Study on the Torque Rheological Behavior of Wood Flour/Chitosan/Polyvinyl Chloride Composites

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Torque rheological properties of wood flour/chitosan/PVC (WF/CS/PVC) compounds were measured by a torque rheometer using roller-style rotating blades at various setting temperatures (175 and 185 °C) and rotation speeds (30, 45, 60, and 75 rpm). The torque rheological parameters were calculated based on the Marquez model and Arrhenius equation. The torque rheological curves of WF/CS/PVC composites were similar to WF/PVC composites without chitosan. The classical Marquez model was verified to be suitable for both WF/PVC and WF/CS/PVC composites. Specifically, the activation energy (ΔE), n value, and range of $C(n)m$ for the former and latter were 27.698 $kJ \cdot mol^{-1}$ and 29.237 $kJ \cdot mol^{-1}$, 0.382 and 0.381, and 4.415 to 5.749 $N \cdot m \cdot s^n$ and 4.652 to 6.079 $N \cdot m \cdot s^n$, respectively. The rheological properties of WF/CS/PVC composites did not show a great qualitative enhancement compared to WF/PVC composites.

Keywords: Chitosan; Wood flour; PVC; Torque rheological behavior

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INTRODUCTION

Wood plastic composites (WPC) are a subset of natural fiber plastic composites (NFPCs) that combine cellulose-based fibers (wood, bamboo, kenaf, hemp, and sisal) of high strength and elasticity with thermoplastic resin (polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC)). The fibers exhibit excellent flexibility and fatigue durability (Segerholm *et al*. 2012; Kaewkuk *et al*. 2013; Petchwattana and Covavisaruch 2013; Cavdar *et al*. 2014; Li *et al*. 2014; Ren *et al*. 2015), which provide unique properties that include outstanding dimensional stability, water resistance, biological durability, and recyclability (Rangaraj and Smith 2000; Stark 2001). Currently, WPC are enthusiastically used in outdoor decking and landscaping, and in the near future, they are also expected to be used in a number of applications such as outdoor decoration, furniture, sports ground equipment, railing, and in the automobile industry (Clemons 2002; Geng and Laborie 2010; Crookston *et al*. 2011). Certainly there are also some deficiencies like excessive shrinkage, creep, fading, slipperiness for WPC.

Currently, there are three main heat-processing methods for WPC manufacture: extruder, injection, and hot compression (Matuana and Kim 2007). The most common method of production is to extrude the WPC into the desired shape. For the process of extrusion, temperature, processing time, and screw rotational speed are undoubtedly the most significant factors that control the appearance quality and the development of the physico-mechanical properties (density, strength, and water absorption) of WPC (Pilarski and Matuana 2005).

Generally, it is more difficult for WPC to be extruded, as opposed to pure plastic, because of the different properties of the wood flour and thermoplastic resin. Poor process selection conditions can lead to a large amount of generated waste, resulting in low plant productivity. There have been a number of published manuscripts on the factors that cause the rheological properties to improve regarding the processing quality of WPC (Li and Wolcott 2005; Hristov *et al*. 2006; Mohanty and Nayak 2007; Huang and Zhang 2009).

The natural amine in chitosan (CS) serves a similar function as the chemical coupling agents with amino-groups to strengthen the interfacial adhesion between PVC and wood flour. In our previous study, CS was introduced to PVC-based WPC, which led to the effective promotion of interfacial bonding as well as the antibacterial ability of the sample surface at the optimum amount (Xu *et al*. 2014a). Meanwhile, the effects on the basic rheological properties of WF/CS/PVC, at different CS contents and particle size levels, were investigated under specific conditions (Xu *et al*. 2014b).

Research on both the rheological parameters and behavior of WF/CS/PVC composites has not been reported. There has been a need to investigate the rheological characteristics of WF/CS/PVC composites to help provide solid theoretical guidance for producing high-quality and high-value added WPC in the future. Therefore, in this study, three main ingredients (WF, CS, and PVC) were combined with additives. Mixing and the torque rheological properties of the compounds were measured using a torque rheometer with roller-style rotating blades at various setting temperatures (175 and 185 °C) and rotation speeds (30, 45, 60, and 75 rpm). The torque rheological parameters were also calculated based on the Marquez model and Arrhenius equation.

EXPERIMENTAL

Materials

Polyvinyl chloride (PVC) (DG-800) was supplied by Tianjin Dagu Chemical Ltd. Co. (China). This PVC has an average degree of polymerization and density of 800 and 1.35 $g \cdot cm^{-3}$, respectively. Wood flour (*Cunninghamia lanceolata*), with particle sizes ranging from 150 to 180 μm, was obtained from Guangzhou Minshan New Material Ltd. Co. (China). Flakes of chitosan (with a degree of deacetylation and an average molecular mass of 95% and 820,000, respectively) were purchased from Golden-Shell Biochemical Ltd. Co. (China). To complete the formulation, other additives, including heat stabilizers, processing aids, and lubricants, were purchased from local chemical companies.

Methods

Pretreatment of samples

The samples were subjected to the same pretreatment method used in our previous study (Xu *et al*. 2014b). Chitosan flakes were shred and sieved to particle sizes of 180 to 220-mesh. Subsequently, 2 wt.% acetic acid was used as a solution to dissolve chitosan, with mechanical stirring at 40 °C for 20 min. The solution was cooled and stored in a container for later use.

Prior to mixing with thermoplastic resin (PVC), WF was dried at 105±2 °C for 72 h in an oven. The WF and PVC were mixed in a high speed mixer (SHR-10A, Zhangjiagang, China) at 1600 rpm, with a temperature of 80 °C for 5 min. Other additives, including heat stabilizer, lubricant, and processing aids, were added and mixed for 10 min at a temperature of 110 °C. The diluted CS solution was sprayed onto the compounds to blend for 10 min. The proportions of all ingredients are listed in Table 1.

Table 1. Formulations of the WF/CS/PVC Composites

Ingredient	PVC	Wood flour	Chitosan	Calcium-zinc Heat stabilizer	Processing aid compounds	Lubricants
Proportion (phr)	100	40	30	5	6	0.8

Torque rheological properties measurement

The torque rheological properties were measured with a torque rheometer (PLF-651, Thermo Fisher Scientific Co., USA) with roller-style rotating blades. The rheological curve tests were carried out at various temperature and rotation speed conditions, as listed in Table 2. The weight of the compounds for each group was set at 65 g.

Table 2. Various Conditions for Torque Rheological Testing

Temperature (°C)	175	175	175	175	185	185	185	185
Rotation speed (rpm)	30	45	60	75	30	45	60	75

Torque rheological parameters calculation

The calculation of the torque rheological parameters is based on the assumption that the torque-rheometer measuring head can be represented by two adjacent coaxial-cylinder viscometers. The rollers simulate uniform cylinders. The formula that was deduced by Marquez was used as Eq. 1 (Marquez *et al*. 1996),

$$M = C(n) m S^{n} \tag{1}$$

where M is the torque value from torque rheometer (N·m), m is the viscosity coefficient (Pa·s^{n}), S is the rotor speed (rad·s^{-1}), and n is the flow index.

In Eq. 1, $C(n)$ can be derived using Eq. 2,

$$C(n) = 2\pi L R_0^2 \left[\frac{2}{n(\alpha^{-2/n} - 1)} \right]^{n} (1 + b^{n+1}) \tag{2}$$

where L is the chamber length (m), R_0 is the chamber radius (m), b is the ratio of the two rollers; and α is the ratio of R_e and R_0 (R_0 is the external radius, and R_e is an equivalent inner radius, defined as the radius of the inner cylinder that produces the same torque as the roller).

In addition, Arrhenius'equation was used as Eq. 3 for the calculation of the viscosity coefficient (m),

$$m = \mathrm{k}\exp(\Delta E/\mathrm{R}T) \tag{3}$$

where k is the pre-exponential factor (constant), T is Kelvin temperature, K; ΔE is the activation energy, J; and R is the universal gas constant, 8.314 J·mol^{-1}.

The Marquez model (Marquez *et al*. 1996) was used as Eq. 4, based on the Arrhenius equation:

$$M = C(n)mS^n = C(n)k\exp(\Delta E/\mathrm{R}T)S^n \tag{4}$$

Both sides of the equation were taken as a logarithm, resulting in Eq. 5 (Cheng *et al*. 1999).

$$\ln M = \ln(C(n)k) + \Delta E/\mathrm{R}T + n\ln S \tag{5}$$

The equilibrium temperature data, torque at different temperature intervals, and rotation speed were fitted using Eq. 5. The activation energy (ΔE), flow index (n), and $C(n)k$ were calculated *via* multiple regression analysis using SPSS software of version 17.0 (IBM, USA). Then, α and $C(n)$ were further calculated using Eq. 2.

RESULTS AND DISCUSSION

Torque Rheological Properties Analysis

Figure 1 and Table 3 show the torque rheological curves and specific numerical values of WF/PVC composites without chitosan, at various temperature settings and rotation speeds. Two peaks can be clearly observed in Fig. 1. These peaks represent the sample loading and state transition of the compounds from particle to fusion flow, respectively. Fusion time can be defined as the interval between the two peaks. Figure 1 illustrates that the fusion time decreases with increasing rotation speed when the temperature is constant. The fusion time also decreased as the temperature increased at constant rotation speed.

As can be seen in Table 3, it was found that the equilibrium temperature and torque were increased, respectively, from 186.7 to 196.6 °C and from 8.9 Nm to 11.5 Nm with the rotation speed increasing from 30 to 75 rpm, at a constant temperature of 175 °C. Equilibrium temperature increased as the equilibrium torque was reduced when the temperature was elevated from 175 to 185 °C, with a constant rotation speed.

Table 3. Equilibrium Torque and Temperature of WF/PVC without CS under Various Conditions

Setting temperature (°C)	Rotation speed (rpm)	Equilibrium temperature (°C)	Equilibrium torque (Nm)
175	30	186.7	8.9
175	45	190.2	10.2
175	60	193.6	10.8
175	75	196.6	11.5
185	30	196.4	8.2
185	45	199.7	8.7
185	60	202.2	9.3
185	75	205.0	9.7

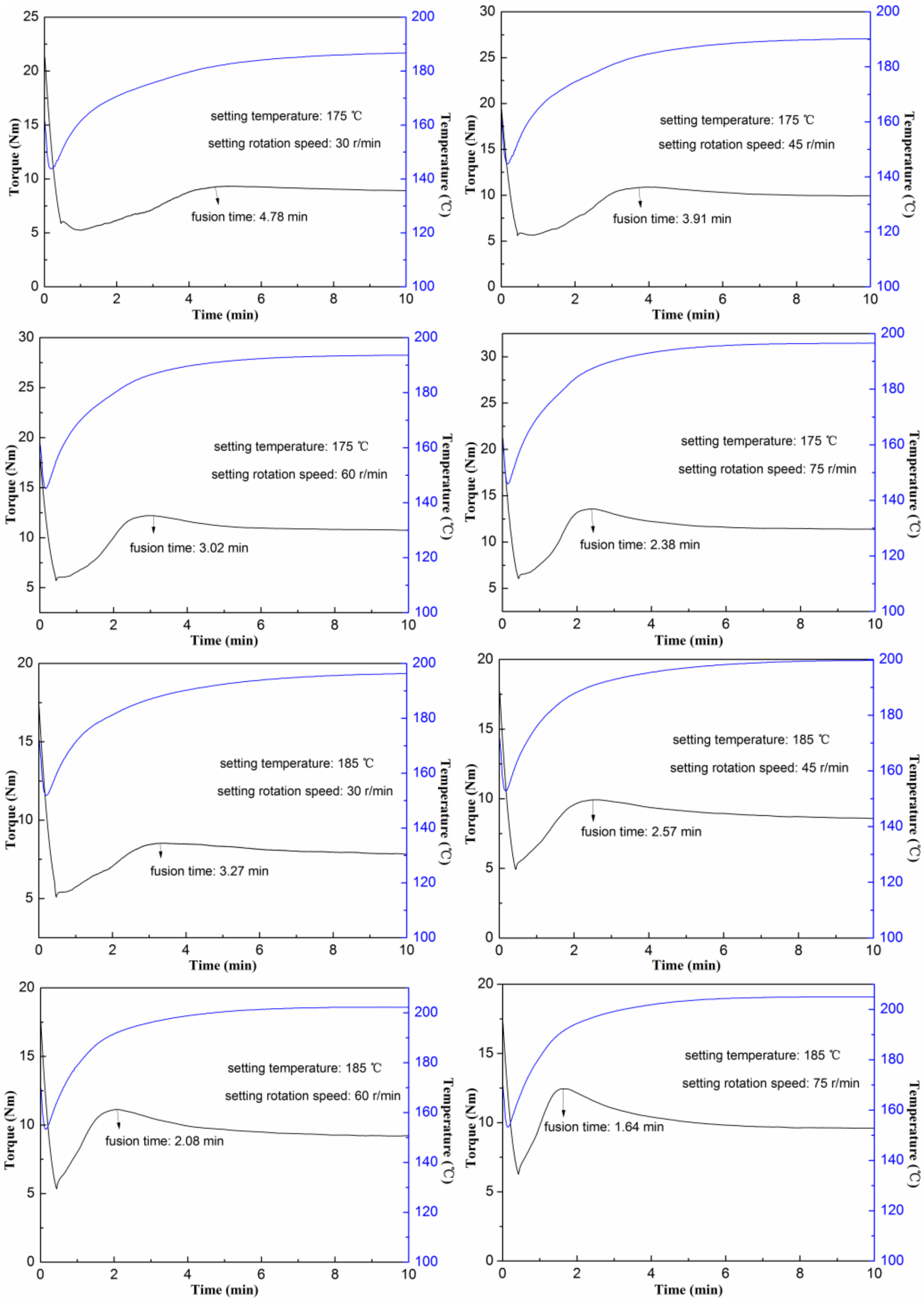

Fig. 1. Torque rheological curves of WF/PVC, without chitosan, under various conditions

Figure 2 and Table 4 show the torque rheological curves and specific values of the WF/CS/PVC composites. The variation trends of WF/CS/PVC composites were similar to that of WF/PVC composites without chitosan. However, compared to WF/PVC, WF/CS/PVC had almost the same fusion time, but higher equilibrium temperature and torque at the same temperature settings and rotation speeds. This was because chitosan has a higher heat capacity than PVC grains (Matuana and Kim 2007). The addition of chitosan proved to be extremely effective in creating interfacial bonds to molecular chains of PVC and wood flour particles.

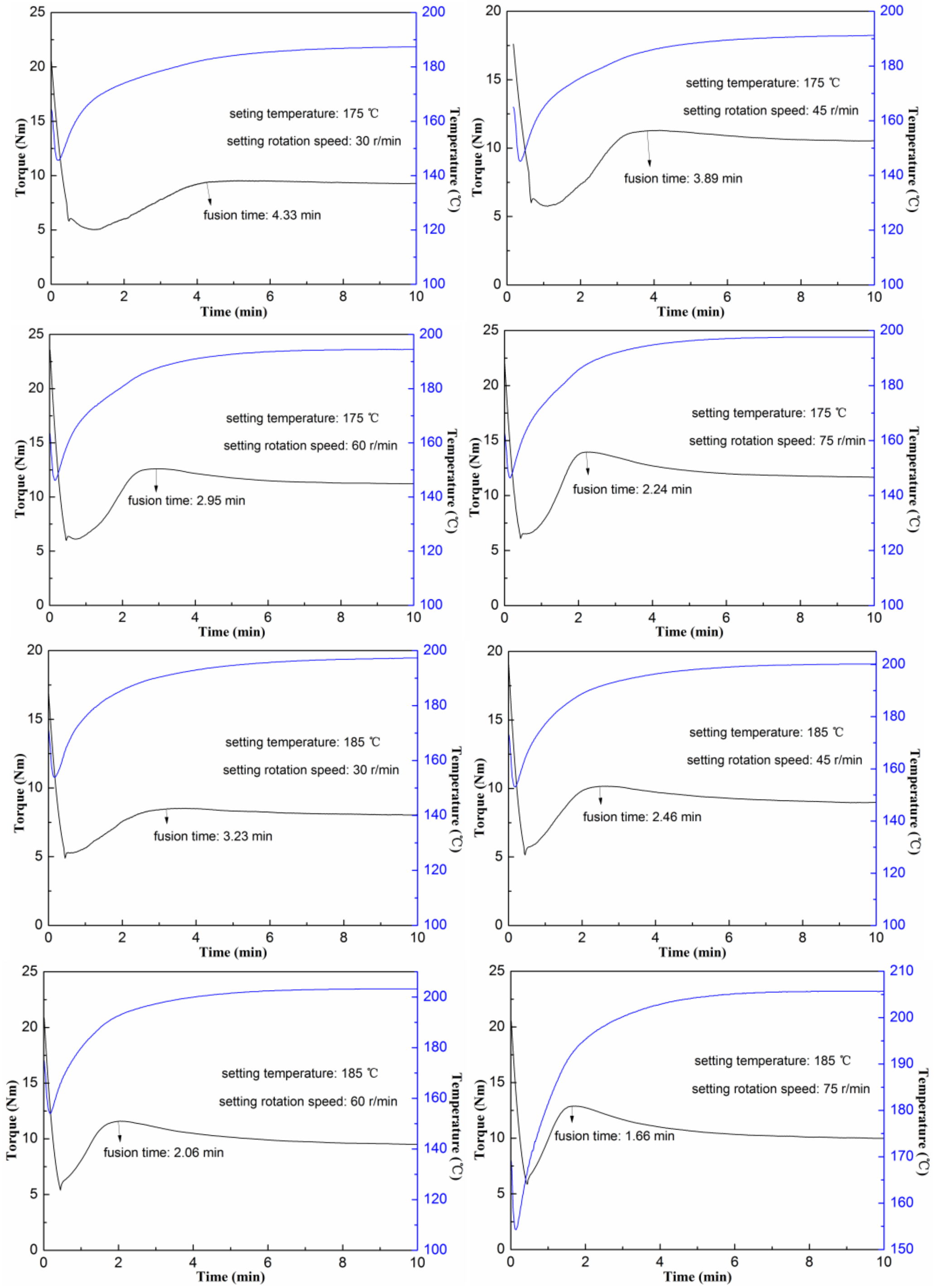

Fig. 2. Torque rheological curves of WF/CS/PVC under various conditions

Table 4. Equilibrium Torque and Temperature of WF/CS/PVC under Various Conditions

Setting temperature (°C)	Rotation speed (rpm)	Equilibrium temperature (°C)	Equilibrium torque (Nm)
175	30	187.4	9.4
175	45	191.2	10.8
175	60	194.5	11.3
175	75	197.6	11.8
185	30	197.3	8.5
185	45	200.3	9.1
185	60	203.2	9.6
185	75	205.7	10.2

Torque Rheological Parameters Analysis

Equation 5, describing the relationships among equilibrium torque (*M*), equilibrium temperature (*T*), and rotation speed (*S*), was transformed to a multivariate linear equation,

$$y = a_1 x_1 + a_2 x_2 + b \tag{6}$$

where $y = \ln M$, $a_1 = \Delta E/\mathrm{R}$, $x_1 = 1/T$, $a_2 = n$, $x_2 = \ln S$, and $b = \ln(C(n)k)$.

The equilibrium torque and equilibrium temperature data in Table 3 for WF/PVC composites were treated by the multiple linear regression method, and the results are shown in Tables 5 and 6. There were high significance levels for the regression equation and regression coefficient, which indicated that there was a high fitting degree for the equation. This suggests that the WF/PVC composites are suitable for the Marquez formula.

Activation energy (*ΔE*) is defined as the minimum input energy required for polymer chains to overcome molecular binding and move to an adjacent position. Generally, the activation energy increases as the rigidity of molecular chains and intermolecular forces increase.

There is an important formula, called the power-law equation, which depicts the rheological behavior of fluid material. The formula is depicted below as Eq. 7,

$$\tau = K\gamma^n \tag{7}$$

where τ is shear stress (Pa), K is fluid viscosity (Pa·s), γ is shear rate (s^{-1}), and n is the non-Newtonian index. The non-Newtonian index (n) is the extent to which the flow properties of a fluid differ from those of Newtonian fluids. The fluid is pseudoplastic fluid when $n<1$; conversely, $n>1$ represents a dilatant fluid.

The known torque rheometry parameters (dictated by the instrument type) were as follows: L was 0.048 m, R_e was 0.0186 m, R_0 was 0.0196 m, α was 0.949, and b was 1.5. The activation energy (*ΔE*) and n of WF/PVC were 27.698 kJ·mol^{-1} and 0.382, respectively, according to Table 6. Additionally, the specific values for m and $C(n)m$ are given in Table 7.

Previous researchers demonstrated that pseudoplastic fluid was at the middle level when n fell within the range $0.35<n<0.70$, and $C(n)m$ was in the range of 2 to 7 N·m·s^n (Mallette and Soberanis 1998). The n value and $C(n)m$ for fusion fluid of WF/PVC compounds was 0.382 and in the range of 4.415 to 5.749 N·m·s^n, which clearly indicated that the fluid type was pseudoplastic and the pseudoplastic level was at the middle. Fluid viscosity was kept constant at the low shear rate, but fluid viscosity decreased as the shear rate increased, in accordance with the power-law equation, resulting in a shear thinning action.

Table 5. Regression Equation Results for WF/PVC

Model	Sum of squares	df	Mean square	F	Significance
Regression	0.088	2	0.044	57.935	0.000[a]
Residual	0.004	5	0.001		
Total	0.092	7			

a. predictors: constant, x_2, x_1

Table 6. Regression Coefficient Results for WF/PVC

Model	Coefficient	t	Significance
Intercept	-5.464	-5.257	0.003
x_1	3331.504	7.075	0.001
x_2	0.382	10.737	0.000

Intercept was the value of $\ln(C(n)k)$, x_1 represented $\Delta E/\mathrm{R}$, x_2 represented n

Table 7. Fluid Parameters of WF/PVC under Various Conditions

Rotation speed (rpm)	Equilibrium temperature (°C)	m (kPa·s^n)	$C(n)m$ (N·m·s^n)
30	186.7	6.168	5.749
45	190.2	6.054	5.643
60	193.6	5.744	5.353
75	196.6	5.616	5.234
30	196.4	5.683	5.296
45	199.7	5.164	4.813
60	202.2	4.946	4.610
75	205.0	4.737	4.415

The equilibrium torque and temperature data in Table 4 for WF/CS/PVC composites were calculated using multiple linear regression, and the results are shown in Tables 8 and 9. The equation showed a high fitting degree, according to the regression results and regression coefficients for WF/CS/PVC. These good fitting results suggest that the Marquez formula could be used for WF/CS/PVC compounds. Meanwhile, ΔE and n values were obtained using the data in Tables 8 and 9, and the results were 29.237 kJ·mol^{-1} and 0.381, respectively. Compared to WF/PVC composites without chitosan, ΔE was increased by 1.539 kJ·mol^{-1}, but n was decreased by 0.001. This implied that the compounds needed more energy to undergo fusion after adding chitosan with a higher heat capacity, which was consistent with our previous conclusion.

On the other hand, although the range of $C(n)m$ was expanded to 4.652 to 6.079 N·m·s^n (in Table 10), the fluid type was still pseudoplastic at the middle level. It was concluded that the addition of chitosan would not lead to a qualitative enhancement of the torque rheological properties of WF/PVC composites.

Table 8. Regression Equation Results for WF/CS/PVC

Model	Sum of squares	df	Mean square	F	Significance
Regression	0.087	2	0.043	77.008	0.000[a]
Residual	0.003	5	0.001		
Total	0.089	7			

a. predictors: constant, x_2, x_1

Table 9. Regression Coefficient Results for WF/CS/PVC

Model	Coefficient	t	Significance
Intercept	-5.800	-6.399	0.001
x_1	3516.598	8.551	0.000
x_2	0.381	12.342	0.000

Intercept was the value of $\ln(C(n)k)$, x_1 represented $\Delta E/R$, x_2 represented n

Table 10. Fluid Parameters of WF/CS/PVC Composites under Various Conditions

Rotation speed ($r \cdot min^{-1}$)	Equilibrium temperature (°C)	m ($kPa \cdot s^n$)	$C(n)m$ ($N \cdot m \cdot s^n$)
30	187.4	6.536	6.079
45	191.2	6.435	5.984
60	194.5	6.034	5.611
75	197.6	5.787	5.382
30	197.3	5.910	5.497
45	200.3	5.422	5.042
60	203.2	5.126	4.767
75	205.7	5.002	4.652

CONCLUSIONS

1. The torque rheological curves for WF/CS/PVC composites were similar to those of WF/PVC composites. Compared to WF/PVC composites without chitosan, WF/CS/PVC showed an early identical fusion time, but higher equilibrium temperature and torque at a constant temperature and rotation speed.
2. The classical Marquez model was verified to be suitable for both WF/PVC and WF/CS/PVC composites. The activation energy (ΔE), n value, and the range of $C(n)m$, for the former and the latter were 27.698 $kJ \cdot mol^{-1}$ and 29.237 $kJ \cdot mol^{-1}$; 0.382 and 0.381; and 4.415 to 5.749 $N \cdot m \cdot s^n$ and 4.652 to 6.079 $N \cdot m \cdot s^n$, respectively. This indicates that the compounds need more energy for fusion to take place after adding chitosan. Although the range of $C(n)m$ was increased, the fluid type was still pseudoplastic at the middle level. The rheological properties of the WF/CS/PVC composites did not show great qualitative enhancement compared to WF/PVC composites. This implied that the process technology of WF/CS/PVC in practical production could be controlled as the same with WF/PVC except for a relatively higher temperature.

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