Non-isothermal Crystallization Behavior of Rice Husk Powder/HDPE Composites

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Abstract — Application of wood plastic composites (WPC) has been increased in recent years because of their good processability, mechanical properties and environmental-friendly features. We prepared the rice husk powder/ high-density polyethylene (HDPE) by extrusion-molding. Using Differential Scanning Calorimeter (DSC), we analyzed the non-isothermal crystallization behavior of the composites. With cooling rate increasing in the DSC experiments, crystallization time decreased, whilst crystallization enthalpy and relative crystallinity increased. The results show that rice husk powder exhibits the role of heterogeneous nucleation in the composites. Rice husk powder promots crystallization behavior of the composites. The DSC data show a better linear relationship that is analyzed successfully by the Mo Zhishen method. The rice husk powder increases the crystallization rate of composites at the same crystallinity.

Keywords - Rice husk powder; Composites; Non-isothermal crystallization; Mo Zhishen method

I. INTRODUCTION

WPC is a kind of composite with dual advantages of wood and plastic. WPC has been rapidly developed not only because of its excellent quality, but also because of its environmentally friendly features[1]. WPC has been widely used in different fields such as construction, decoration, furniture, gardens, transportation, packing, cars, traffic, sports and other industries[2]. Physical and mechanical properties of the composites is affected by many factors, especially incompatibility of wood powder and plastic, processing temperature, strength of wood particles, wood-polymer adhesion, and type of wood powders[3-5]. These factors limit its application in the fields of construction and engineering materials. The emphasis of studying WPC composites has been placed on mechanical properties, water absorption, and rheological properties in recent years. An important influencing factor for the physical and mechanical properties of WPC is crystallization behavior of semi-crystalline polymers[6]. Research on the crystallization behavior of WPC is very necessary because The addition of biomass has a significant effect on the crystallization behavior of the polymer. In this paper the WPC is made of husk powder and HDPE. The non-isothermal crystallization of composites is carried out by differential scanning calorimeter[7,8] and experimental data is analyzed using Mo's equation[9]. The results of crystallization process of the rice husk powder/HDPE composites provided a theoretical basis for the use of rice husk powder as the main filler in WPC.

II. EXPERIMENTAL

A. Experimental Materials

High density polyethylene (HDPE), DMDY 1158 (MFI = 1.4~2.8g/10 min), was purchased from China's Qilu Petrochemical Co., Ltd. The rice husk powder was pulverized in the laboratory from rice husk collected from local farm in Zibo. The average size of rice husk powder used in the experiment was in the range of 40-60 mesh. Rice husk powder was dried at 105 ℃ for 24 h to moisture content less than 2% and then stored in sealed containers. Polyethylene wax and Maleated polyethylene(MAPE) was purchased from Nanjing Deba Chemical Co. Ltd (NDC), Polyethylene wax was used as lubricant and MAPE was used as a compatibilizer. other additives were bought from the market. The size distribution of rice husk powder was determined using an automatic vibratory sieve shaker (Vibrating Screen Plant of Zhejiang). The photo of the rice husk powder is shown in Fig.(1).

B. Preparation of The Samples

The mixture of rice husk powder, HDPE, Polyethylene wax and MAPE was mixed in a high speed mixer for 8 min before dynamically vulcanized composites were prepared using an internal mixer with counter rotating roller rotors[10]. The speed of the internal mixer was set up at 40 rpm and the temperature was set up at 170 ℃. 10 min later, the composites were quickly taken out of the internal mixer and placed in the plate vulcanizing machine. The temperature of plate vulcanizing machine mold was set up at 170 ℃ and the plate vulcanizing machine pressure was set up at 10 MPa. The composites

were hot-pressed for 10 min at 170 ℃ and cold-pressed for 3 min at room temperature. Table I shows the composition of all systems.

Fig.1 The Rice Husk Powder

TABLE I. COMPOSITION OF HDPE AND WOOD PLASTIC COMPOSITES

Designation	Rice husk powder	HDPE	Polyethylene wax	MAPE
HDPE	0	100	2	4
MS28	20	80	2	4
MS46	40	60	2	4

C. DSC Measurements

The non-isothermal crystallization of the composites were investigated with a differential scanning calorimeter analyzer[11](DSC- Q100, TA Instrument, USA) . All samples (5-10 mg) were rapidly heated to 180 ℃ at a rate of 120 ℃/min and conserved 2 minutes to eliminate mechanical and thermal prehistory, and then cooled to room temperature at rates of 10, 15, 20, 25 ℃/min respectively. All the DSC experiments were carried out under pure nitrogen.

III. RESULTS AND DISCUSSION

A. Crystallization Behavior

Fig.(2).- Fig.(4). showed the DSC curve of non-isothermal crystallization for all samples at different heating rates. Fig.(5). showed the DSC curve of non-isothermal crystallization for all samples at 10 ℃/min. The crystallization curves of heat flow were recorded as a function of temperature to analyze the non-isothermal crystallization behavior of HDPE and its composites. It can be seen that every crystallization curve appeared crystallization peak under different cooling rates.

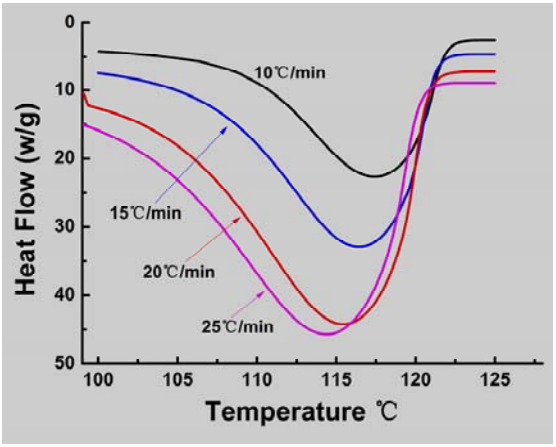


Fig.2 DSC Curve of Non-isothermal Crystallization for the Sample of HDPE at Different Heating Rates

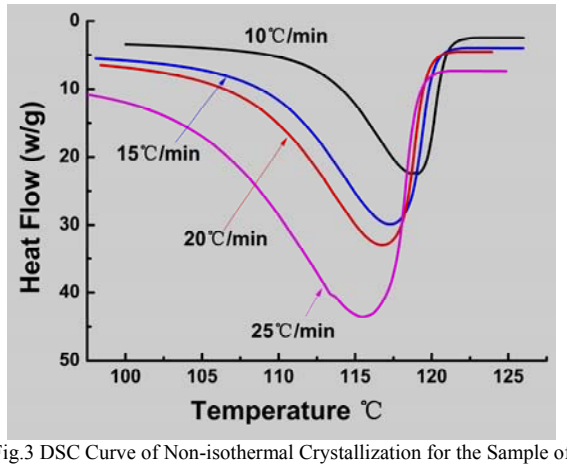
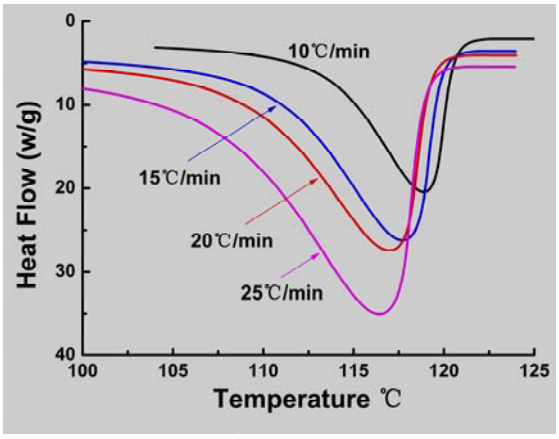


Fig.3 DSC Curve of Non-isothermal Crystallization for the Sample of MS28 at Different Heating Rates



(c) MS46

Fig.4 DSC Curve of Non-isothermal Crystallization for the Sample of MS46 at Different Heating Rates

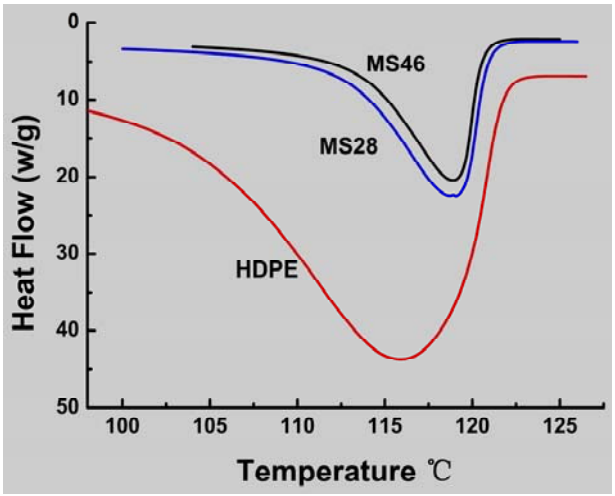


Fig.5 DSC Curve of Non-isothermal Crystallization for the Samples at 10℃/min Heating Rate

Table II lists the crystallization parameters at different cooling rate (D). There were the cooling peak temperature (T_p), the crystallization onset temperature (T_0), melt crystallization enthalpies (ΔH), relative crystallinity (X_c), total crystallization time(t). The X_c of the composites was estimated from the following E_q.

$$X_C = \frac{\Delta H}{\Delta H_0} \qquad \Delta H_0 = 293 \text{ J/g} \tag{1}$$

Cooling peak temperature T_p and crystallization onset temperature T_0 all reduced with cooling rate increasing. The increase of different cooling rate D also resulted in the crystallization peaks of rice husk powder/HDPE composites lower and wider. And as a result of this, increasing crystallization degree of super cooling reduced T_0 and T_p. Low temperatures limited the movement of molecular chain, so these problems leaded to the formation of imperfect crystals and a wider range of melting temperature. That was displayed in Fig.(2)- Fig.(4) with broadening of crystallization peak. Increasing D not only shorten total crystallization time t of composites, but also increased X_c and ΔH . Fig.(5) showed that T_0 and t decreased at the same D producing an increase in rice husk powder content. This indicated that the rice husk powder induced the formation of crystals as heterogeneous nucleation sites, thus promoting the crystallization rate and degree of crystallinity in the composites. The addition of rice husk powder promoted the formation of a branched chain, in turn, reduced the crystallization time. The branched chain also caused the crystallization temperature and melt crystallization enthalpies to decrease. The relative crystallinity at any time (X_t) can be calculated by the following formula[12,13]. T_∞ is the temperature at which the crystallization completes. T_0 is the temperature at which crystallization begins.

Total crystallization time (t) was evaluated from the crystallization temperature using the following E_q [12,13]:

$$t = \left| T_0 - T_t \right| / D \tag{2}$$

TABLE II. CRYSTALLIZATION PARAMETERS AT DIFFERENT COOLING RATES

Designation	D /□/min	T_p /□	T_0 /□	ΔH / J/g	X_c /%	t/s
HDPE	10	117.5	121.9	130.6	44.6	106
	15	116.5	121.3	136.1	46.5	80
	20	115.5	120.8	137.3	46.9	69
	25	114.5	120.3	147.6	50.4	66
MS28	10	119	120.9	107.8	36.8	96
	15	117.3	120.1	101.5	34.6	81
	20	116.7	119.6	102.5	35.0	60
	25	115.4	119	112.0	38.2	53
MS46	10	118.9	120.5	74.9	25.5	91
	15	117.7	119.8	76.5	26.1	64
	20	117	119.2	76.6	26.1	52
	25	116.4	118.8	80.5	27.5	46

$$X_t = \frac{X_C(t)}{X_C(t_\infty)} = \frac{\int_0^t \frac{dH(t)}{dt} dt}{\int_0^{t_\infty} \frac{dH(t)}{dt} dt} = \frac{\Delta H_t}{\Delta H_\infty} \tag{3}$$

Fig.(6).- Fig.(8). showed the X_c curve of the samples versus temperature. Fig.(9).- Fig.(11). showed the X_c curve of the samples versus times. The X_c of the samples was highly dependent upon the crystallization time, having an exponent relation with the time. This illustrated that the crystallization process of composites was concentrated. The molecular chain can easily obtained more energy at temperatures higher than 125 ℃, so that intense molecular activity caused the difficulty in composites crystallization. The crystallization phenomenon was found when the temperature dropped to 122℃, where the crystallization rate accelerated. The crystallization process occurred at a rate of 90% , or near 105 ℃. The crystallization rate of the composites and cooling rate was related. In the experiment, the faster cooling rate can increase the crystalline speed and shorten the crystallization time.

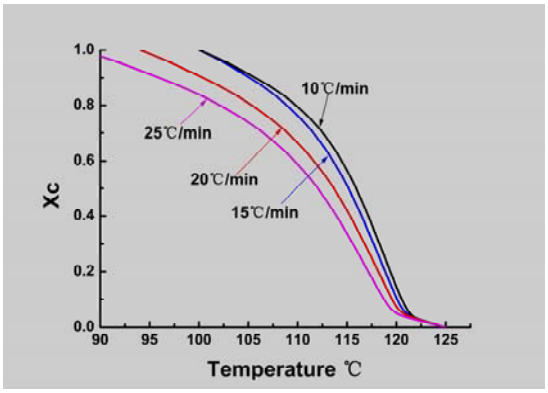


Fig.6 The Curve about X_c for the Sample of HDPE Versus Temperature

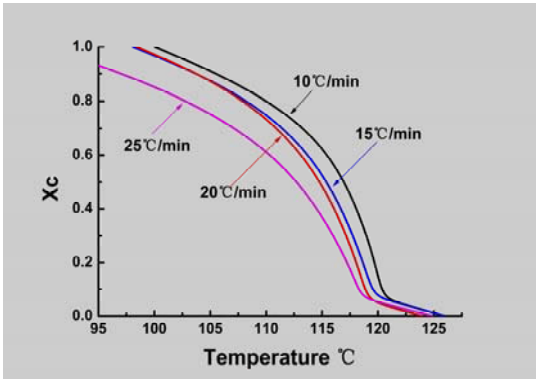


Fig.7 The Curve about X_c for the Sample of MS28 Versus Temperature

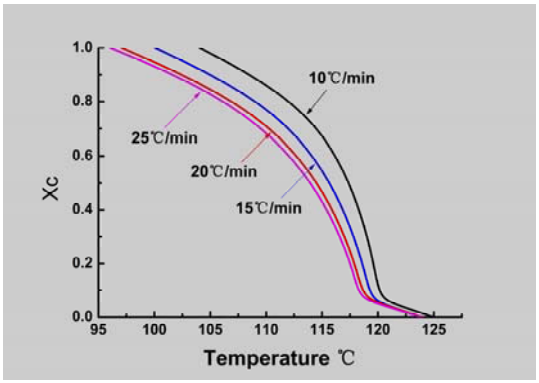


Fig.8 The Curve about X_c for the Sample of MS46 Versus Temperature

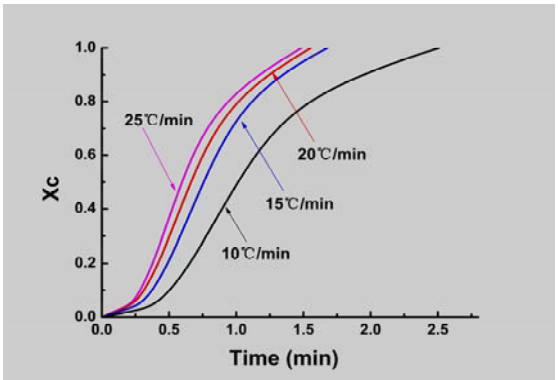


Fig.9 The Curve about X_c for the Sample of HDPE Versus Times.

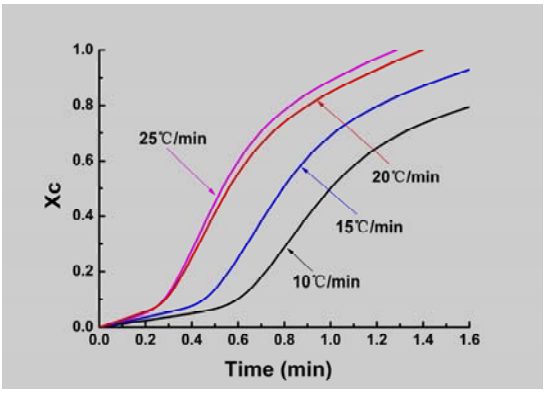
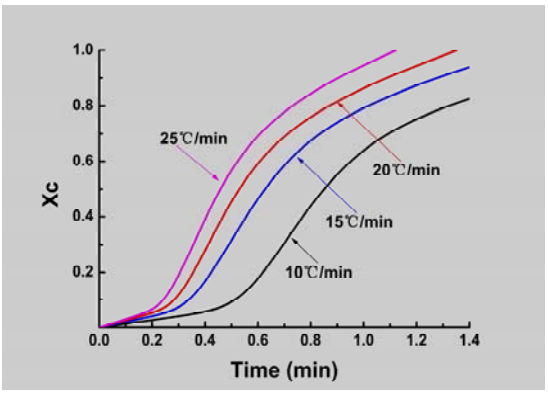


Fig.10 The Curve about X_c for the Sample of MS28 Versus Times.



(c) MS46

Fig.11 The Curve about X_c for the Sample of MS46 Versus Times.

B. Non-isothermal Crystallization Kinetics

Zhishen Mo proposed an equation in order to analyze the polymer non-isothermal crystallization kinetics problems[9]:

$$\ln D = \ln F(T) - a \ln t \qquad (4)$$

where $F(T)$ = chosen cooling rate per unit time in order to reach a certain degree of crystallinity; $a = n/m$, n = Avrami constant, m = Ozawa index.

Fig.(12)-Fig.(14). showed the curve of ln$D$～ln$t$ for all samples at a certain relative crystallinity. The curve showed a good linear relationship between ln$D$ and ln$t$ with the Mo ' s method in dealing with non-isothermal crystallization kinetics of rice husk powder/HDPE composite. The $F(T)$ and α can be extracted from intercept and slope of the simulating line of Fig.(12).- Fig. (14).

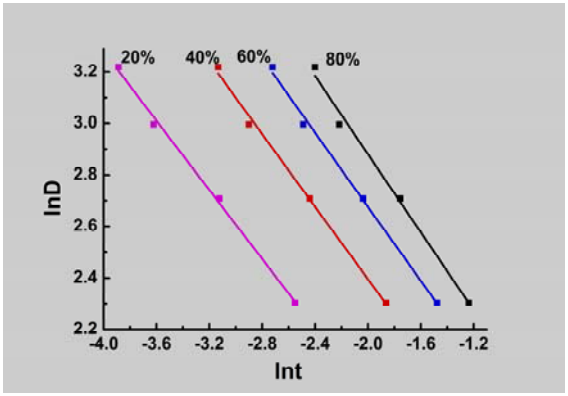


Fig.12 Plots the ln*D* Versus ln*t* for the Non-isothermal Crystallization for the Sample of HDPE

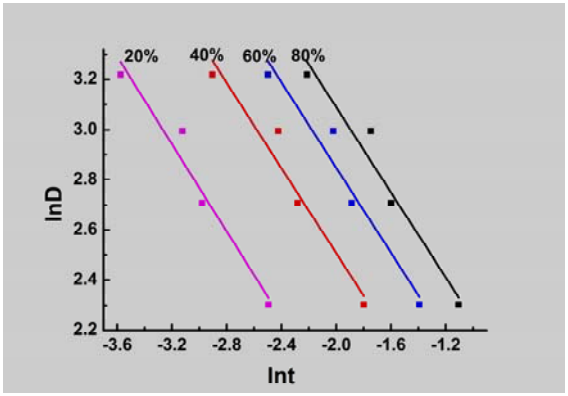


Fig.13 Plots the ln*D* Versus ln*t* for the Non-isothermal Crystallization for the Sample of MS28

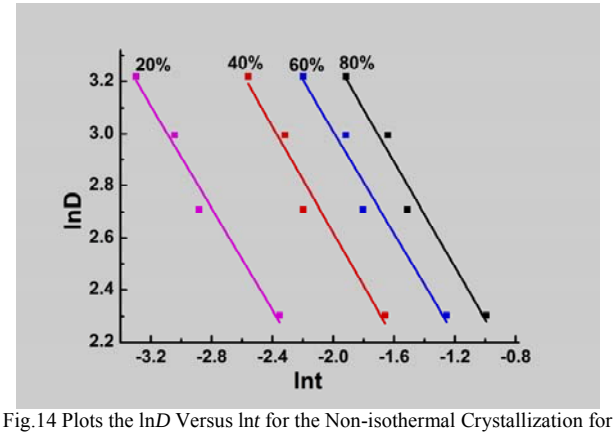


Fig.14 Plots the ln*D* Versus ln*t* for the Non-isothermal Crystallization for the Sample of MS46

These results were shown in table III. The *F(T)* increased with the crystallinity X_c increasing. The *F(T)* of MS28 is greater than MS46 but less than HDPE under the same crystallinity. MS28 required a lower cooling rate than MS46 to achieve the same degree of crystallinity, but a higher rate than that required by HDPE. With increasing rice husk powder content, the spacing among pulverized biomass particles in composite system gradually decreased. The decrease in spacing of pulverized biomass particles creates contact among them and produces obvious aggregation behavior. This kind of behavior produces a discernable effect on the melt crystallization of composites.

TABLE III. CRYSTALLIZATION PARAMETERS AT DIFFERENT COOLING RATES

Designation	HDPE				MS28				MS46			
X_c	20	40	60	80	20	40	60	80	20	40	60	80
F(T)	0.60	0.99	1.24	1.37	0.15	0.80	1.13	1.32	0.03	0.58	1.05	1.27
α	0.67	0.70	0.71	0.75	0.87	0.84	0.84	0.84	0.98	1.02	0.98	1.01

IV. CONCLUSIONS

Crystallization behavior is an important characteristic in the mechanical properties of wood plastic composites. The effects of crystallization condition on the non-isothermal crystallization behaviors for HDPE and its composites were comparatively investigated by DSC. The results showed that with cooling rates increasing, relative crystallinity increased so relatively rapid cooling rate is favorable for HDPE crystallization. The rice husk powder as a heterogeneous nucleation agent promoted crystallization of the composite. The more the contents of rice husk powder, the more influence on the crystallization of HDPE. The DSC data was analyzed successfully by the Mo Zhishen method and it revealed a good linear relationship. The preparation of wood plastic composites using rice husk powder is at least theoretically possible.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGMENT

This work is supported by Agricultural Science and Technology Transformation Fund of China. (Contract serial

number 2013GB2C600274).

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