# Mechanical Properties, Thermal, and Crystallization Behavior of Polypropylene Composites Reinforced by Starch and Wasted Cotton Cloth

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**ABSTRACT:** In this study, wasted cotton cloth was bonded with soluble starches as an adhesive, then dried, cut into fiber fragments and filled into polypropylene (PP) to achieve resource efficiency. The mechanical, thermal, and crystallization properties of the composites were characterized. The results indicated that with the addition of wasted cotton cloth treated without or with silane coupling agent (RC or TRC), PP composites' tensile strength, impact strength, and flexural strength have been improved. The heat distortion temperatures increased slowly, indicating that wasted cotton cloth filled into PP can be turned back into useful items without degradation of PP composites exhibited. Thus, it is a good avenue for the utilization of an otherwise wasted cotton cloth resource. The crystallization activation energy, nucleation constant, and folding surface free energy of PP were markedly reduced in PP/RC composites and its compatibilized composites. The value of F(T) gradually increased with the increasing relative degree of crystallinity. The addition of wasted cotton cloth could significantly reduce the spherulitic size of PP. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 562–570, 2012

**Key words:** blends; composites; crystallization; differential scanning calorimetry; mechanical properties

#### INTRODUCTION

Polypropylene (PP) has been widely used in everyday products, packaging materials, household appliances, automobile industry, building operations, and other industries due to its excellent performance.<sup>1-4</sup> Meanwhile, its consumption maintains strong economic growth momentum on a global basis. With the exhaustion of petroleum resources, PP industry using petroleum products as raw materials is faced with increasing cost pressures. The key to solving this problem is to use low-cost filler for PP. Woodplastic composite materials are drawing the attention of the researchers. The filling materials are mainly wood flour, bamboo powder, straw, chaff etc.<sup>5-10</sup> Alternatively, other cellulosic resources can be derived from cloth. With the continuous improvement in living standards in China (population > 1.3B), consumers peruse higher quality comfort from clothing. An issue with high consumerism and rapid fashion style changes is the increase in waste, currently in the order of several hundred thousand tones of wasted cloth generated each year. It is very difficult to recycle and reuse these clothes due to the diversity of clothing components and the large quantity of the abandoned clothes. Most of the wasted clothes are now being dumped in landfills or incinerated, which exerts great pressure on the ecological environment. Therefore, the recycling and resource utilization of wasted clothing is a pressing concern. If wasted clothing can be used as the filler of plastic matrix, it would be able to reduce costs as well as mitigate environmental pollution.

In this study, wasted clothing was filled into thermoplastics to achieve resource utilization. Since wasted cotton cloth is soft and light, it can't be mixed with PP in a twin-screw extruder when being mixed with PP pellets. Thus, a certain amount of soluble starch was dissolved into solution and served as the glue for wasted cotton cloth. Multilayer wasted cotton cloth was bonded with soluble starch solution, and then dried and cut into waste cotton sheets of a certain thickness, which can exhibit melt compounding with PP by the twin-screw extruder.

Starch and recycled cotton particle is a polar hydrophilic material while the PP is a hydrophobic material with nonpolar. The compatibility between them is poor<sup>11,12</sup> and therefore one needs to consider a means to improve this paring of starch and recovery cotton into PP. The performance of the bond

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The Composition of PP/RC Composites									
Component (wt %)	PP	PP-g-MA	Cotton cloth	KH-550	Sample	PP	PP-g-MA	Cotton cloth	KH-550
Sample									
PP	100	_	_		TRC2	93	5	2	Treated
RC2	93	5	2	Untreated	TRC5	90	5	5	Treated
RC5	90	5	5	Untreated	TRC10	85	5	10	Treated
RC10	85	5	10	Untreated	TRC15	80	5	15	Treated
RC15	80	5	15	Untreated					

TABLE I The Composition of PP/RC Composite

behavior determines the capacity of transferring the strain from the polymer matrix to the fiber, and further determines the strength of composite materials. The fiber was modified by adding additives to enhance the interfacial bonding strength. The addition of silane coupling agent was used as the important method of fiber surface modification through its chemical bonding with the surface of cellulose fiber. By using this method, the number of hydrophilic hydroxyl groups was reduced, and the organic functional groups were connected with the polymer to improve the compatibility and dispersion between fiber and plastics.<sup>13,14</sup> In addition, with the addition of compatibilizer maleic anhydride (MA) grafted PP (PP-g-MA), esterification reaction was conducted between the carboxyl of PP-g-MA and hydroxyl groups on the starch and wasted cotton particles, which is effective in improving the compatibility of fibers and plastics.<sup>15,16</sup> Silane coupling agent and PP-g-MA were used to improve the compatibility. Meanwhile, the mechanical properties, thermal stability and crystallization behavior were studied.

#### **EXPERIMENT**

#### Materials

A commercial grade isotactic PP (H030SG, MFR = g/10 min at 200°C) used in this study was supplied by Reliance Industries Limited. Soluble starch was obtained from Shanghai Richjoint Chemical Reagents Co. Wasted cotton cloth was obtained from the recycled clothing marked with 100% cotton in a salvage station of China. PP grafted with MA (PP-g-MA) was supplied by Guangzhou Lushan Chemical Materials Co. of China with MA grafting ratio of 1.0% and MFI of 15 g/10 min. Silane coupling agent (KH550) was obtained from Jiangsu Chenguang Coincident Dose Co..

#### Sample preparation

Soluble starch was dissolved into 30% concentration of the solution with hot water. Subsequently, the soluble starch solution was used as adhesive. The mass ratio of the soluble starch and recycled cotton cloth was fixed as 1 : 2, and then, multilayer recycled cotton cloth was bonded with soluble starch solution. The products prepared were dried and made into pellets. 5% of PP-g-MA was chosen as the compatibilizer. Starch and recycled cotton pellets were treated as silane coupling agent KH550. PP, PP-g-MA and starch recycled cotton pellet were mixed according to the composition in Table I, which RC and TRC are the abbreviations of recycled cotton and treated recycled cotton, respectively. The mixtures were blended in a twin-screw extruder (SHJ-20 co- rotating twin-screw extruder with screw diameter of 21.7 mm, which provided by Nanjing Jieya Extrusion Equipment Co.) at the temperatures of 16  $\sim$  190°C (screw speed = 150 rpm, feed rate = 15 rpm). The extruded products were dried completely and molded into standard samples through injection machine (Model HM7DENKEY, Nissei Plastic Industrial Co.) at the temperatures of  $160 \sim 190^{\circ}$ C.

#### Mechanical testing

Tensile, flexural and Izod impact tests were carried out according to ASTM Standard. For each test and each type of the composites, five specimens were tested and the average values were reported. Tensile tests were conducted according to ASTM D 638 using a Universal Testing Machine (Zwick/Roell Z005, Zwick Roell Testing Machines Pvt.) at a crosshead speed of 50 mm/min. Static flexural tests were carried out according to ASTM D 790 using the same testing machine mentioned above at a crosshead speed of 2 mm/min. Izod Notch impact tests were conducted according to ISO 179 using a Universal Impact Testing Machine (ZBC-50, China Shenzhen SANS Testing Machine Co.).

#### Microstructure analysis

The impact specimens were frozen in liquid nitrogen for 3 h, and then quickly smashed. The fracture surfaces of the specimens were sputter-coated with gold before SEM analysis. The fracture surface morphology of the composites was observed on a Philips XL-30 ESEM scanning electron microscope with an acceleration voltage of 15 kV.

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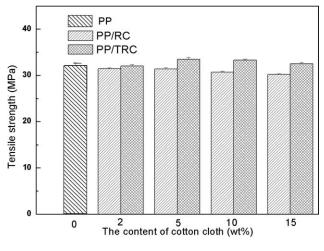


Figure 1 Tensile strength of PP/RC composites.

### **DSC** characterization

A TA Instruments Q200 differential scanning calorimeter (DSC) was used to study the thermal behavior of the PP/RC composites, and was calibrated using the melting temperature and enthalpy of a pure indium standard. About 8–9 mg of the sample was accurately weighted for DSC testing, and all measurements were performed in nitrogen atmosphere.

In nonisothermal crystallization and melting behavior characterization, a composite sample was rapidly heated to 220°C and held for 5 min. Subsequently, it was cooled to 60°C at the cooling rate of  $10^{\circ}$ C/min for crystallization behavior study. The sample was then reheated to 220°C at  $10^{\circ}$ C/min for melting behavior observation.

In nonisothermal crystallization kinetics study, a composite sample was rapidly heated to 220°C and held for 5 min. Subsequently, it was cooled to 60°C at selected cooling rates ranging from 5 to 40°C/ min. Each sample was used only once.

#### Polarized optical microscopy

The spherulite morphology and growth of PP/RC composite were studied using a polarized optical microscope (POM, Zeiss) equipped with a hot stage (Linklam LTM350). The samples were hot pressed into films with the thickness of 0.02 mm. The crystallization process was recorded in the second heating and cooling scan at the rate of  $0.5^{\circ}$ C/min.

# **TGA** analysis

The thermal decomposition behavior of the composites was studied by a thermogravimetry (model Q500, TA Instruments) in nitrogen atmosphere with the heating rate of  $10^{\circ}$ C/min.

### Vicat softening temperature testing

The vicat softening temperature of the composites was tested on a heating deflection and vicat softening temperature measuring apparatus (GT2HV2000, Taiwan Gotech Testing Machines Co.) according to ASTM D1525 Standard.

### Water absorption testing

The sample with the size of 10 mm  $\times$ 10 mm  $\times$ 4 mm was put into the drying oven at 50°C for 24 h, and then soaked into distilled water for 48 h at room temperature Subsequently, wipe off the water on the surface of the sample with a filter quickly. Weigh the sample immediately after water immersion. The ratio of the weight gained after being soaked is the water absorbing capacity.

# **RESULTS AND DISCUSSION**

# The effect of silane coupling agent on the mechanical properties

Figures 1–3 show the mechanical properties of unmodified PP/RC, silane coupling agent modified PP/RC composites. It can be seen that the tensile strength of silane coupling agent modified PP/RC composites is higher than that of pure PP and unmodified PP/RC with silane coupling agent, while the impact strength of silane coupling agent modified PP/RC composites is lower than that of unmodified PP/RC with silane coupling agent. Compared with those of pure PP, the impact strength and flexural strength of unmodified PP/RC composites and silane coupling agent modified PP/ RC composites are increased together, and the biggest increases are 19.7% and 19.9% for impact strength, 32.2% and 38.8% for flexural strength respectively. With the increasing RC content, the

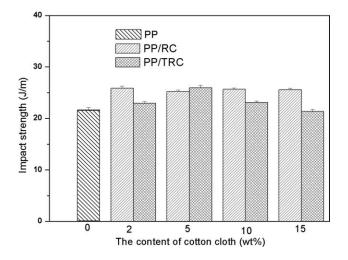


Figure 2 Impact strength of PP/RC composites.

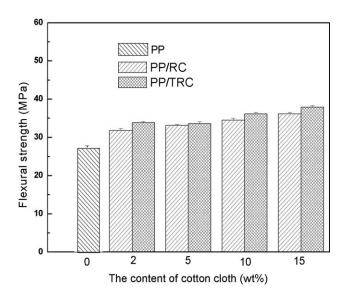


Figure 3 Flexural strength of PP/RC composites.

impact strength presents a downward trend, but the flexural strength presents an upward trend. This suggests that PP-g-MA is favorable to the toughness of PP/RC composites while silane coupling agent is favorable to the reinforcement of PP/RC composites. This observation was attributed to the reaction between MA on the main chain of PP and the hydroxyl group in the starches and wasted cotton cloth particles with a strong chemical bond formed. As a result, the compatibility between the two phases is improved, which increases the impact strength. As the hydrophobic agent, the silane coupling agent can infiltrated the filler as well as promote the dispersion of fillers in plastics. The hydroxyl group on the surface of the fillers can form strong covalent bonds with silane coupling agent. The effect of reinforcing fiber and bonding at the interface between fiber and matrix is exhibited due to the physical and chemical cross-linking between components.

#### Water absorption study of PP/RC composites

The water absorption data of unmodified PP/RC composites and silane coupling agent modified PP/ RC composites are shown in Table II. With the increase of starch and wasted cotton cloth particles, the water absorption rate of PP/RC composites is higher than that of pure PP due to the increased hydroxyl groups. Although starch and wasted cotton cloth particles are treated with silane coupling agent,

the water absorption rate decreases significantly compared with that of unmodified PP/RC composites. This indicates that silane coupling agent is beneficial for maintaining the dimensional stability of PP/RC composites.

### SEM observation of PP/RC composites

There is a good dispersion of the fillers in PP/RC composites due to the effect of the compatibilizer PP-g-MA. Granular material seen in Figure 4(a,e) should be starch, and the fiber materials seen in Figure 4(b-d) and (f-h) should come from the wasted cotton cloth in the course of shear melting in a twin-screw extruder. The content of starch and wasted cotton cloth particles varies from 2 wt %(15 wt %, and there is no aggregation taking place. However, after starch and wasted cotton cloth is treated with a silane coupling agent, the arrangement of the fibers is parallel to the directions of the substrate seen in Figure 4(f-h) while the arrangement of the fibers in unmodified PP/RC composites with silane coupling agent is perpendicular to the substrate. Thus, in the process of melt drawing, the fibers parallel to the direction of the substrate are inclined to orientation, which may be the reason of the higher tensile strength and slightly lower impact strength for silane coupling agent modified PP/RC composites. It can be observed in the SEM that bonding is poor for PP/RC compositions that would make stress transfer from matrix to fiber less effective, hence poorer mechanical reinforcement, seems to be reflected in the flexural properties.

#### Thermal properties of PP/RC composites

The thermal decomposition (TG) behavior and heat distortion temperatures reveal the material thermal stability at high temperatures and service conditions respectively. Figure 5 shows the TG curves of the unmodified PP/RC composite and silane coupling agent modified PP/RC composite with 10 wt % of RC. Meanwhile, the related thermal stability parameters are provided in Table III. Only one decomposition stage occurs on the TG curves of pure PP and all the composites studied. The jointing of RC makes the onset decomposition temperature ( $T_d$ <sup>onset</sup>), decomposition peak temperature ( $T_d$ ) and vicat softening temperature of the PP/RC composites higher than that of pure PP. The  $T_d$ <sup>onset</sup> are listed from high to low as follows: RC10 > TRC10 > PP. This might

TABLE II Water Absorption Data of PP/RC Composites PP RC2 RC5 **RC10** RC15 TRC2 TRC5 TRC10 Sample 0.08 0.11 0.13 0.15 0.19 0.03 0.09 0.10 Water absorption rate (%)

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TRC15

0.14

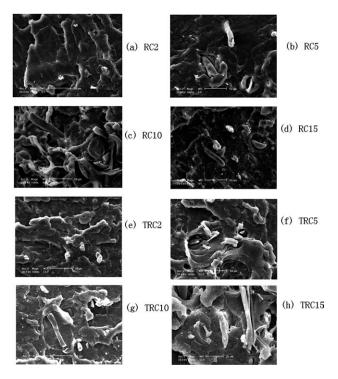
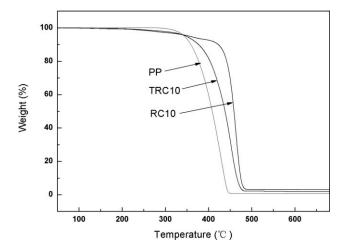


Figure 4 SEM photos of PP/RC composites.

be due to the fact that the  $T_d$  of RC is higher than that of PP, so the RC melt retarded the decomposer of PP to release. Till the  $T_d$  of RC, the decomposer of RC releases with that of PP. However, the decomposition peak temperature ( $T_d$ ) and vicat softening temperature of the PP/RC composites modified by silane coupling agent are lower than those of unmodified PP/RC composites, which might be due to the silane coupling agent with inferior thermal stability.

# Nonisothermal crystallization and melting behavior

Figures 6 and 7 show the DSC crystallization and melting curves of pure PP and PP/RC composites. Meanwhile, the corresponding data are listed in Table IV, in which the crystallization enthalpy ( $\Delta H_c$ ) and melting enthalpy ( $\Delta H_m$ ) were normalized by the weight percent of PP. It can be seen that the crystallization temperatures ( $T_c^P$ ) of PP are improved when being blended with RC. Moreover,  $T_c^P$  of the composites increases with the increasing RC content. This



**Figure 5** TG curves of unmodified PP/RC composites and silane coupling agent modified PP/RC composites at 10 wt % of RC content.

indicates that RC exhibits heterogeneous nucleation effect on PP crystallization and enables PP crystallization at higher temperatures. Both  $\Delta H_c$  and  $\Delta H_m$  of the PP/RC composites are smaller than those of pure PP, which might be attributed to the disturbance of cotton fibers on the crystal growth of PP. The X-ray diffractograms of PP/RC composites are shown in Figure 8. The crystallinity data indicated that with the addition of RC, the crystallinity was increased compared with that of pure PP, due to the heterogeneous effect of RC, which is consistent to the result of DSC.

# Nonisothermal crystallization kinetics

Four methods have been widely adopted to describe the nonisothermal crystallization process, namely Avrami equation, Ozawa equation, Jeziorny equation and Mo's method. The double logarithmic form of Avrami equation is<sup>17</sup>:

$$\ln[-\ln(1 - X(T))] = \ln Z_t + n \ln t \tag{1}$$

where X(T) is the relative crystallinity after the crystallization time t,  $Z_t$  and n are the crystallization kinetic constant and Avrami exponent, respectively, and both are related to the rate and mechanism of crystallization.

		1	1	
Sample	Onset decomposition temperature (°C)	Decomposition peak temperature (°C)	Residual weight (wt %)	Vicat softening temperature (°C)
PP	276.05	430.57	0.69	153.0
RC10	419.6	464.5	3.04	155.3
TRC10	366.3	452.3	1.86	153.5

TABLE III Thermal Properties Data of PP/RC Composites

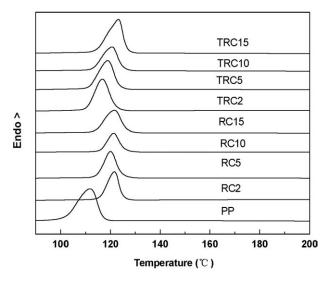


Figure 6 DSC exothermic curves of PP/RC composites at the cooling rate of  $10^{\circ}$ C/min.

Jeziorny<sup>18</sup> calibrated the crystallization kinetic constant of Avrami equation using cooling rate  $\Phi$ :

$$\log Z_c = \log Z_t / \Phi \tag{2}$$

where  $Z_c$  is the calibrated crystallization kinetic constant.

Ozawa derived an equation whose double logarithmic form is<sup>19</sup>:

$$\log[-\ln(1 - X(T))] = \log K(T) - m \log R$$
 (3)

where *R* is the cooling rate, K(T) is a function related to the overall crystallization rate that indicates how fast crystallization proceeds, and *m* is the Ozawa index, which is somewhat similar to the Avrami exponent and depends on the type of nucleation and growth dimensions.

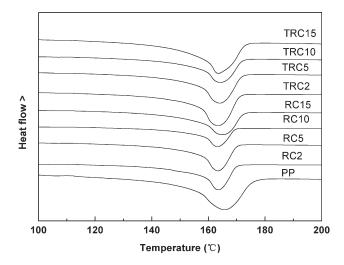


Figure 7 DSC endothermic curves of PP/RC omposites at the heating rate of  $10^{\circ}$ C/min.

Mo and coworkers<sup>20</sup> proposed a different equation by combining the Avrami and Ozawa equations, giving rise to the relationship between cooling rate R and crystallization time t at a given relative crystallinity:

$$\log Z_t + n \log t = \log K(T) - m \log R \tag{4}$$

$$\log R = \log F(T) - \alpha \log t \tag{5}$$

where the kinetic parameter,  $F(T) = [K(T)/Z_t]^{1/m}$ , refers to the value of the cooling rate, which has to be chosen at unit crystallization time when the measured system amounts to a certain degree of crystallinity; the Mo exponent  $\alpha$  is the ration of the Avrami exponent n to the Ozawa exponent m, that is,  $\alpha = n/m$ . F(T) has a definite physical and practical meaning, the smaller the value of F(T) is, the higher the crystallization rate becomes.

Moreover, Kissinger<sup>21</sup> suggested a method to determine the activation energy for the transport of the macromolecular segments to the growing surface,  $\Delta E$ , by calculating the variation of  $T_p$  with the cooling rate  $\Phi$ :

$$d[\ln(\Phi/T_p^2)]/d(1/T_p) = -\Delta E/R \tag{6}$$

where *R* is the gas constant.

According to eqs. (1)–(6), nonisothermal crystallization kinetic plots of RC10 composite (see Fig. 9) were obtained and showed a nice linearity in Avrami method, Mo method and Kissinger method. This suggested that the above three methods may provide a satisfactory description to the composites in this study. All nonisothermal crystallization kinetic parameters of the composites with 10 wt % fabric content are listed in Table V according to the same processing procedures as those of RC10 composite. It can be observed that pure PP gave a value of about 2.8 < n < 3.4, suggesting a spherulitic growth from nuclei initiated at time zero,

TABLE IV Non-Isothermal Crystallization and Melting Parameters of Pure PP, Unmodified PP/RC, Silane Coupling Agent Modified PP/RC Composites

<i>T<sub>c</sub></i> <sup>p</sup> (°C)	$T_c^{\text{onset}}$ (°C)	$\Delta H_c$ (J g <sup>-1</sup> )	$T_m^p$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )			
111.69	116.88	98.13	165.63	95.64			
121.59	124.95	96.32	163.57	87.86			
120.00	124.48	74.95	163.46	71.23			
121.31	125.63	90.47	163.19	81.31			
121.58	126.51	90.39	164.92	82.59			
116.76	122.02	87.99	163.37	82.88			
118.86	123.49	95.84	164.04	89.68			
120.65	124.95	78.86	164.33	70.76			
123.22	126.52	87.34	163.53	72.81			
	$\begin{array}{c} T_c^{\rm P} \\ (^{\circ}{\rm C}) \\ \hline 111.69 \\ 121.59 \\ 120.00 \\ 121.31 \\ 121.58 \\ 116.76 \\ 118.86 \\ 120.65 \end{array}$	$\begin{array}{c c} T_c^{\ p} & T_c^{\ onset} \\ \hline (^\circ C) & (^\circ C) \\ \hline 111.69 & 116.88 \\ 121.59 & 124.95 \\ 120.00 & 124.48 \\ 121.31 & 125.63 \\ 121.58 & 126.51 \\ 116.76 & 122.02 \\ 118.86 & 123.49 \\ 120.65 & 124.95 \\ \hline \end{array}$	$\begin{array}{c c} T_c^{\rm P} & T_c^{\rm onset} & \Delta H_c \\ \hline (^{\circ}{\rm C}) & (^{\circ}{\rm C}) & (J~{\rm g}^{-1}) \\ \hline 111.69 & 116.88 & 98.13 \\ 121.59 & 124.95 & 96.32 \\ 120.00 & 124.48 & 74.95 \\ 121.31 & 125.63 & 90.47 \\ 121.58 & 126.51 & 90.39 \\ 116.76 & 122.02 & 87.99 \\ 118.86 & 123.49 & 95.84 \\ 120.65 & 124.95 & 78.86 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			

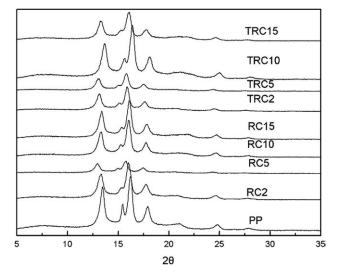


Figure 8 X-ray diffractograms of PP/RC composites.

which was in accordance with what has been reported in the literature.<sup>22</sup> The n value of RC10, and TRC10 composites ranged mostly around 3, which means that wasted cotton cloth, starch, PP-g-MA and silane coupling agent would not signifi-

cantly influence the nucleation form and crystalline growth form of PP. With the increasing cooling rate, the  $t_{1/2}$  and  $T_p$  of pure PP, RC10, and TRC10 composites decreased. At the same cooling rate, the  $t_{1/2}$  and  $T_p$  of RC10 and TRC10 composites were higher than those of pure PP, especially for the RC10 composite. The F(T) and  $\alpha$  of pure PP, RC10, and TRC10 composites increased with the increase of X(T), suggesting that it needs a higher cooling rate to reach certain X(T) at the same crystallization time. At the same X(T), the values of F(T) for these specimens are ranked as: PP > RC10 > TRC10. That is to say, to reach the same X(T), the crystallization time needed by PP is the longest and the crystallization time of TRC10 composite is the shortest. This demonstrates the heterogeneous nucleation effect of starch, cotton fiber, silane coupling agent, and PP-g-MA. Moreover, the values of  $\Delta E$  for these specimens are ranked as: PP > TRC10 > RC10, indicating that the addition of wasted cotton cloth obviously depressed the  $\Delta E$  of PP in the composites and made the crystallization of PP in the composites easier on nonisothermal crystallization conditions.

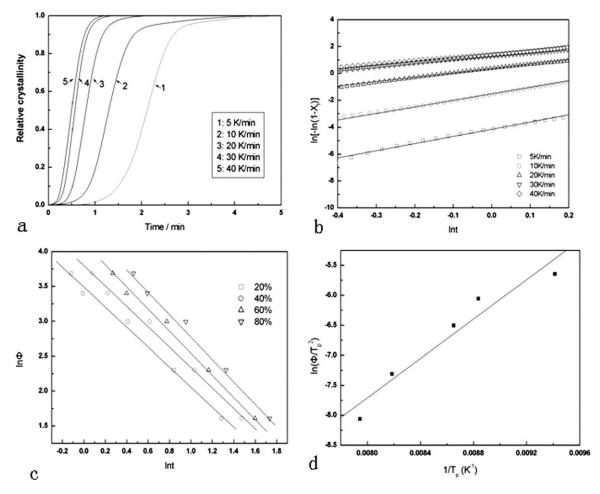


Figure 9 Nonisothermal crystallization kinetic plots of RC10 composite.

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$\Phi$ (°C min <sup>-1</sup> )	п	$Z_c$	$t_{1/2}$ (min)	$T_p$ (°C)	$\Delta E$ (kJ mol <sup>-1</sup> )	X(T) (%)	F(T) (K min <sup>a-1</sup> )	α
5	3.4	0.62	1.71	115.45	221.16	20	7.1	1.4
10	3.1	0.95	0.96	111.72		40	9.3	1.4
20	3.3	1.06	0.59	107.14		60	11.5	1.5
30	2.8	1.07	0.48	105.44		80	14.4	1.6
40	3.0	1.06	0.45	103.82				
5	5.1	0.43	2.13	125.85	136.57	20	2.3	1.3
10	3.7	0.86	1.29	122.16		40	2.6	1.4
20	3.6	1.01	0.82	115.59		60	2.8	1.5
30	3.5	1.05	0.58	113.17		80	3.0	1.5
40	2.9	1.04	0.50	106.25				
5	4.6	0.47	2.06	124.07	144.61	20	2.2	1.3
10	3.3	0.90	1.18	120.11		40	2.5	1.4
20	3.2	1.03	0.70	114.59		60	2.7	1.5
30	3.7	1.05	0.60	112.76		80	3.0	1.6
40	3.0	1.04	0.51	105.83				
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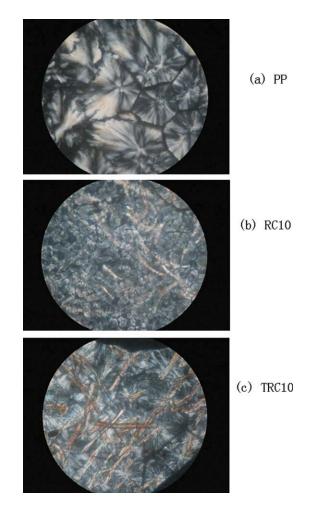
TABLE V Non-Isothermal Crystallization Kinetic Parameters of Pure PP, PP/RC, Silane Coupling Agent Modified PP/RC Composites with 10 wt % RC

# POM observation

The final performance of crystalline polymer-matrix composites depends on the crystallization behavior and crystal morphology of polymer-matrix to a large degree. Our previous studies indicated that RC exhibited heterogeneous nucleation on PP, and improved crystallization temperatures. In this article, the crystal morphology of pure PP, unmodified PP/RC composite, silane coupling agent modified PP/RC composite at 10 wt % of RC were observed by polarized optical microscopy (POM) (see Fig. 10). The spherulites with black cross extinction phenomena and the obvious crystal interface were observed in pure PP [Fig. 10(a)]. In the unmodified RC10 composite [Fig. 10(b)] and silane coupling agent modified TRC10 composite [Fig. 10(c)], the cotton fiber could be observed clearly. The trivial crystals were seen in RC10 and TRC10 composite no matter their distances from the fiber surface. This might be due to the fact that PP-g-MA and silane coupling agent which exhibited heterogeneous nucleation effect dispersed uniformly in PP matrix. When the temperature reached the crystallization temperature, lots of nuclei formed in an instant which retarded the growth of crystal.

# CONCLUSIONS

In this study, the PP/RC composites were prepared by extrusion blending and injection molding. Meanwhile, compatibilizer PP-g-MA and silane coupling agent KH550 were used to modify the interface of PP/RC composites. The results indicated that the addition of RC led to the increase of tensile strength, impact strength and flexural strength of PP. PP-g-MA modification was more conducive to the improvement in impact strength. If silane coupling agent was used further to treat the RC, it would be more helpful to improve the tensile properties and flexural strength. The two types of PP/RC composites have higher thermal decomposition temperatures and



**Figure 10** POM micrographs of PP/RC composite, silane coupling agent modified PP/RC composite with 10 wt % of RC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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Vicat softening temperatures and dimensional stability. In summary, compared with the mineral fiber reinforcements (such as glass fiber), RC is a more lightweight, inexpensive plastic reinforcement of high quality. Four methods were used to deal with the nonisothermal crystallization process for PP/RC composites and silane coupling agent modified PP/RC composites. The Avrami equation, Ozawa equation, Jeziorny's and Mo's methods can give a satisfactory description of the nonisothermal crystallization behavior of PP/RC composites. According to the results obtained by Avrami equation, the primary crystallization stage for nonisothermal melt crystallization might be in accordance with a three-dimensional spherical growth with heterogeneous nucleation. The values of the kinetics parameter F(T) reveal that the addition of RC, compatibilizer and silane coupling agent obviously increases the crystallization rate of PP from molten state. The results of DSC and polarized optical microscopy techniques indicate that RC can increase the crystallization temperature and the nucleation density of PP. Thus, RC is an effective nucleating agent for PP. When RC is treated with silane coupling agent, the tensile strength and flexural strength would be increased.

### References

1. Cantero, G.; Arbelaiz, A.; Llano-Ponte, R.; Mondragon, I. Compos Sci Technol 2003, 63, 1247.

- Nunez, A. J.; Sturm, P. C.; Kenny, J. M.; Aranguren, M. I.; Marcovich, N. E.; Reboredo, M. M. J Appl Polym Sci 2003, 88, 1420.
- 3. Potschke, P.; Kretzschmar, B.; Janke, A.; Compos Sci Technol 2007, 67, 855.
- 4. La Mantia, F. P.; Morreale, M.; Ishak, Z. A. M. J Appl Polym Sci 2005, 96, 1906.
- 5. Ashori, A.; Nourbakhsh, A. Bioresource Technol 2010, 101, 2515.
- 6. Ayrilmis, N.; Buyuksari, U. J Mater Sci 2010, 45, 1336.
- Malkapuram, R.; Kumar, V.; Negi, Y. S. J Reinforc Plast Compos 2009, 28, 1169.
- Yuan, Q.; Wu, D. Y.; Gotama, J.; Bateman, S. J Thermoplast Compos 2008, 21, 195.
- Correa, C. A.; Razzino, C. A.; Hage, E. J Thermoplast Compos 2007, 20, 323.
- 10. Stark, N. M.; Rowlands, R. E. Wood Fiber Sci 2003, 35, 167.
- 11. Ramaraj, B. J Appl Polym Sci 2007, 103, 3827.
- 12. Vinidiktova, N. S.; Ermolovich, O. A.; Goldade, V. A.; Pinchuk, L. S. Mech Compos Mater 2006, 42, 273.
- Ansari, M. N. M.; Ismail, H. J Reinforc Plast Compos 2009, 28, 3049.
- Lin, O. H.; Akil, H. M.; Ishak, Z. A. M. Polym Compos 2009, 30, 1693.
- 15. Lertwilmolnun, W.; Vergnes, B. Polymer 2005, 46, 3462.
- Taepaiboon, P.; Junkasem, J.; Dangtungee, R.; Amornsakchai, T.; Supaphol, P. J Appl Polym Sci 2006, 102, 1173.
- 17. Avrami, M. J Chem Phys 1940, 8, 212.
- 18. Jeziorny, A. Polymer 1978, 19, 1142.
- 19. Ozawa, T. Polymer 1971, 12, 150.
- Liu, T. X.; Mo, Z. S.; Wang, S. E.; Zhang, H. F.; Polym Eng Sci 1997, 37, 568.
- 21. Kissinger, H. E. J Res Nat'l Bureau Stand 1956, 57, 63.
- Wu, D. F.; Wu, L.; Wu, L. F.; Xu, B.; Zhang, Y. S.; Zhang, M. J Polym Sci Part B Polym Phys 2007, 45, 1100.