THERMOPHYSICAL PROPERTIES OF POLY(PROPYLENE)-BASED COMPOSITE POLYMER

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Abstract

The thermal diffusivity and the thermal conductivity of polypropylene-based composite polymer were simultaneously measured with a temperature wave analysis method. We can measure the thermal properties under cooling process which are important to consider the polymer processing. The effect of filler in the composite was analyzed by thermal diffusivity and thermal conductivity as a function of temperature. The thermal conductivity of particle dispersed composite was confirmed as a reasonable value and was explained with a series model.

Keywords: composite, poly(propylene), temperature wave, thermal conductivity, thermal diffusivity

Introduction

Poly(propylene) (PP) is one of the major polymeric materials, which has high cost competitiveness, good rigidity and impact resistance. In many cases, poly(propylene) composites are extensively used in a wide range of industrial end products including automotive parts, wire, cable coating, etc. [1–3]. Recently, the PP base composite containing rubber materials was introduced as a new functional polymer. These polymers are called the super olefin polymers that show high rigidity, impact resistance and good fluidity [4]. The related result was reported about the preparation of modified material [5, 6], the effect of filler [7–9], and the structure [10–12].

　　Thermophysical properties are important factors to control and simulate the polymer processing system particularly in cooling process. Moreover, these are applied as useful tools for analyzing the structure in a composite material [13]. However, especially for the multi-phase materials, thermal conductivity or thermal diffusivity has not been completely understood even in the used temperature range.

　　The new thermal analytical method named temperature wave analysis (TWA) has been developed to determine thermal diffusivity of polymer thin films [14, 15]. The change of phase or amplitude in a periodical temperature wave was used to measure the thermal diffusivity. The temperature wave, which is generated at the front

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surface of the polymer thin film, can be observed at the rear surface. As characteristics of this method, a small amount sample of the laboratory level can be measured in the wide temperature range from solid to liquid state including the melting point. The application of TWA has been already reported about various polymers, paper [16], and composite materials [17].

The present work deals with the simultaneous measurement of thermal diffusivity and thermal conductivity as a newly modified method of TWA. The measurement was carried out during melt-crystallization process in poly(propylene)-based composite material filled with inorganic or rubber component. The data of composite materials was also considered with some thermal conduction models.

Experimental

Sample

Materials used were isotactic-polypropylene (PP), poly(ethylene-co-propylene) (EPR), poly(ethylene-co-butene) (EBR) produced by Sumitomo Chemical Co. Ltd. Talc was chosen as an inorganic filler for increasing hardening. The blends of PP/EPR, PP/EBR, and PP/talc were prepared from the melting state by twin screw extruder. A flow rate was maintained uniformly for all the blends. Table 1 shows the mixing ratio and density.

Table 1 poly(propylene) base composites used in this work

Components/mass%				Density/g cm^{-3}
PP(HY100G)	EBR(NO 416)	EPR(E100)	talc(JR-37)	
100	–	–	–	0.9074
90	10	–	–	0.9029
80	20	–	–	0.8996
70	30	–	–	0.8957
60	40	–	–	0.8916
80	–	20	–	–
70	–	30	–	–
90	–	–	10	0.9719
80	–	–	20	1.0449
70	–	–	30	1.1303
–	100	–	–	0.8728
–		100	–	0.86
–			100	2.7

The sample was molded to film with hot press at 180°C under pressure of 100 kg cm^{-2}. Because the film has an unstable structure by molding process, the sample was heated to 175°C in 1°C min^{-1} and held at 175°C for 30 min before measure-

ment. The backing material was used Pyrex 7740 (Corning Inc.), which was also used as reference material for measuring the thermal conductivity.

Measurement

The thermal diffusivity was measured by TWA method. The details of apparatus and the principle of this method were reported previously [14, 15]. The sample was held with 2 Pyrex glass pieces used as heater and sensor coated with gold thin film in area of 1×4 mm. Polyimide film as spacer was inserted with sample for preventing the change of sample thickness. The thickness of sample was measured after the heat treatment.

The thermal diffusivity is calculated from the relationship of the frequency and the phase delay of temperature wave or the amplitude at the rear surface of the sample [14]. The temperature wave decay in amplitude (*A*) and phase delay is progressed with propagating to the sample. The phase delay ($\Delta\theta$) and amplitude term in temperature wave are shown in Eqs (1) and (2), respectively.

$$\Delta\theta = -\sqrt{\frac{\pi f}{\alpha}}\, d - \beta \tag{1}$$

$$\ln(A\sqrt{f}) = -\sqrt{\frac{\pi f}{\alpha}}\, d + \ln\left(\frac{2c\sqrt{\alpha}}{(C\sqrt{\alpha} + C_b\sqrt{\alpha_b})^2}\right) + \ln(J) \tag{2}$$

where *d* is the thickness of sample, *C* is the heat capacity per unit volume, β is a constant depending on the equipment characteristics, and subscript b means backing material. From Eqs (1) and (2), the phase delay or amplitude shows a linear relation with a square root of the frequency. α can be calculated from the slope of these relationships. The remaining term that intercept with y-axis also contains some information. In Eq. (1), it indicates the constant depending on the equipment characteristics that
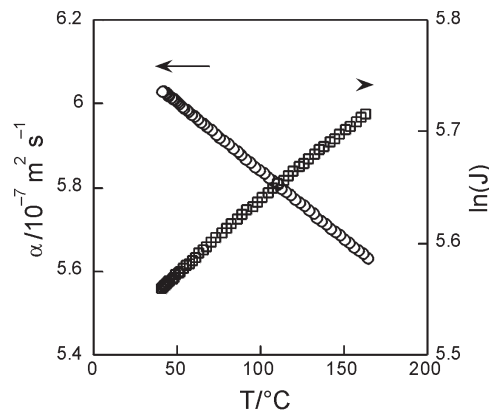
Fig. 1 Thermal diffusivity of PYREX7740 with PYREX7740 as a backing material; measuring condition –1 K min^{-1}, 6 Hz, thickness: 482 μm
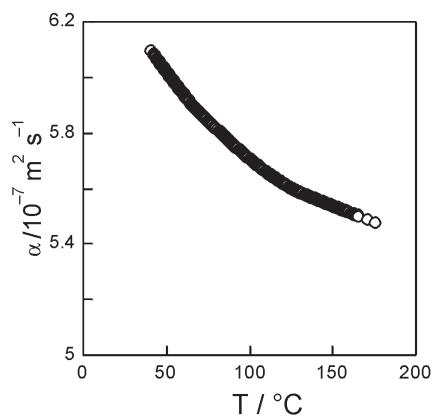
Fig. 2 Thermal diffusivity of PYREX7740 with poly(propylene) as a backing material; measuring condition -1 K min^{-1}, 6 Hz, thickness: 482 μm

shows a constant value according to equipment assembly. The right hand side of Eq. (2) is divided into three terms. The first term is identical as that of phase delay. The second term contains the heat capacity per unit volume of backing materials and sample. The third term, which is dependent on the measuring conditions such as the resistance value of thin coating and input voltage, is impossible to calculate directly by the detected signal. However, this value has no effect on the change of sample at the same measuring condition. In other words, the third term shows similar value from the measurement of sample or reference material in identical measuring conditions.

This value changes depending on cell, so ln(J) has to be measured for each cell. If the reference material is measured with the same material as the backing material, then Eq. (2) is rewritten as follows.

$$\ln(A\sqrt{f}) = -\sqrt{\frac{\pi f}{\alpha_b}}d_b + \ln\left(\frac{1}{2(C_b\sqrt{\alpha_b})^2}\right) + \ln(J) \tag{3}$$

Using the known properties of the reference material, ln(J) is easily determined from Eq. (3). This value is the same as that of Eq. (2), so the heat capacity per unit volume of sample is calculated from the second term of Eq. (2). Figure 1 shows the measured α values and the third term ln(J) calculated by Eq. (3) with same material PYREX7740 as a backing material.

As the other measurement method, it is considered that the two surfaces of backing material is covered with samples. In the former method, the thickness of the samples has to account for keeping up a fixed measuring condition and identical measuring frequency. However, the second method is measured at constant thickness with some backing materials, so that the measuring condition is easily controlled, and the error of measurement is less than in the former method. For this system, Eq. (2) is turned to Eq. (4)

$$\ln(A\sqrt{f}) = -\sqrt{\frac{\pi f}{\alpha_b}}\, d_b + \ln\left(\frac{2C_b\sqrt{\alpha_b}}{(C\sqrt{\alpha} + C_b\sqrt{\alpha_b})^2}\right) + \ln(J) \tag{4}$$

Figure 2 shows measured α values of PYREX7740 with PP as a backing material. The measurement was controlled with similar conditions as these used in Fig. 1. Therefore, $C\alpha^{1/2}$ is calculated from Eq. (4) and the $\ln(J)$ of reference material described in Fig. 1. The thermal conductivity is taken from the measured and calculated results with the relation of $\lambda = \alpha C$.

Results and discussion

Thermal diffusivity

Figure 3 shows the temperature dependence of thermal diffusivity in poly(propylene) by the conventional TWA. The result of first heating shows lower value than that measured during the second heating at the low temperature side, because the sample has an unstable structure due to quenching. Generally, α becomes smaller as a function of temperature and shows almost a constant value in melt state. In the cooling process, α increases with decreasing temperature and sharp change occurs at crystallization. The temperature dependence of second heating shows similar value as that of cooling, but the melting process is observed at higher temperature than the crystallization process.
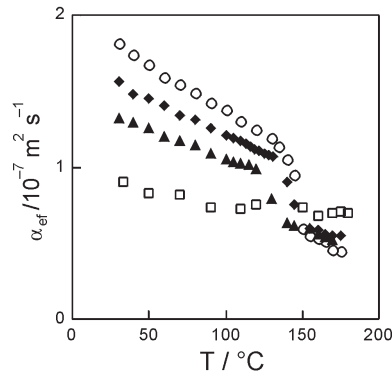
Figure 4 show the temperature dependence of the effective thermal diffusivity (α_{ef}) in cooling process of PP/EPR composite. Since EPR has lower α than PP below 150°C, α_{ef} of composite at room temperature is decreased with increasing the content of EPR. In contrast, α_{ef} shows opposite tendency in liquid state, because the temperature dependence in EPR is relatively small. In the crystallization process, it is observed that α_{ef} suddenly increases with decreasing temperature similarly to PP. However, the change of α_{ef} is smaller due to the addition of EPR. The change of slope is related to crystallinity from Fig. 3. These results indicate that the decrease of α_{ef} means decreasing crystallinity [18]. As a result, the addition of EPR affected the decrease of crystallinity of PP matrix.

As for the content of crystalline part in the composite, the addition of EPR means the increase of the total non-crystalline part in PP/EPR blends. Accordingly, the crystallinity of the blend decreases by the addition of EPR or EBR. Figure 5 also shows the temperature dependence of α_{ef} in cooling process of PP/EBR composite. The addition of EBR shows the same tendency with PP/EPR

Figure 6 shows the temperature dependence of α_{ef} in cooling process of PP/talc composite. Talc has higher α_{ef} value than PP in whole temperature, so that the α_{ef} of composite is increased with increasing of talc content. The influence of talc on thermal diffusivity is estimated in 3 temperature regions: solid state, crystallization process, and melt state, based on crystallization temperatures T_{c_1} and T_{c_2} as shown in Fig. 6. Table 2 shows the change of α_{ef} regarding the change of temperature ($\Delta\alpha/\Delta T$) of PP/talc composites in each state. $\Delta\alpha/\Delta T$ increases with increasing talc content in
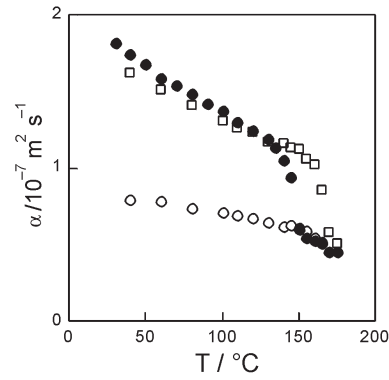
Fig. 3 Thermal diffusivity of poly(propylene) for the melting and cooling processes;
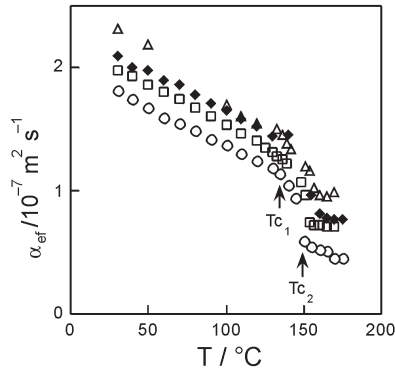o – 1st heating, ● – cooling, □ – 2nd heating

Fig. 4 Temperature dependence of thermal diffusivity of poly(propylene)/EPR com-
posite for cooling process; o – PP, ◆ – PP/EPR=80/20 mass%, ▲ – PP/EPR=
70/30 mass%, □ – EPR
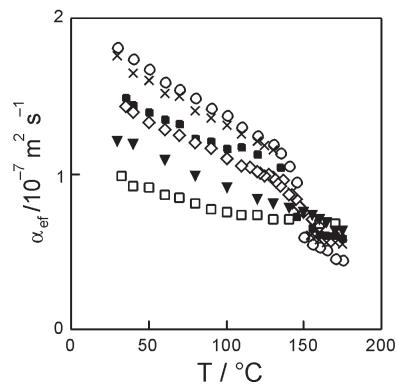
Fig. 5 Temperature dependence of thermal diffusivity of poly(propylene)/EBR com-
posite for cooling process; o – PP, X – PP/EBR=90/10 mass%, ■ – PP/EBR=
80/20 masst%, ◊ – PP/EBR=70/30 mass%, ▼ – PP/EBR=60/40 mass%, □ – EPR

all the measured temperature ranges. In crystallization process, talc acts the nucleating agent for PP [19], so the addition of talc accelerates the crystallization of PP.

Fig. 6 Temperature dependence of thermal diffusivity in poly(propylene)/talc composite for cooling process; o – PP, □ – PP/talc=90/10 mass%, ◆ – PP/talc= 80/20 mass%, Δ – PP/talc= 70/30 mass%
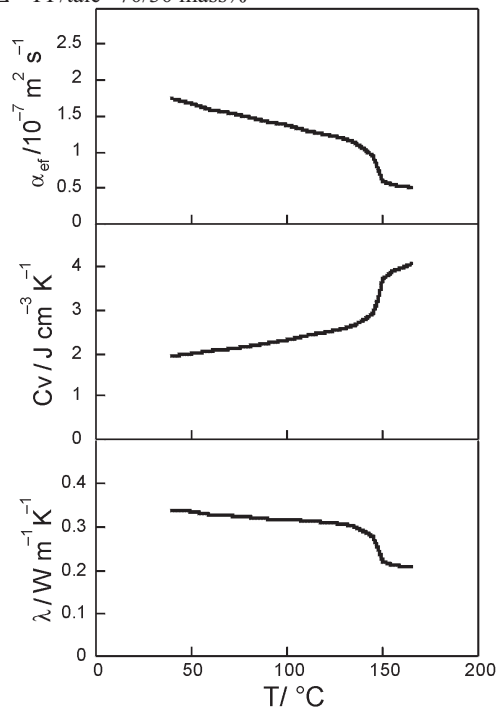
Fig. 7 Temperature dependence of thermal properties of poly(propylene)

Table 2 The change of α_{ef} about the change of temperature of PP/talc composites during the process tempreature

Mass fraction/%	T_{c_1}/°C	T_{c_2}/°C	ΔT_{c_1}/°C $T_{c_2}-T_{c_1}$	$\Delta\alpha/\Delta T$ (10^{-7} m^2 s^{-1} K^{-1})		
				$50\sim T_{c_1}$	$T_{c_1}\sim T_{c_2}$	$T_{c_2}\sim 170$
100/0	135.3	149.8	14.5	6.42	32.0	6.88
90/10	137.7	151.6	13.9	7.02	33.5	8.86
80/20	139.5	152.6	13.1	7.80	35.5	10.0
70/30	141.4	153.5	12.1	8.66	36.5	9.8

The change of ΔT_c ($=T_{c_2}-T_{c_1}$) for crystallization process is also related to the influence of talc. The addition of talc leads to decrease of the crystallization period. The resulting α_{ef} shows a good correspondence with these relations.

Thermal conductivity

Thermal conductivity was calculated from $C\alpha^{1/2}$ measured by the second measuring method. Figure 7 shows the temperature dependence of α, C, and λ in poly(propylene). α and λ showed an upward tendency about decrease temperature, but C shows an opposite tendency. Nevertheless, all properties have a sharp change during the crystallization process.

The accuracy of measured λ of PP was confirmed with the data obtained by other methods [20]. However, it is difficult to compare this for PP-base composites, because of insufficient number of the measurements. As for the unknown materials, the numeric model is effective for comparing the high order structure. Table 3 shows α_{ef} and λ_{ef} at 40 and 165°C of PP-base composites.

**Table 3** Thermal property of poly(propylene)-based composites at solid and liquid state

Material	Comp./ mass%	Thermal diffusivity (10^{-7} m^2 s^{-1})		Thermal conductivity (W m^{-1} K^{-1})	
		40°C	165°C	40°C	165°C
PP	100	1.74	0.512	0.339	0.208
PP/EPR	80/20	1.48	0.534	0.314	0.206
	70/30	1.30	0.561	0.286	0.218
PP/EBR	90/10	1.65	0.565	0.329	0.226
	80/20	1.45	0.607	0.309	0.229
	70/30	1.40	0.616	0.306	0.228
	60/40	1.19	0.686	0.260	0.220
PP/talc	90/10	1.93	0.707	0.352	0.242
	80/20	2.00	0.783	0.363	0.258
	70/30	2.26	0.959	0.382	0.283

The morphology in PP/EPR is the so-called sea and island structure as observed by microscopy [21]. The structure of these materials corresponds to a parallel structure as thermal conduction model. So it can be assumed that PP/EPR or EBR has a
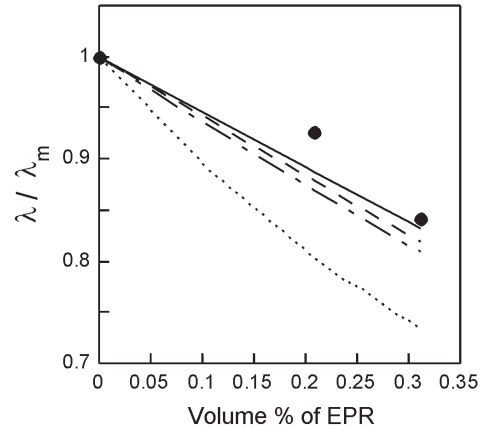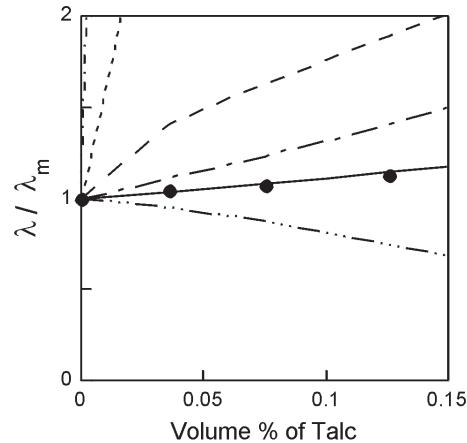
Fig. 8 Comparing the measured and the calculated thermal conductivity with some
models in PP/EPR composites; — parallel, ⋯⋯ series, – - – Ray–Maxwell,
– – – Russel, ● – measured
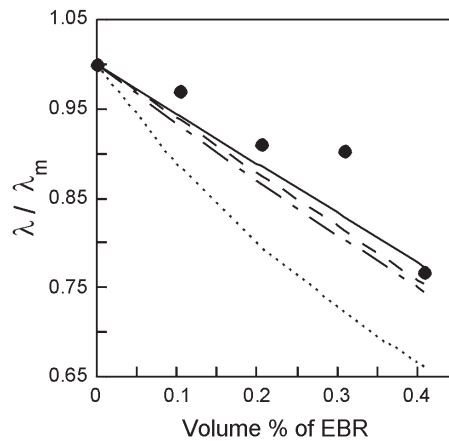
Fig. 9 Comparing the measured and the calculated thermal conductivity with some
models in PP/EBR composites; — parallel, ⋯⋯ series, – - – Ray–Maxwell,
– – – Russel, ● – measured

parallel structure. Figures 8 and 9 show a comparison of the results obtained by the
measured λ_{ef} and the useful thermal conductance model [13] in PP/EPR and PP/EBR
composite, respectively. The calculated values by parallel model show a lower value
than the measured λ_{ef} (closed circle in figure). From the previous reported data about
a parallel structure model, it is known that the parallel structure had a preferential
conductance path regardless of volume contents [17]. Moreover, the tendency of
preferential conductance is different with the component sets, so these blends may
have a parallel structure. However, it is hard to define the structure of PP/EPR or
EBR composite as a parallel model.

Fig. 10 Comparing the measured and the calculated thermal conductivity with some
models in PP/talc composites; ····· parallel, ── series, – - – Ray–Maxwell,
– – – Russel, -·-·- Ribaud, –···–Tye, ●– measured

Figure 10 shows the compared result with the measured λ_{ef} and the various thermal conduction models in PP/talc. The measured λ_{ef} shows a good agreement with a series model. In the case of PP/talc, the surface of talc acts as a nucleating agent for crystallization and increases the crystallinity [19]. Accordingly, it is considered that PP/talc composite has a series structure composed with a thin talc membrane and PP phase.

Conclusions

The heat capacity per unit volume and thermal conductivity of a PP-based composite was measured by temperature wave analysis that is measured by changing the dimension of sample and backing materials. The thermal diffusivity of PP-based composite showed different temperature dependencies in the melting and the crystallization process. The effect of EPR, EBR and talc was confirmed in the thermal diffusivity and thermal conductivity of the composite. The measured thermal conductivity was conformed as a reasonable value and the structure of PP/talc was analyzed as a series type from the measured results and the thermal conductance model.

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