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Preparation and Properties of Cornstarch Adhesives

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Abstract: The main goal of this study was to use cornstarch in the production of environmentally sound adhesives. 'Three-formaldehyde glue' pollutes the environment and harms to human health strongly, which widely used for wood-based panels preparation. Environment-friendly cornstarch adhesives were prepared using method of oxidation-gelatinization, insteading of the three formaldehyde glue. The effects of the quality ratio of starch and water, temperature and shear rate on the apparent viscosity of the adhesive were studied. The rheological eigenvalue of apparent viscosity was studied through nonlinear regression. The results showed that the apparent viscosity of cornstarch adhesives increased and then decreased with the increasing of temperature and the maximum value was obtained at 10°C; the apparent viscosity decreased slowly with the increasing of rotor speed; the phenomenon of shear thinning appeared wither cornstarch adhesives which was pseudo-plastic fluids. Cornstarch adhesives with characteristics of non-toxic, no smell and pollution could be applied in interior and upscale packaging.

Keywords: Apparent viscosity, rheological eigenvalue, starch adhesives

INTRODUCTION

Currently, the resin system used in wood-based panel preparation was the three-formaldehyde glue, which mainly consists of Urea-Formaldehyde resin adhesive (UF), Phenolic resin adhesive (PF) and Melamine-Formaldehyde resin adhesive (MF), however, there was a fatal drawback of this type of resin adhesives, such as the release of free formaldehyde which not only polluted the environment but also harmed to humans strongly (Wu *et al*., 2009; Li *et al*., 2008; Zhang and Zhang, 2008). Starch had advantages of resource-rich, low-cost, versatile, non-toxic, no smell, pollution etc. What's more, the starch adhesive with well adhesion and film-forming properties was a class of natural adhesives (Ding, 2008; Chen *et al*., 2007, 2006).

As a renewable natural polymer materials, the starch which not only has active functional groups, as well as the outstanding characteristics to adapt to the requirements of environmental protection, but also with the advantages of resource-rich, low-cost, non-toxic and biodegradable is payed more and more attention in the field of adhesives. However, as an adhesive, the pure starch has a lot of inadequacies, such as water resistance, fluidity, permeability, storage stability and mechanical properties (Guo and Guo, 2007; Li-Hong and Li-Xue, 2008; Syed *et al*., 2001; Liu *et al*., 2008; Santayanon and Wootthikanokkhan, 2003; Jun-you and Shu-Min, 2006), the properties of starch could be improved by physical and chemical methods, for example, it was an effective way to change the solubility, viscosity and related properties to meet the performance requirements of different application areas. In both methods, the chemical modification was an important means of preparation of starch adhesives (Liu *et al*., 1999; Jun-you and Shu-Min, 2006; Lin *et al*., 2007). The starch molecules contained the glycosidic bond and reactive hydroxyl groups could chemically react with many substances, which was the basis of chemically modified starch (Li *et al*., 2007).

In this study, we reported an easy method to prepare cornstarch adhesives through oxidation-gelatinization, insteading of the three formaldehyde glue. The aim of this work is to improve the apparent viscosity of cornstarch adhesives. Also, the effects of the quality ratio of starch and water, temperature and shear rate on the apparent viscosity of the adhesive

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Table 1: The raw materials of experiments

The main raw material	Trademark	Manufacturer
Cornstarch	Edible starch	Shandong Jincheng Food Co., Ltd.
30% H_2O_2	AR	Nanjing Chemical Reagent Co., Ltd.
NaOH solution	AR	Nanjing Chemical Reagent Co., Ltd.
$Na_2S_2O_3$	AR	Nanjing Chemical Reagent Co., Ltd.
$FeSO_4 \cdot 7H_2O$	AR	Nanjing Chemical Reagent Co., Ltd.

Table 2: Formula of preparing starch adhesives

The appellation	H_2O_2	Fe^{2+} solution	NaOH solution	$Na_2S_2O_3$ solution
Concentration	26%	6%	10%	6%
Dosage	0.5 mL	1 mL	18 mL	2 mL
Effect	Oxidizer	Oxidizer	Pasting agent	Blockers

were studied. The rheological eigenvalue of apparent viscosity was studied through nonlinear regression.

MATERIALS AND METHODS

The raw materials, reagents and their grades and manufacturers, are listed in Table 1.

Methods: There are many methods to prepare starch adhesives and in this test, the method of oxidation-gelatinization was used to prepare cornstarch adhesives. Table 2 is the formula of preparing starch adhesives.

Analysis methods: In accordance with the national standard GB/T 2794-1995 "the adhesive viscosity measurement", the NDJ-5S digital viscometer was used to test the starch adhesive viscosity. Before measuring, the viscosity of the liquid to be measured should be estimated firstly and then the suitable rotor and rotational speed of the digital viscometer were selected. To ensure the accuracy, the percentage of the range should be accurately controlled in the range of 10 to 90% and the sample of starch adhesives should be uniformly and without bubbles during the measurement. The samples were measured after half an hour of the temperature converted and the temperature should been reached the set value each time.

Starch adhesives put into the beaker which placed in the bath pot with a constant temperature while measuring the viscosity of starch adhesives. The rotor immersed into the adhesive in depth properly and then selected the appropriate speed by the control panel keys. The average of five measurements of the apparent viscosity of the starch adhesive was considered to be the result.

RESULTS AND DISCUSSION

Adhesive viscosity has an important role on the bonding strength, tensile strength and other mechanical properties in the composite materials. The starch adhesives apparent viscosity depends on the dispersion of the starch molecules in solution expand capacity, where the starch molecules increase the content area and reinforce mutually during the adhesive preparation process and ultimately enhance the adhesion strength.

Figure 1 shows the effect of temperature on apparent viscosity of cornstarch adhesives. As can be seen from the figure, when the ratio of starch and water quality is 1/6, corn starch adhesives apparent viscosity increased and then decreased with the increase of the temperature and the maximum value is obtained at 10°C. The corresponding value was 1860, 1763, 1568 and 1318 mPa.s, respectively and the decline of the rate of the apparent viscosity decreased gradually (Fig. 1a). When the ratio was 1/8 and the rotor of the apparent viscosity (255 and 202.5 mPa.s, respectively) was obtained at 15°C and when the speed was 30 and 60 PRM, the apparent viscosity (178 and 137.5 mPa.s, respectively) was obtained at 10°C (Fig. 1b). While the ratio was 1/10 and the rotor speed of corn starch adhesive was 6 and 12 PRM, the peak of the apparent viscosity (120 and 97.5, mPa.s, respectively) was obtained at 10°C and when the speed was 30 and 60 PRM, the apparent viscosity decreased gradually with the increase of the temperature (Fig. 1c). While the ratio was 1/6, the adhesive prepared apparent viscosity was significantly better than that the two precious. As is portrayed in Fig. 1d, when the speed was 30 PRM, the peak values (156.8, 178 and 90.5 mPa.s, respectively) were obtained, the apparent viscosity increased and then decreased with the increase of the temperature, what's more, the higher the temperature was, the smaller the difference between the apparent viscosity of the different adhesives, this may be due to the raise in temperature make the frictional resistance among starch molecules smaller, which manifested as the decrease of the viscosity.

Figure 2 shows the effect of rotate speed on apparent viscosity of cornstarch adhesives. As can be seen from the figure, the apparent viscosity decreased slowly with the increase of the speed of the rotor, that's can be explained that the phenomenon of shear thinning appears in cornstarch adhesives, when the ratio was 1/6, adhesives prepared apparent viscosity was significantly better than that the two precious, the peak values (886, 180 and 70.5 mPa.s, respectively) were obtained at 2°C.

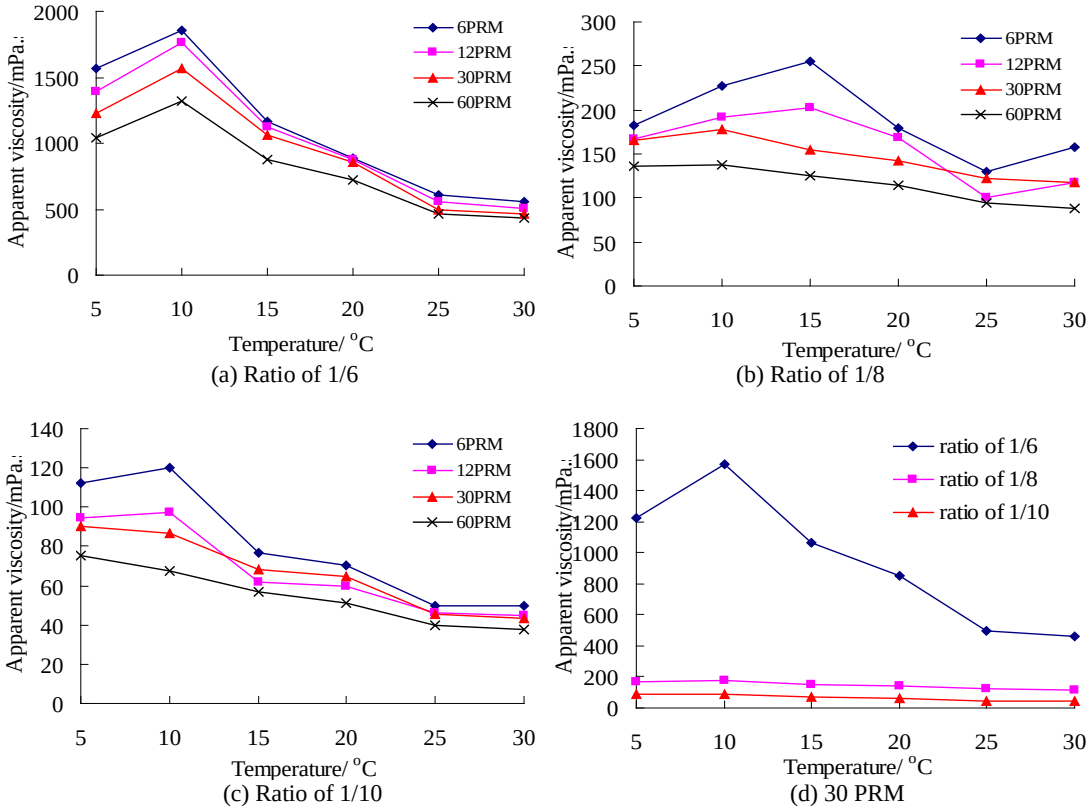

Fig. 1: Effect of temperature on apparent viscosity of cornstarch adhesives

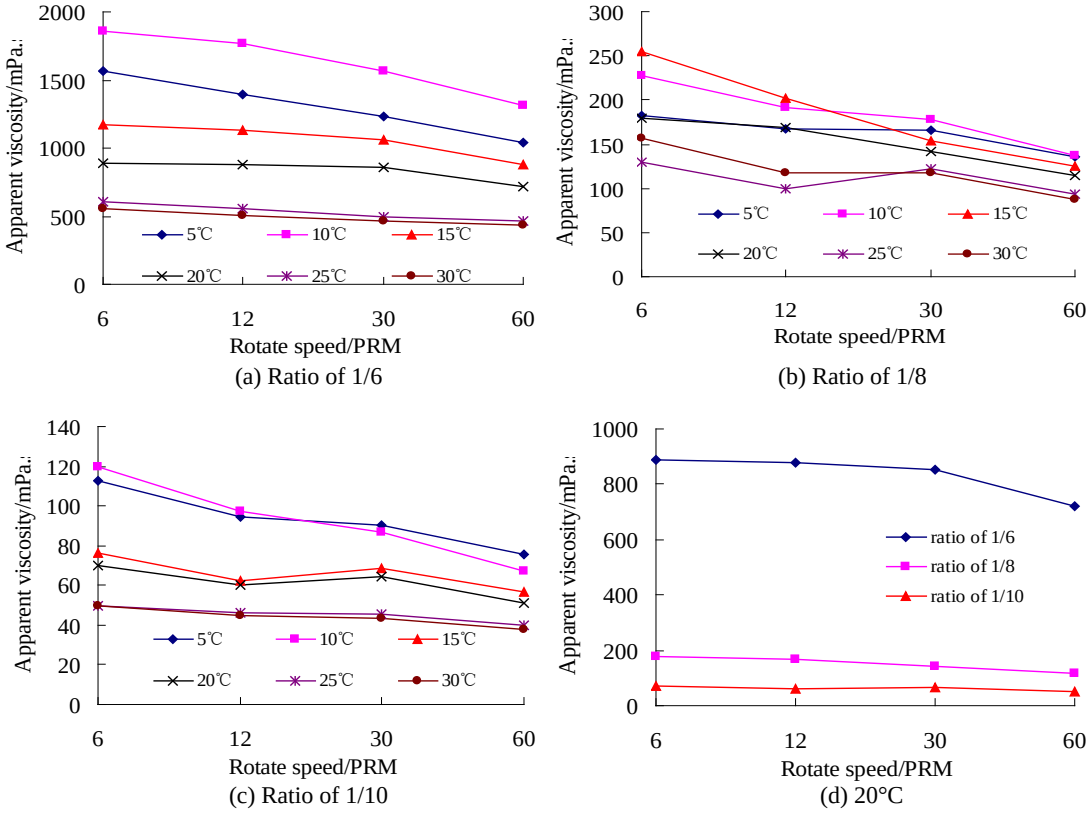

Fig. 2: Effect of rotate speed on apparent viscosity of cornstarch adhesives

Table 3: Rheological eigenvalue of cornstarch adhesives (ratio of 1/6)

Temperature/°C	k/Pa.s^n	n	Expression	R^2
5	2136.60	-0.1709	$\eta = 2136.6v^{-0.1709}$	0.9878
10	2484.20	-0.1466	$\eta = 2484.2v^{-0.1466}$	0.9459
15	1474.80	-0.1145	$\eta = 1474.8v^{-0.1145}$	0.8568
20	1058.60	-0.0821	$\eta = 1058.6v^{-0.0821}$	0.7886
25	750.62	-0.1185	$\eta = 750.62v^{-0.1185}$	0.9960
30	665.63	-0.1067	$\eta = 665.63v^{-0.1067}$	0.9978

Table 4: Rheological eigenvalue of cornstarch adhesives (ratio of 1/8)

Temperature/°C	k/Pa.s^n	n	Expression	R^2
5	225.94	-0.1134	$\eta = 225.94v^{-0.1134}$	0.8289
10	325.82	-0.2001	$\eta = 325.82v^{-0.2001}$	0.9341
15	437.99	-0.3062	$\eta = 437.99v^{-0.3062}$	0.9994
20	263.83	-0.1940	$\eta = 263.83v^{-0.194}$	0.9585
25	172.93	-0.1518	$\eta = 172.93v^{-0.1518}$	0.9677
30	223.56	-0.2182	$\eta = 949.03v^{-0.2182}$	0.8633

Table 5: Rheological eigenvalue of cornstarch adhesives (ratio of 1/10)

Temperature/°C	k/Pa.s^n	n	Expression	R^2
5	146.100	-0.1560	$\eta = 146.1v^{-0.156}$	0.9284
10	180.790	-0.2336	$\eta = 180.79v^{-0.2336}$	0.9679
15	86.875	-0.0954	$\eta = 86.875v^{-0.0954}$	0.5776
20	83.763	-0.1079	$\eta = 83.763v^{-0.1079}$	0.6578
25	58.139	-0.0853	$\eta = 58.139v^{-0.0853}$	0.8770
30	60.338	-0.1080	$\eta = 60.338v^{-0.108}$	0.9306

As can be seen from Fig. 1 and 2, with many strongly hydrophilic functional hydroxyl groups in the main chain of the starch molecules, the hydroxyl groups bonded to each other to form hydrogen bonds, so that the starch adhesive would have a certain adhesion force, however, the cohesion of the hydroxyl group with water molecules is much larger than the binding force among the starch molecules, the absorption of hydroxyl on glued materials was desorbed by water molecules, as a result, the wet bonding strength of the starch adhesive degraded severely and the effect of temperature on adhesives was greater than the two precious.

The value of k, n and the correlation coefficient R^2 of adhesives were obtained by using one unknown nonlinear regression to analyze the apparent viscosity and shear rate. Table 3, 4 and 5 show the rheological eigenvalue of cornstarch adhesives apparent viscosity with the ratio of 1/6, 1/8 and 1/10, respectively.

As is depicted in Table 3, 4 and 5, cornstarch adhesives prepared in this test were pseudo-plastic fluids because all of the n were less than zero. When the rheological curve of cornstarch adhesives was described by the pseudo-plastic fluid model, the model could better describe the rheological properties of cornstarch adhesives curve if R^2 was between 0.5776 and 1.000.

CONCLUSION

- Cornstarch adhesives apparent viscosity increased and then decreased with the increase of the temperature and the maximum value is obtained at 10°C.
- The apparent viscosity decreases slowly with the increase of the rotor speed and the phenomenon of shear thinning appears in corn starch adhesives.
- Cornstarch adhesives are pseudo-plastic fluids.

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