the loss tangent, and n is the relaxation exponent at the gel point. The frequency independence of the $\tan\delta$ in the vicinity of the gel point has been widely examined for gelation [37], and has also been employed to determine the gel point. Fig. 4 shows the time dependence of $\tan\delta$ at different constant shear frequencies and 65 °C. Obviously, there was a critical aging time for all the samples at which $\tan\delta$ is frequency independent. This indicated that the system has reached the gel point and the cluster of the fractal structure was macroscopically percolated, in good agreement with Winter–Chambon criterion. It also validated that the Winter–Chambon theory can be used to determine the gel point of the complex system containing natural polymer. From the crossover in Fig. 4, the gel point (t_{gel}) for the samples with different starch contents was obtained, and the results are shown in Fig. 5. t_{gel} increased with the addition of starch, and the beginning of gelation process was delayed. This could be explained that the crosslinking of WPU molecules and the decreased inter-particle distance caused by water evaporation induced the gelation process. With an increase of the starch paste, the η^* value of the system increased to prevent the formation of the crosslinked WPU network and also to induce a lower rate of water evaporation. In view of the above results, the Winter–Chambon criterion can be applied in the WPU/starch aqueous dispersion system to clarify their rheological behaviors.

3.2. Behaviors of critical WPU/starch gels

It is well-known that the shear relaxation modulus $G(t)$ is predicted to obey a power law relaxation at the gel point [38]:

$$G(t) = S_g t^{-n} \qquad (4)$$

where S_g is the gel strength and has an unusual dimension of Pa s^n. n is the same as that in Eq. (2). S_g can simply be considered as the relaxation modulus at the gel point when the relaxation time t was

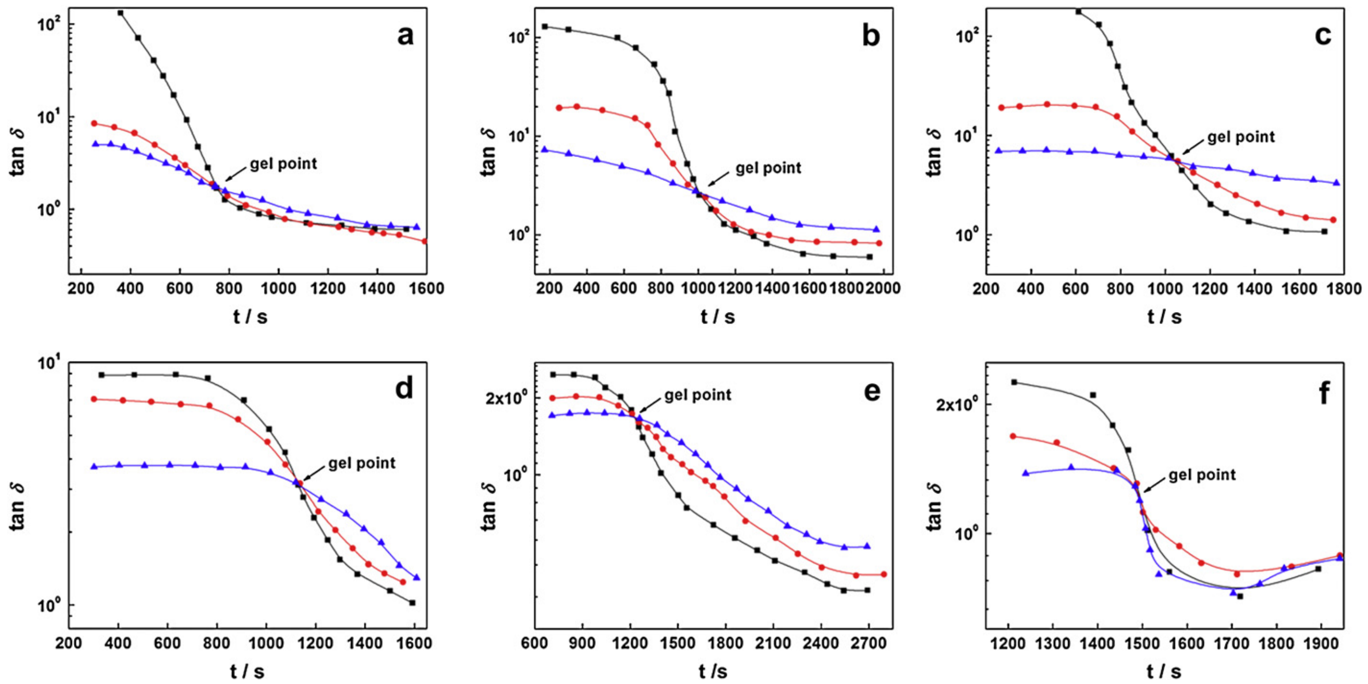


Fig. 4. Time dependence of tan δ at different constant shear frequencies (0.4 rad s^{-1} ■, 1 rad s^{-1} ● and 4 rad s^{-1} ▲) and 65 °C with different starch contents: (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, and (f) 70 wt%. The arrow shows the value of t_{gel}.

1 s. To express S_g as $S_g = G(t)t^n$, a similar expression can be applied to $G'(\omega)$ and $G''(\omega)$ at the gel point as [39]

$$G'(\omega) = G''(\omega)/\tan\delta = S_g\omega^n\Gamma(1-n)\cos(n\pi/2) \tag{5}$$

where $\Gamma(1-n)$ is the Γ function. By testing the n value, S_g can be calculated from $G'(\omega)$ or $G''(\omega)$ at the gel point using Eq. (5) above.

By using Eq. (3), the n values were obtained, and the dependence of n on the starch contents is shown in Fig. 6. In general, the n value is related to the physically fractal dimension, and reflects the degree of compactness of the network. A lower n value suggests the formation of a more highly elastic gel [40–42].Our finding indicated that the n value varied with the changing starch content. For US10-l, a relatively low n value of 0.66 indicated that the crosslinked WPU matrix formed a tight network. With an increase of starch content, n increased and reached the highest value of 0.89 for US30-l. This result revealed that the crosslinking density of the WPU matrix changed to the lowest when the starch content was 30 wt%, because of the phase separation. The high n value also suggested a less elastic nature, namely, a weak interaction in the gels. With the further addition of starch, the interactions between the particles increased, leading to a reduction of the n value. Interestingly, the n values of US60-l and US70-l were similar and lower than the others. This could be explained by the small changes, if any, in the structure of the high elastic gel with starch matrix with decrease of the WPU content.

In addition, the physical nature of a gelling system at the gel point can be described by the gel strength (S_g) defined in Eqs. (4) and (5), which is related to the physical strength of the gel network.

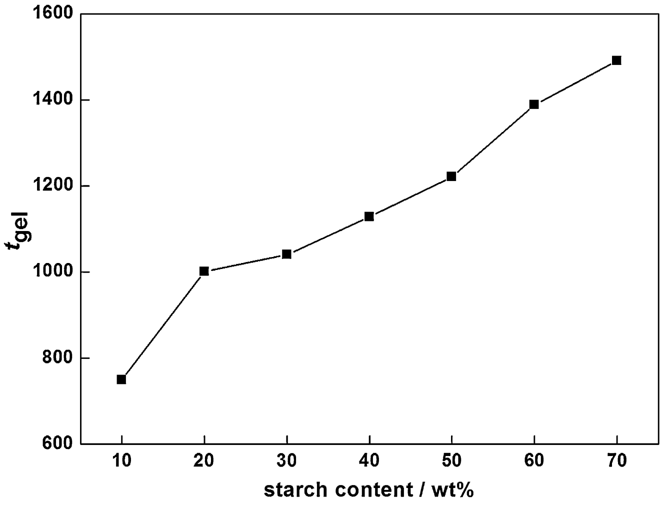


Fig. 5. Dependence of the gel point (t_{gel}) of crosslinked WPU/starch aqueous dispersions on the starch contents.

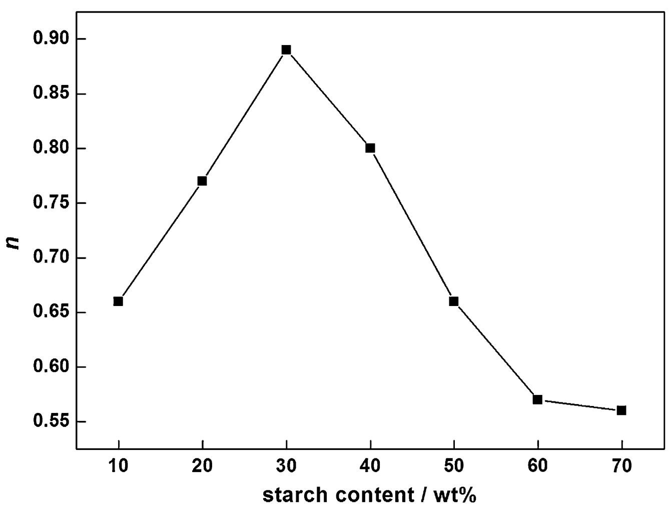


Fig. 6. Dependence of the relaxation exponent (n) of crosslinked WPU/starch aqueous dispersions on the starch contents.

Table 1
The experimental values of gelation time t_{gel}, tan δ, the relaxation exponent n, and the gel strength S_g of crosslinked WPU/starch aqueous dispersions.

Starch content (wt%)	tan δ	t_{gel} (s)	n	S_g (Pa s^n)
10	1.70	750	0.66	0.0089
20	2.69	1001	0.77	0.0084
30	5.66	1040	0.89	0.0081
40	3.17	1128	0.80	0.070
50	1.69	1221	0.66, 0.57	0.38
60	1.25	1388	0.57	8.41
70	1.23	1491	0.56	21.5

The S_g values calculated are summarized in Table 1, and they are plotted against the starch content in Fig. 7. The S_g values of US10-l, US20-l and US30-l were much lower than the others, indicating weak gels. However, with an increase of the starch content, the S_g values increased rapidly. The addition of starch would affect the S_g value in two opposite directions. In one aspect, the intermolecular hydrogen bonds between the starch and the WPU matrix can enhance the interaction in the gel, leading to an increase of S_g value. In another, the starch component can prevent the formation of tight crosslinking network of WPU, resulting in a reduction of S_g value. When the starch content was more than 30 wt%, the S_g values increased dramatically, indicating that the emergence of the continuous phase of starch led to the enhancement of the gel strength. In total, the dramatic changes observed in n and S_g revealed clearly the transitions of the internal structure of WPU/starch composites with increased starch content.

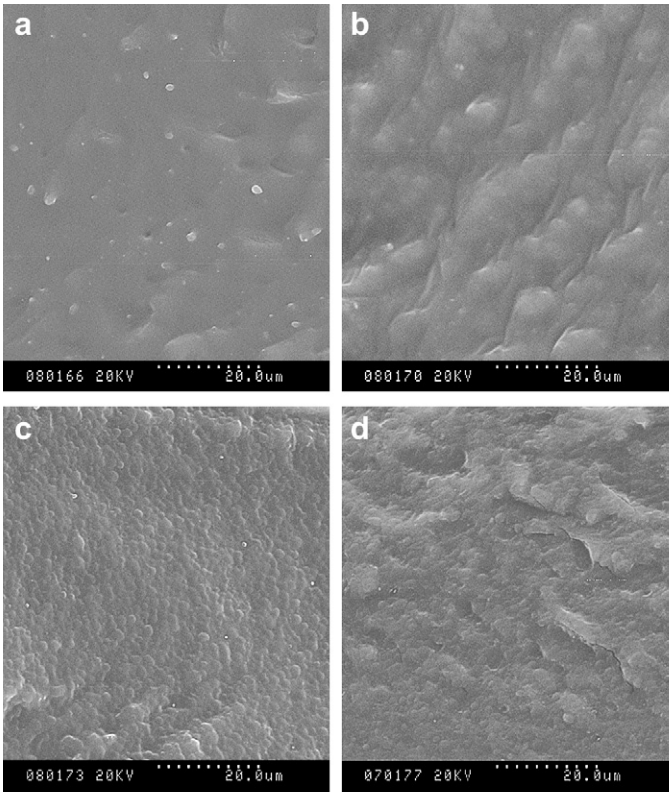


Fig. 8. SEM images of the fractured surfaces of crosslinked WPU/starch composite sheets with different starch contents: (a) 10, (b) 30, (c) 50, and (d) 70 wt%.

3.3. Morphology and mechanical properties of composite materials

To understand the relationship between the viscoelastic behaviors of the dispersions and the structures and properties of the solid sheets, the morphology and the mechanical properties of the WPU/starch composites were measured. SEM images of the fractured surface (cross-section) of US10-s, US30-s, US50-s and US70-s are shown in Fig. 8. A homogeneous distribution of the starch aggregates with the dimension of 1–2 μm in the WPU matrix was observed for US10-s, and its fractured surface was relatively smooth, indicating tight architecture of the crosslinked WPU. However, the US30-s sheet exhibited a coarse and fluctuant fracture surface, as a result of the formation of big aggregations of starch and the WPU network became less compact. When the starch content increased to 50 wt%, the starch component existed as the matrix, and the crosslinked WPU was dispersed in the continuous starch phase. It suggested the transitions of the internal structures of the WPU/starch composites as a function of the starch content, which supported the results of rheological measurements. Furthermore, DMTA test was carried out to determine the modulus and the segmental motion of molecules of the composite sheets with different matrices as observed by SEM. Fig. 9 shows the temperature dependence of the storage modulus (E') and loss peaks (tan δ) of US10-s, US30-s, US50-s and US70-s. The drop in E' of the

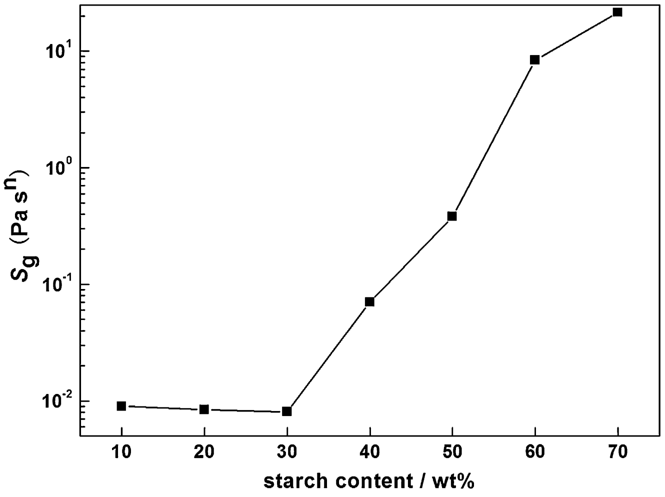


Fig. 7. Dependence of the gel strength (S_g) of crosslinked WPU/starch aqueous dispersions on the starch contents.

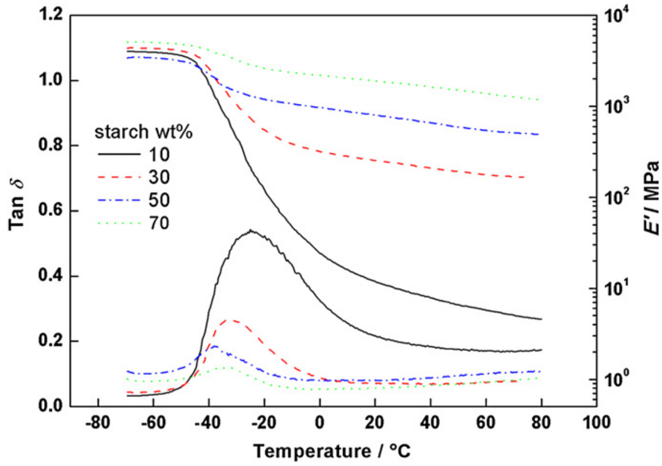


Fig. 9. Temperature dependence of the storage modulus (E') and loss peaks (tan δ) of the crosslinked WPU/starch composite sheets with different starch contents.

composite sheets at T_α was therefore ascribed to energy dissipation phenomena involving cooperative motions of long amorphous sequences likely to rotate and translate in different surroundings [1]. This modulus drop was not as obvious as in synthetic polymers (usually more than three orders of magnitude) [43], and reduced with the increase of starch content. The T_α values were assigned to WPU. For US10-s, the T_α value was −24.97 °C which was higher than the others, as a result of the formation of tight WPU network. However, the T_α value of US30-s was −32.32 °C, as a result of the phase separation and the reduced interaction between WPU segments. Interestingly, the T_α value of the composite sheet having a high starch content (50 wt%) appeared at −38.15 °C, because WPU network (with higher mobility) was broken and dispersed in the starch matrix. For US70-s, the strong hydrogen-bonding interactions between WPU and starch restrict the mobility of WPU segment, leading to the increase of T_α value (−33.10 °C). These results further supported strongly the transitions in the microstructures of composite materials.

The photographs of US10-s and US70-s and the mechanical properties of the WPU/starch composite sheets are shown in Fig. 10. The results of the mechanical properties were the averages of five parallel measurements. The tensile strength (σ_b) and the Young's modulus (E) of the composite sheets increased with an increase of the starch content. They exhibited soft elastomeric character when the starch content was low (Fig. 10a), and act like rigid plastic at a higher level of starch content (Fig. 10b). Interestingly, the trends of changes in the values of E', E and σ_b of the WPU/starch composite sheets were similar to those of G' and S_g of the corresponding aqueous dispersions on the whole. The results revealed that the mechanical properties of the materials were relative to the microstructure of the gels, and the S_g value can be used to judge σ_b to a certain extent. Especially, relatively weaker mechanical properties were observed in US20-s, US30-s and US40-s, in good agreement with those predicted by the G', G'' and η^* results. Therefore, we can judge the structures and σ_b of the composite materials by the rheological measurements. It is a useful and reliable method to guide the designing and preparation of composite materials with different functions via casting and evaporating.

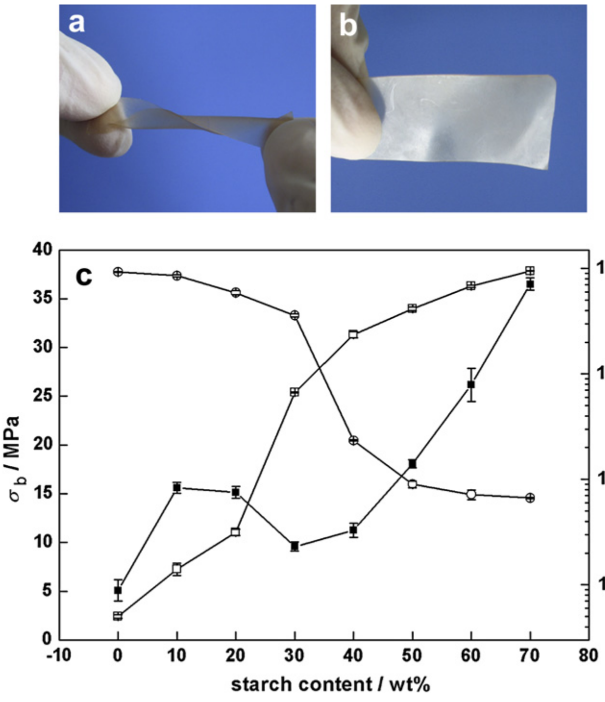


Fig. 10. Photographs of US10-s (a) and US70-s (b) and the dependence of the tensile strength (σ_b) (■), the Young's modulus (E) (□) and the elongation at break (ε_b) (○) of crosslinked WPU/starch composite sheets on the starch contents.

4. Conclusions

The isothermal rheological behaviors of waterborne polyurethane/starch aqueous dispersions during the curing process were characterized satisfactorily by small-amplitude oscillatory shear flow experiments. An abrupt increase in G', G'' and η^* of several orders of magnitude was observed to reveal the formation of a fractal polymer gel. It was validated that the Winter–Chambon theory can be used to determine the gel point of the complex system of waterborne polyurethane/starch dispersions. The t_{gel} value increased with the addition of starch content. The mechanical properties of the composite materials were related to the microstructure of the gels, and the n and S_g values at the gel point can be used to judge the structure and tensile strength of the resultant materials. The starch with relatively low content (less than 40 wt%) dispersed in the crosslinked WPU matrix, leading to the formation of weak gels. With an increase of the starch content, the systems underwent a transition from dual-phase continuity to starch matrix, creating a strong gel, leading to the improvement of the mechanical strength. Furthermore, the relationship between the viscoelastic behaviors of the dispersions as well as the structures and mechanical properties of the WPU/starch composite sheets was confirmed to be concerned. Therefore, this work provided a new applicable approach to predict the mechanical properties by measuring the rheological behaviors of the aqueous dispersions of natural polymer-based composite materials during the curing process.

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