Novel Intercalated Nanocomposites of Polypropylene/Organic-Rectorite/Polyethylene-octene Elastomer: Rheology, Crystallization Kinetics, and Thermal Properties

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ABSTRACT: The melt blending method was applied to prepare ternary composites of polypropylene (PP)/organic-rectorite (OREC)/polyethylene-octene elastomer (POE) at constant content of 2 phr (parts per hundred PP) of OREC and 5, 10, 15 phr of POE (named PRE25, PRE210, and PRE215, separately) via twin-screw extruder. At the same time the binary composites of OREC/PP at 2 phr loading of OREC, named PR2 were prepared in order to investigate effects of OREC and POE on rheology and crystallization properties of composites. The rheology was characterized on capillary rheometer, nonisothermal crystallization kinetics on differential scanning calorimetry (DSC), and thermal stability properties on thermogravimetric analysis (TG). It is found that melting PR2 and PRE systems conform to the law of Non-Newton and shear-thinning behavior is observed for both systems. The apparent viscosity of the melt decreases with the increase of POE loadings. The crystallization half-time ($t_{1/2}$) of PRE is shorter, the rate constant Zc larger, which indicates OREC and POE has the heterogeneous nucleation effect and the crystallization rate of PP was increased. The enthalpy of PRE is lower than that of PR2 and pure PP at the same conditions, which shows that the relative crystallinity of PRE composites are reduced. TG curves show that the ternary systems have higher thermal stability in contrast with pure PP.© 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1915–1921, 2005

Key words: polypropylene; polyethylene-octene elastomer; rectorite; crystallization; rheology; thermal properties

INTRODUCTION

Polymer/clay nanocomposites have received increasing attention in recent years because of their significant improvement in physical properties over their neat polymer and conventional composites.[1–3] Polypropylene (PP)/clay nanocomposite is one of the pioneer researched nanocomposites since PP is one of the most widely used polyolefin polymers, and its properties are greatly affected by the intercalation and exfoliation of clay in the PP matrix.[4,5]

Rectorite (REC) is a useful kind of clay mineral, which is a sort of regularly interstratified clay mineral with alternate pairs of a dioctahedral micalike layer (nonexpansible) and a dioctahedral smectitelike layer (expansible) existing in a 1:1 ratio. The exchangeable hydrated cations lie in the interlayer region of 2:1 smectitelike layers, which can make REC cleave easily between smectitelike interlayers, forming monolithic REC layers.

Rectorite can be used as nanoscale filler for PP after being modified with dodecylbenzyldimethylammonium bromide, but the mechanical properties of the resulting nanocomposites can only be enhanced slightly because of the small polarity of PP and poor intercalation performance.[6] The toughness of PP can be enhanced significantly by the addition of elastomer, which, however, is a compromise in strength.[7,8] To obtain PP systems with higher strength and toughness, we prepared the ternary systems of PP/organic rectorite (OREC) polyethylene–octene elastomer (POE) (named PRE systems) at constant content of OREC via conventional melt blending process as well as the binary composites of PP/OREC (same content of OREC, named PR2) and studied the intercalation performance of OREC in composites and their mechanical properties in another paper.

The polymorphism of PP has attracted considerable attention because the final mechanical properties are significantly affected by the crystallinity and crystallization rate of the semicrystalline polymer, which can be influenced by additional component and processing conditions. In this experiment, we investigated the influences of OREC and POE on the

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crystallization properties of PP. Moreover, the processing behavior and thermal properties are also important for the modified PP, so we also investigated the effect of OREC and POE on the melt rheology of composites by capillary rheometer and thermal stability by thermogravimetric analysis (TG).

EXPERIMENTAL

Materials

Polypropylene, T30S, common grade, was supplied by Fushun Petroleum Chemical Co., People's Republic of China. Rectorite, with cation exchange capacity of 40 meq/100 g and the *d*-space of REC 2.2 nm, was obtained from Hu Bei Zhongxiang Rectorite Mine (Wu Han, HuBei, People's Republic of China). OREC was prepared in our laboratory. Sodium REC was screened with a sieve of 300-mesh to remove impurities. A certain amount of screened clay was suspended in deionized water in a glass vessel using a glass rod. Dodeceylbenzyldimethylammonium bromide, supported by Xi'an Chemical Agent Factory, was dissolved in a certain amount of water and then added to the suspended clay–water solution under continuous vigorous stirring for several minutes at room temperature. The mixture was transferred into a three-neck flask, heated to 85°C, and stirred for 5 h. The treated products were washed and filtered repeatedly to ensure a complete removal of bromide ions by the titration of $AgNO_3$ solution. Thereafter, the product was dried under vacuum at 100°C for several hours. The *d*-space of OREC was 2.56 nm measured by X-ray diffraction. The POE is a commercial product of Dupont Dow Elastomers under the trade name Engage 8150. Other reagents used were chemical grade.

Preparation of composites

The composites can be obtained after kneading PP, OREC, POE, and necessary additives for 5 min at room temperature on a high-speed mixing machine (GH-10DY, Beijing Plastic Factory, Beijing, China) and then extruding the mixtures in a twin-screw extruder (PEL330, Brabender, Duisburg, Germany). The screw speed was set at 50 rpm, and the barrel temperatures were set from 170°C at the first barrel to 190°C at the last barrel. Table I shows the systems of the composites

TABLE I
The Systems of Composites

System[a]	PR2	PRE25	PRE210	PRE215
Content of POE/g	0	5	10	15

[a] The content of OREC is 2 g; PP is 100 g.

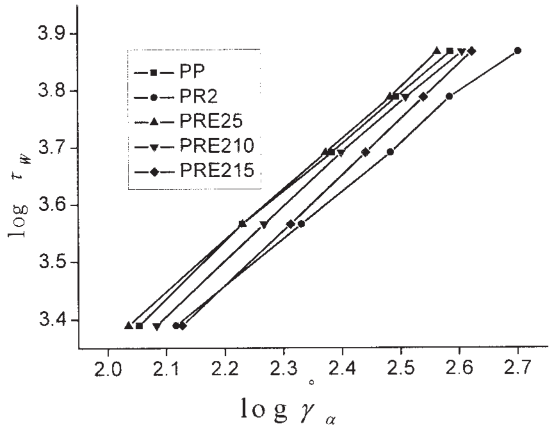


Figure 1 Plots of $\log \tau_w$ versus $\log \mathring{\gamma}_\alpha$ for PP and the composites.

Characterization

The measurement of rheologic property was carried out on an XLY-IIcapillary rheometer (Kejiao Instrument Factory, Ji Lin University, Chang Chun, Ji Lin, China) with a height-to-diameter ratio of 40:1. A pressure–flow diagram of the different systems was obtained at a certain temperature, and then it was transformed to wall shear stress-apparent shear rate ($\tau_w - \mathring{\gamma}_\alpha$) and apparent viscosity shear rate ($\eta - \mathring{\gamma}$) curves. Nonisothermal crystallization kinetics was studied using a differential scanning calorimeter (DSC-2910) made by TA Co (New Castle, DE). The samples were heated at a heating rate of 20°C/min to 210°C first under nitrogen atmosphere for 15 min to eliminate thermal history and then cooled down to room temperature at three kinds of constant falling temperature rates of 5, 10, and 15°C/min, respectively. Thermal stability properties of composites were conducted in nitrogen atmosphere on TG (TGA Q50, TA. Co. New Castle, DE).

RESULTS AND DISCUSSION

Rheology of PR2 and PRE systems

PP and composites were heated to 200°C and then pressured 20, 30, 40, 50, and 60 Kg/cm^2, and the corresponding rheology curves were obtained. The $\log\tau_w \sim \log \mathring{\gamma}_\alpha$ curve is plotted in Figure 1, in which τ_w and $\mathring{\gamma}_\alpha$ is shear stress and apparent shear rate at pipe wall, respectively. Obviously each group of τ_w and $\mathring{\gamma}_\alpha$ satisfied the equation $\tau_w = K\mathring{\gamma}_\alpha^n$ in a certain range of shear rates.

The values of slope determined from the linear regression of rheology curves are non-Newton exponent

TABLE II
The Values of Non-Newton Exponent *n* for PP and the Composites

Systems	Shear rate (s^{-1})	*n*
PP	113.2–386.0	0.89
PR2	130.9–504.2	0.83
PRE25	108.5–366.5	0.90
PRE210	121.2–404.4	0.92
PRE215	134.1–420.3	0.96

n. All the data are listed in Table II. All the values of *n* are less than 1, implying that PP and modified composites exhibit typical shear-thinning behavior. The shear rate $\mathring{\gamma}$ can be calculated from Eq. (1):

$$\mathring{\gamma} = \frac{(3n+1)\mathring{\gamma}_\alpha}{4n} \tag{1}$$

The apparent viscosity η of composites can be calculated by the following equation according to various *n* values:

$$\eta = \frac{\tau_w}{\mathring{\gamma}} = K \cdot \mathring{\gamma}^{(n-1)} \tag{2}$$

The curves of log $\eta \sim$ log $\mathring{\gamma}$ (shown in Fig. 2) show that the higher shear rate carries less apparent viscosity for all of the composites, which indicates that molecular chains deviate from equilibrium configuration to molecular orientation along the flow direction under high temperatures and pressures. The apparent viscosity of the PR2 system is lower than that of the PP and PRE systems, while the apparent viscosity of PRE210 and PRE215 is lower than that of pure PP, and the apparent viscosity of PRE215 is the lowest in three PRE systems. The change of apparent viscosity shows that a higher content of POE can carry better fluidity to PRE composites. Additionally, the apparent viscosity of pure PP and PRE is not affected significantly by shear rate in contrast with PR2.

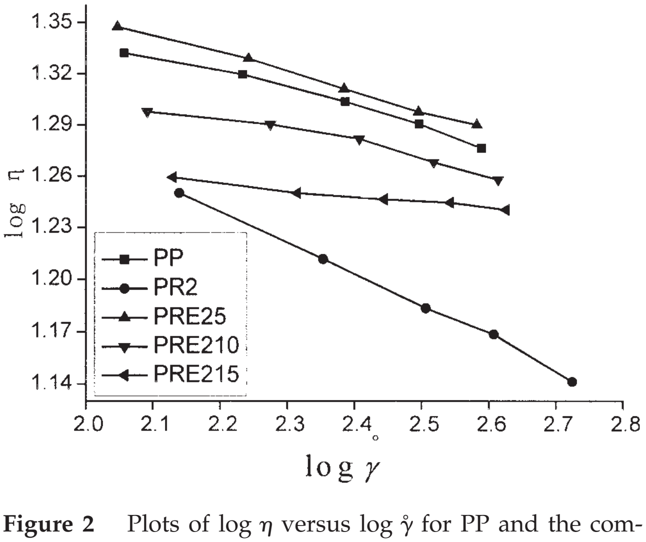


Figure 2 Plots of log η versus log $\mathring{\gamma}$ for PP and the composites.

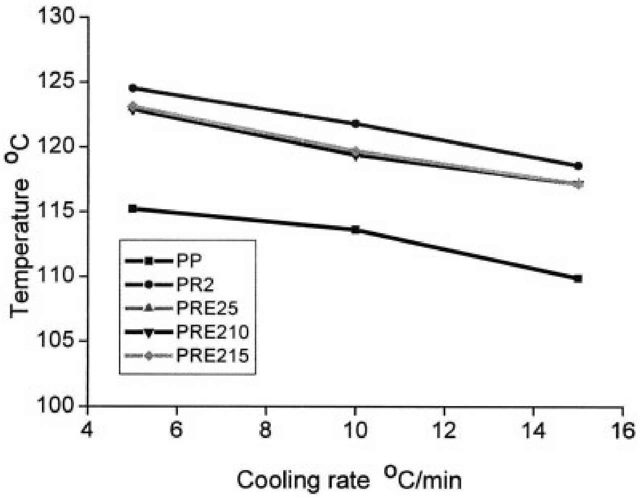
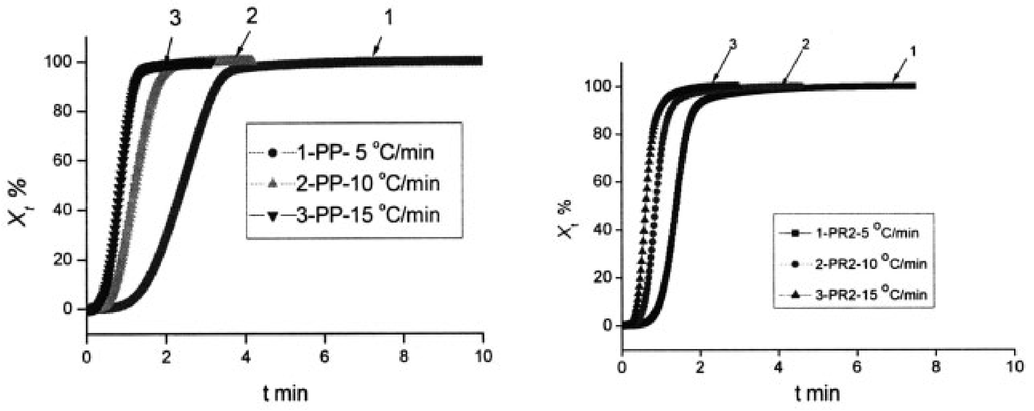


Figure 3 Tp of PP and composites from DSC thermograms.

The melt fluidity of composites is relative to the structure of each component in the blends, free volume, and interfacial interaction between every two blends. The apparent viscosity of PRE25 is higher than that of PP, probably because the soft chain of POE can insert into the free volume of PR2 and lead to more geometry interwinding and the synergistic effect of stronger interface force among PP, POE, and OREC, and the viscosity of PRE is increased when the loading of POE is relatively low. But when PRE systems have more soft chains of polymer, the increase in free volume may decrease the viscosity of the PRE systems. The improvement of processing behaviors of the PR2 system is due to a part of the macromolecules intercalating into layers of clay and breaking of the interwinding structure. Then the van der Waals force between the clay layers and macromolecules is faded and the macromolecules are prone to orientation at high temperature shear force, which can help to increase the mobility of the macromolecule chain segment in the polymer matrix.

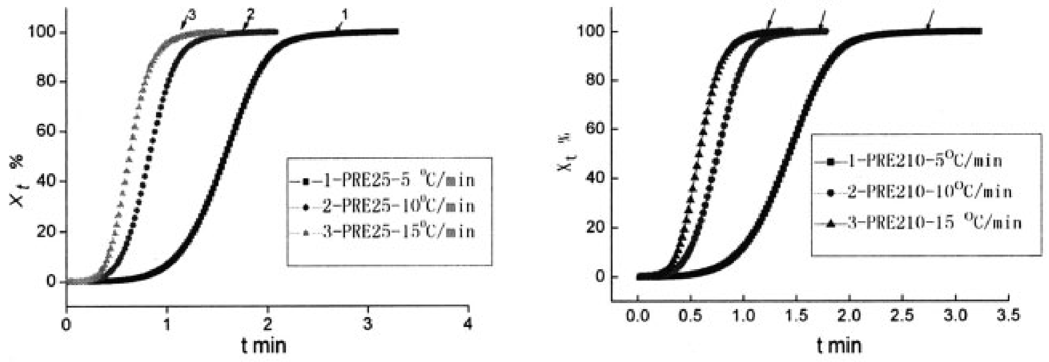
Nonisothermal crystallization properties of PR2 and PRE

From the thermal spectrum of nonisothermal crystallization, we can obtain the curves of crystalline peak temperature (T_p) dependence of falling temperature rates for PP and composites (showed in Fig. 3). The T_p tends to shift to lower temperatures with the falling temperature rate increase, which indicates that the supercooling de-



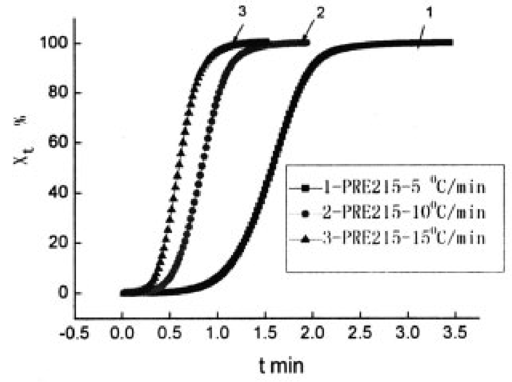
(a) PP

(b) PR2



(c) PRE25

(d) PRE210



(e) PRE215

Figure 4 Plots of X_t versus t for crystallization of PP and the composites.

gree of crystallizing increases in this course. Additionally, the value of T_p of PRE is between that of PR2 and PP at the same cooling temperature rate, indicating that the clay can act as an effective nucleus and significantly enhance the crystallization temperature and crystallization rate of PP.

TABLE III
Parameters of Sample During Nonisothermal Crystallization Process

Systems	ϕ (°C/min)	m	Z_c	t_{l2} (min)	T_p (°C)	ΔH_c (J/g)
PP	−5	4.0	0.46	2.44	115.4	102.50
	−10	3.9	0.89	1.24	113.8	95.30
	−15	3.8	1.01	0.88	110.1	93.30
PR2	−5	4.8	0.57	1.62	124.4	101.90
	−10	5.0	1.01	0.90	121.7	103.59
	−15	4.9	1.13	0.63	118.6	84.30
RE25	−5	4.94	0.59	1.56	123.0	90.96
	−10	4.43	1.05	0.82	119.5	89.64
	−15	4.55	1.12	0.63	117.2	89.96
RE210	−5	4.46	0.67	1.44	112.9	90.34
	−10	4.07	1.08	0.76	119.4	88.15
	−15	4.21	1.14	0.58	117.2	87.73
RE215	−5	5.18	0.58	1.58	123.1	83.82
	−10	4.59	1.04	0.84	119.7	82.59
	−15	4.23	1.13	0.60	117.2	82.09

The relative crystallinity at different crystallization time, X_t, can be obtained from the ratio of the area of the exotherm up to time t divided by the total exotherm at infinite time t_∞ with an equation given as

$$X_l = \frac{X_c(t)}{X_c(\infty)} = \frac{\int_0^l \frac{dH(t)}{dt}dt}{\int_0^\infty \frac{dH(t)}{dt}dt} \tag{3}$$

where $X_c(t)$ is absolute crystallinity at time t, $X_c(\infty)$ is maximum absolute crystallinity, and $\frac{dH(t)}{dt}$ is the rate of heat evolution at given fall temperature rates.

From the data of DSC, we can obtain the curves of crystallinity dependence of crystalline time (t) shown in Figure 4), and crystalline halftime ($t_{1/2}$) during nonisothermal crystallization is listed in Table III.

The crystalline kinetics parameters of PP and composites can be calculated from the data provided by DSC according to crystalline kinetics theory.[9] Isothermal crystallization of the polymer can be calculated using the Avrami equation, which shows the relationship of crystalline time (t) versus relative crystallinity by the equation

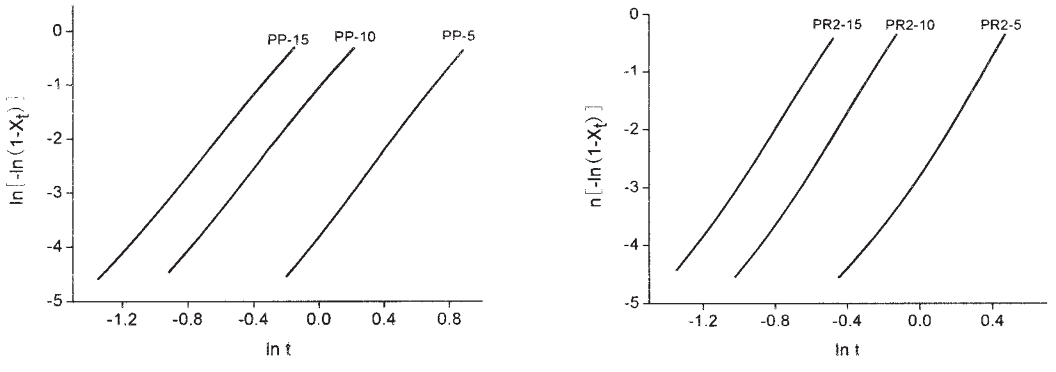
$$1 - \chi_t = \exp(-Z_t t^m) \tag{4}$$

In which χ_t is the relative crystallinity as mentioned above at crystalline time t, m is the Avrami power, which describes the nucleation and growth process, and Z_t is the isothermal crystallization rate constant associating with fixed crystallization temperature.

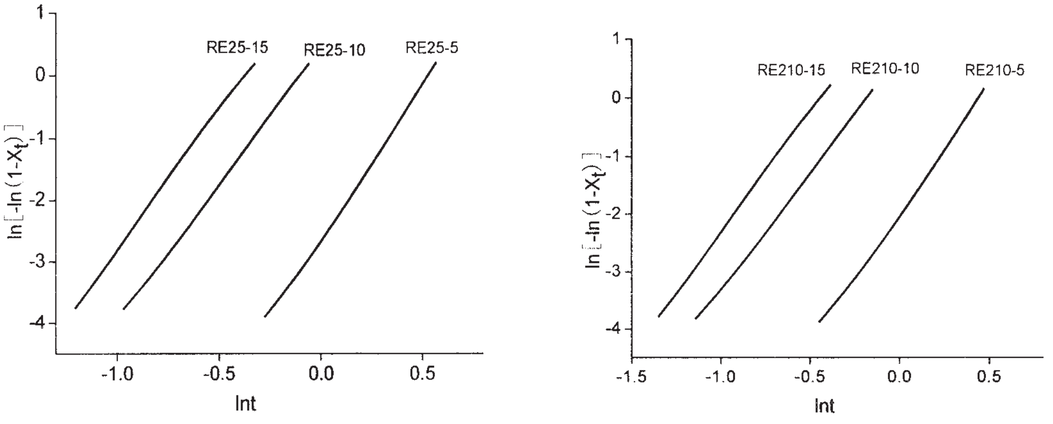
Take the logarithm toward Eq. (4) and obtain Eq. (5):

$$\ln[-\ln(1-\chi_t)] = \ln Z_t + m \ln t. \tag{5}$$

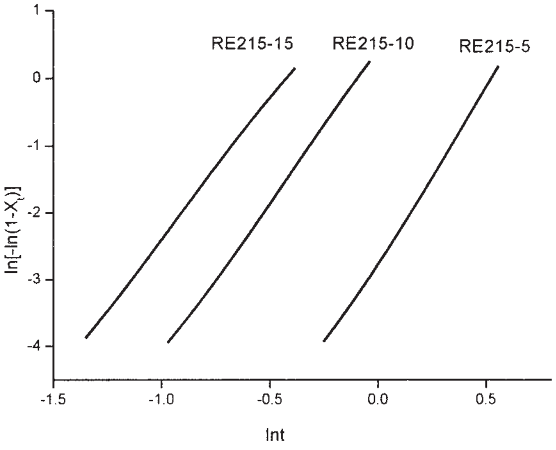
Convert the form of t in the Avrami equation (5) into $t = \frac{T_0 - T}{\phi}$, here, T_0 is the crystallization initial temperature, T is the crystallization temperature, ϕ is the falling temperature rate, and plot $\ln[-\ln(1-\chi_t)] \sim \ln t$ curves are shown in Figure 5. The $\ln[-\ln(1-\chi_t)] \sim \ln t$ curves of various composites are relatively ideal linearity, which reveals that the method for nonisothermal crystallization parameters (i.e., the Jeziorny method) applied to PP and composites is available. For nonisothermal crystallization, take the revised factor by the falling temperature rate, the revised Avrami parameters (Z_t) according to $\ln Z_c = \ln Z_t/\varphi$, then obtain the nonisothermal crystallization rate constant Z_c, and the results are listed in Table III. The Avrami exponent m of PR2 and PRE composites is in the range of 4–5, and that of pure PP is always less than 4, which implies that the addition of OREC and POE has the heterogeneous nucleation effect for PP, while the $t_{1/2}$ of PRE becomes shorter, and the Z_c becomes larger than that of pure PP and PR2 at the same falling temperature rates, which indicates that the addition of POE can accelerate the crystallization rate of PP and PR2. Otherwise, the values of enthalpy (ΔH_c) of PRE are lower than that of PR2 and pure PP at the same conditions, showing that OREC and POE can accelerate the crystallization rate of PP, but the relative crystallinity of the resulting composites are reduced.



(a) PP (b) PR2



(c) PRE25 (d) PRE210



(e) PRE215

Figure 5 Plots of $\ln[-\ln(1 - X_t)]$ versus $\ln t$ for crystallization of PP and the composites.

Thermogravimetric analysis of PP and composites

Figure 6 shows the TG curves of PP and composites. It is obvious that the PRE systems and PR2 nanocomposite begin to decompose at higher temperature. The enhanced thermal stability of the polymer–clay nanocomposites is attributed to the finer dispersment of OREC in the composites, which can carry unexpected hybrid properties synergistically derived from the interforces between components.

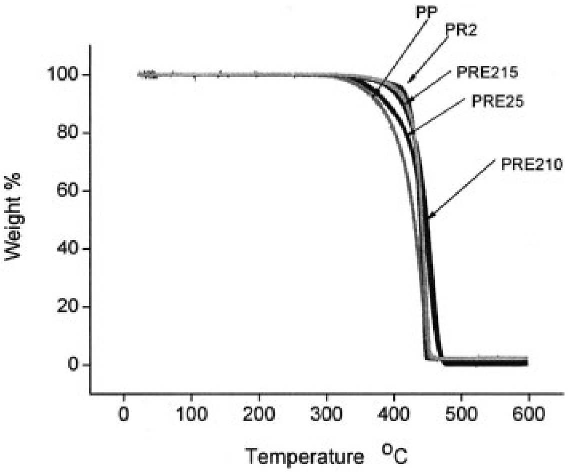


Figure 6 The curves of thermogravimeric analysis (TG) of modified PP.

CONCLUSIONS

The melting PP, PR2, and PRE systems conform to the law of non-Newton and shear-thinning behavior is observed for the systems. More content of POE in PRE systems leads to lower apparent viscosity and better processability when the constant loading of OREC is 2 phr. POE and OREC in PP can act as nucleating agents and improve the crystallization rate of PP, but the relative crystallinity of the resulting composites is reduced. The decomposition temperature of PRE systems is higher than that of pure PP, which indicates that the ternary systems have higher thermal stability.

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