Thermal Characteristics of Silver Powder-Filled Polypropylene Composites

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SYNOPSIS

The thermal properties of silver powder-filled polypropylene composites were studied as a function of filler concentration. Thermal conductivities of the composites increased with filler content. Comparison of the data with theoretical predictive models for two-phase systems showed that the Nielsen equation agreed reasonably well with the measured values. A TGA study showed that presence of silver powder increased the thermal stability of polypropylene through an increase in activation energy. The thermal expansion coefficient of the composites exhibited a decrease in the presence of Ag powder. Surface treatment of Ag powder with a titanate coupling agent marginally increased thermal conductivity and decreased thermal expansion coefficient values, implying a degree of enhance adhesion of the filler with the polymer. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Conductive polymer composites made by the incorporation of metal powders into thermoplastics are an emerging group of engineering materials[1-5] suitable for a number of applications such as discharging static electricity, heat conduction, EMI shielding, electrical heating, and converting mechanical to electrical signals. These materials are more cost-effective and noncorrosive than are metals and very often need single-step molding compared to multi-step fabrication for metals. Furthermore, the conductivity level can be "tailor-made" to fit varying levels of conductivity. This offers enormous design flexibility for part fabrication.

It should be noted that with increase in electrical conductivity, thermal conductivity will also be enhanced. Higher rates of heat dissipation could be extremely useful for some applications, either to reduce hot spots or to act as a heat sink, in particular for a thermally sensitive component.

In these particulate-filled systems, a significant problem is caused by the nonuniformity of dispersion of the discrete phase in the matrix, giving rise to fluctuations in the composite properties.[5-8] Surface modification of the filler partly by a suitable coupling agent reduces this problem by enhancing surface interaction between the two phases. Accompanied effects are reflected in the optimization of rheological and mechanical properties and ease of processing.

In this communication, we report a study on the thermal characteristics of silver (Ag) powder-filled isotactic polypropylene (i-PP) as a function of silver content. Thermal conductivity was estimated at varying Ag concentration in the composites and the data were compared with some of the theoretical models for two-phase systems. Thermal stability and the thermal expansion coefficient have also been studied as functions of filler contents. The effect of surface modification of Ag with a titanate coupling agent LICA-38 has also been studied.

EXPERIMENTAL

Materials

The isotactic polypropylene (i-PP) used was Koylene M0030 (density 0.90 g cm^{-3}, MFI 10) obtained from Indian Petrochemicals Corp., Vadodara, India. Laboratory-grade silver metal (Ag) powder packed under argon (density 10.43 g cm^{-3}) was obtained from Sisco Research Laboratories, Bombay. The average particle diameter of Ag powders estimated by a SEISHIN photomicronizer unit was 6.3 μm.

Silver particles were surface-modified by a liquid titanate coupling agent neopentyl(diallyl)oxy, tri(dioctyl pyrophosphato)titanate, LICA-38, of chemical structure

$$CH_2=CH-O-CH_2$$
$$CH_3-CH_2-C-O-Ti-[O-P-O-P-(OC_8H_{17})_2]_3$$
$$CH_2=CH-O-CH_2$$
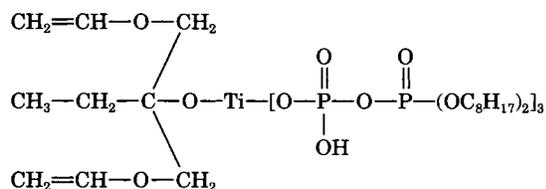
which was obtained from Kenrich Petrochemical Ltd., Bayonne, NJ.

Surface Modification of Ag

Silver powder was surface-modified in a high-speed mixer for 30 min using a toluene solution of LICA-38 (0.4 wt % on the basis of Ag). The treated powders were then dried for 4 h at 373 K and vacuum-dried at 353 K for 24 h.

Preparation of the Composites

Vacuum-dried i-PP and Ag (both untreated and treated) were compounded at 433 K on a two-roll mill for 15 min to prepare thin sheets containing 0–70 phr (0–5.6 vol %) Ag. Sheets of 3 and 8.5 mm in thickness were then compression-molded at 453 K and 34.4 MPa pressure for 5 min using chips from the primary sheets. Square-shaped specimens of 2.5 cm sides were machined from sheets 3 mm thick for the thermal conductivity measurements, while cylindrical bars of diameter 8 mm and length 90 mm were machined from sheets of 8.5 mm thickness for measurement of the coefficient of thermal expansion. Ground powdered samples were used for studying the thermal stability of the composites.

MEASUREMENTS

Thermal Conductivity

Thermal conductivity measurement was performed using a simple probe method suggested by Powell.[9–12] A schematic of the probe is shown in Figure 1. The probe[13] is a copper cylinder with a tapered base, the diameter and length of the probe being 30 and 35 mm, respectively. At its lower end, a similarly tapered stainless-steel cylindrical piece is threaded, which is axially drilled for fitting a small tube of the same metal. This small tube projects slightly beyond the taper section. Two Copper-Eureka thermocouples are differentially connected across the top of the cylinder and the lower end of the tube so that the temperature difference developed across the probe can be measured. Another thermocouple is fixed at the top of the probe to determine its temperature. The probe assembly is wound externally with nichrome wire for heating the probe, and the whole system is covered by insulating material to minimize heat loss.

It has been shown that if T_c is the temperature that is quickly reached at the point of contact by the spherical probe when it touches the experimental material and K_1 is the thermal conductivity of the
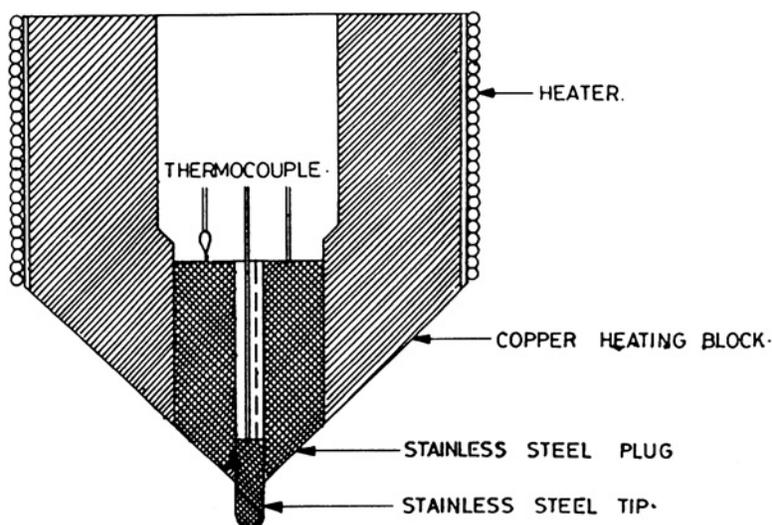
Figure 1   A simple probe for the measurement of thermal conductivity.
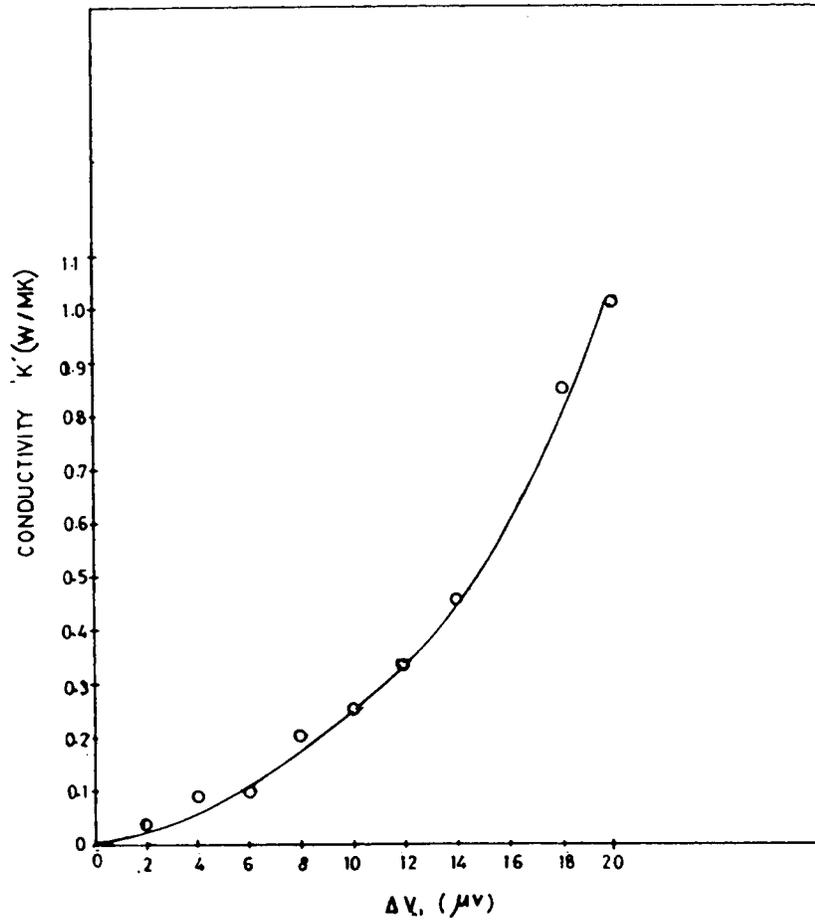
Figure 2 Calibration curve for the probe shown in Figure 1.

probe material, then thermal conductivity K_2 of the experimental material may be given by

$$T_c(K_1 + K_2) = T_0 \cdot K_1 \qquad (1)$$

where T_0 is the initial temperature. The difference between T_0 and T_c measured by differentially connected thermocouples is given by

$$\Delta V = T_0 - T_c \qquad (2)$$

or

$$\Delta V = \frac{K_2}{K_1 + K_2} \cdot T_0 \qquad (3)$$

Plotting known K_2 values for a few materials against ΔV values, a calibration curve[14] for the probe was obtained (Fig. 2). From the calibration curve, the unknown thermal conductivity of a material can be estimated. The calibration curve was generated

from known thermal conductivities of some materials presented in Table I. For best results, the probe should be heated 40 K above the ambient temper-

Table I Thermal Conductivities and Corresponding ΔV Values of Materials

Material	Thermal Conductivity	
	W/MK	ΔV (μV)
Polystyrene	0.037	2
Epoxy B	0.088	4
Epoxy C	0.104	6
Asbestos cement	0.20	8
Polytetrafluoroethylene (PTFE)	0.25	10
Low-density polyethylene (LDPE)	0.33	12
High-density polyethylene (HDPE)	0.45	14
Flint glass	0.85	18
Pyrex glass	1.1	20

ature. A Phillips dc microvoltmeter (Model GM 6020) was used for reading the temperature and the differential emf of the probe.

Thermal Expansion Coefficient

The study of thermal expansion coefficient of solid materials is important for engineering design. This property is a direct function of the bonding forces between the atoms in a solid material.

A push rod dilatometer[15,16] was used for measuring the thermal expansion coefficient values in this

study. This is a simple and reliable method to study the parameter using a cylindrical bar specimen of dimensions 90 mm long and 8 mm diameter. A schematic is shown in Figure 3. The equipment consists of a fused quartz push rod dilatometer, constant temperature bath, and an ice point cell. The dilatometer with a dial gauge attached at its top measures the change in length of the sample when the latter is shifted from the ice point cell to the bath at 353 ± 2 K or vice versa. A Mittotoyo dial gauge of range 0.001–1 mm with a least count of 1 mm was used for the measurement.
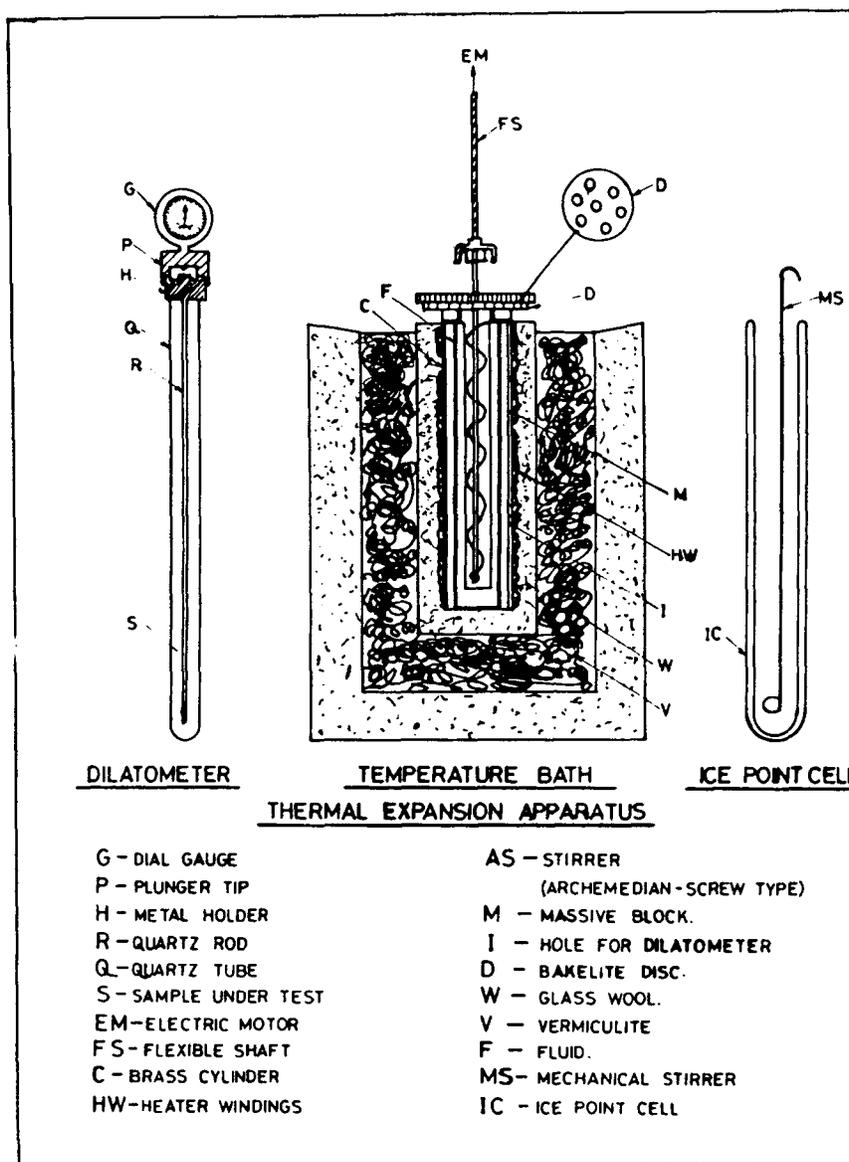
Figure 3 A unit for the measurement of thermal expansion coefficient.

Thermal Stability

A Dupont thermogravimetric analyzer (Model 1090) with Module 951 was used to study the thermal stability of the composites in nitrogen atmosphere, at a constant heating rate of 10 K/min.

RESULTS AND DISCUSSION

Thermal Conductivity

Thermal Conductivity Models

A large number of empirical and theoretical models[17-19] have been used to describe the thermal conductivity of polymer composites in view of the fact that this property is a bulk property analogous to viscosity and modulus. Comprehensive review articles[20,21] have discussed the applicability of many of these models that appear to be more promising. In this study, the models proposed by Maxwell and Eucken,[22] Petersen and Hermans,[23] Cheng and Vachon,[24] and Nielsen[25] were used to compare and describe the thermal conductivity of i-PP/Ag composites due to their wide applicability[4,26] in polymer composites. These models are presented below for reference.

Maxwell-Eucken Equation[22]:

$$K_c = \frac{K_p(B + 2) + 2(B - 1)\phi_f}{(B + 2) - (B - 1)\phi_f} \quad (4)$$

where $B = k_f/K_p$.

Petersen-Hermans Equation[23]:

$$K_c = K_p\left[1 + 3B\phi_f + 3B^2\left(1 + \frac{B}{4} + \frac{B^2}{256} + \cdots\right)\phi_f\right] \quad (5)$$

Table II Properties of Materials

Material	Thermal Conductivity (W/MK)	Thermal Expansion Coefficient α ($\times 10^6$) (M/MK)
i-PP	0.12	58–102
Ag	427	19

Values were taken from Refs. 27 and 28.

where

$$B = \frac{K_f - K_p}{2K_p + K_f}$$

Cheng-Vachon Model[24]:

$$\frac{1}{K_c} = \frac{1 - B}{K_p} + \frac{1}{XYC^{1/2}} \ln\frac{X + B/2C^{1/2}Y}{X - B/2C^{1/2}Y} \quad (6)$$

where

$$B = \left(\frac{3\phi_f}{2}\right)^{1/2}, \qquad C = 4\left(\frac{2}{3\phi_f}\right)^{1/2},$$

$$X = (K_p + B(K_f - K_p))^{1/2},$$

$$\text{and} \quad Y = (K_f - K_p)^{1/2}$$

Nielsen Expression[25]:

$$\frac{K_c}{K_p} = \frac{1 + AB\phi_f}{1 - B\psi\phi_f} \quad (7)$$

where

$$B = \frac{K_f/K_p - 1}{K_f/K_p + 1}, \quad \psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2}\right)\phi_f$$

$A = f$ (geometry of particles) and is expressed as $A = K_E - 1$, where K_E is the generalized Einstein coefficient, and ϕ_m = maximum packing fraction of the particles.

In eqs. (4)-(7), K_c represents composite conductivity; K_p, unfilled polymer conductivity; K_f, conductivity of the filler particles (Ag powder); and ϕ_f, volume fraction of the fillers.

The properties of the materials used are presented in Table II. The thermal conductivity of Ag and i-PP used were measured by the present method. The values show close agreement with published results.[27,28]

Figure 4 exhibits variation of thermal conductivity (K_c) of the composites as a function of volume percent ($\phi_f \%$) of Ag powder. In the i-PP/Ag (untreated) composites, K_c shows quite a sharp increase with ϕ_f. The value at the highest ϕ_f increased by two times that of unfilled i-PP. The increase in the K_c value at such low Ag concentration appears to be somewhat unusual compared to other studies.[29] It may be observed from the SEM photomicrographs of Ag powder (Fig. 5) that Ag particles were considerably agglomerated and a large fraction of these
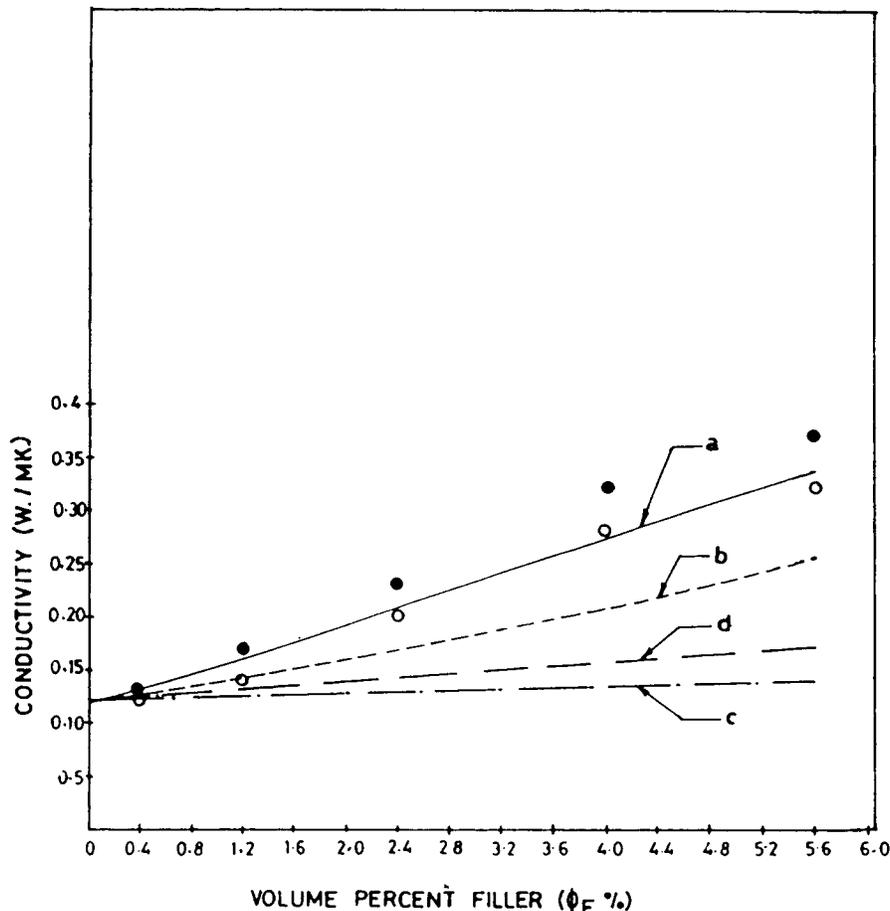
Figure 4 Comparison of experimental and predicted thermal conductivities of PP/Ag (open symbols) untreated and (closed symbols) treated composites: (a) Nielsen equation; (b) Maxwell-Eucken model; (c) Cheng-Vachon model; (d) Petersen-Hermans expression.

agglomerates possessed one dimension significantly larger than the other two. Some of these agglomerates would retain their shape despite the shearing forces acting during processing, so that a degree of dimensionality would be imparted to the composites. Possibly, this dimensionality contributed to the observed increase in thermal conductivity similar to other works.[29]

The variation of thermal conductivity at these ϕ_f values indicate that the conductive system is close to a dispersion system rather than to an attached system. This implies that the filler distribution in the system was random and the possibility of formation of conducting Ag chains was insignificant. However, since heat flow can take place through molecular vibrations and free electron movement, heat transfer is possible through the matrix polymer. Similar observations were reported in other works[29,30] also.

A similar variation of thermal conductivity was observed in i-PP/Ag (treated) composites; the values were, however, greater by 10–20% depending on the composition. These increased values may be partly due to a better degree of dispersion of the Ag particles sequential to breakdown of the agglomerates on surface treatment with the coupling agent (see Fig. 5) and removal of water of hydration as well as nonconducting air at the interphase of filler and matrix.[31]

Thermal conductivity data were compared with the models in Figure 4. For Nielsen's expression, the values of the shape factor A of the filler particles and the maximum packing fraction of the particles ϕ_m chosen were 30 and 0.82, which are the values for random fibers[32] with uniaxial random packing order,[33] in view of the elongated shape of the Ag particles (Fig. 5). For the untreated Ag-filled composites, the data showed reasonably good fit at low
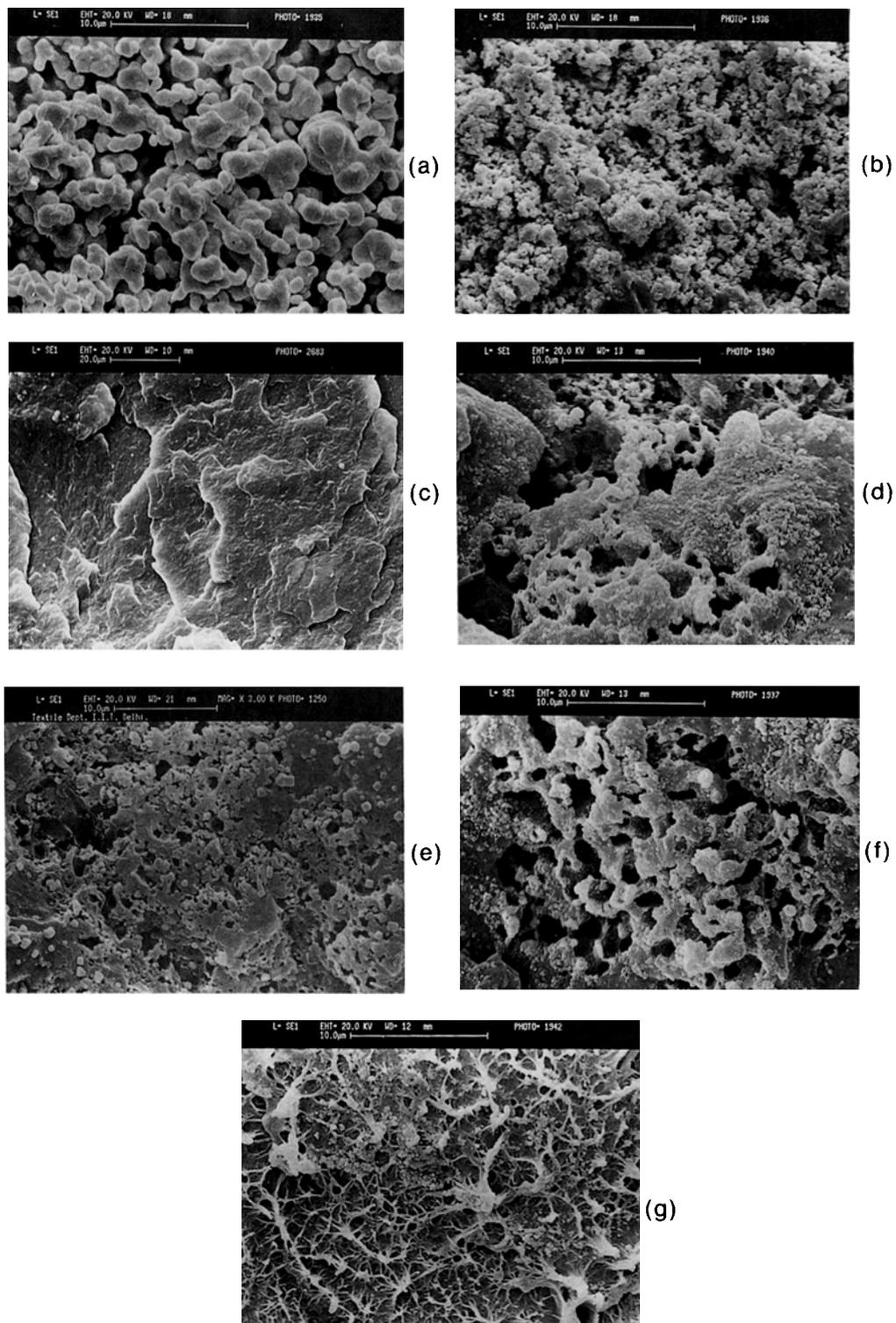
Figure 5 Scanning electron micrographs of (a) untreated Ag, (b) treated Ag, (c) PP, and dispersion of Ag in PP (d) PP/Ag 4.1 vol % untreated, (e) PP/Ag 4.1 vol % treated, (f) PP/Ag 5.6 vol % untreated, (g) PP/Ag 5.6 vol % treated.

Table III   Average Deviation Between Calculated and Experimental Thermal Conductivities for PP/Ag Composites

Sample Composition	Average Deviation (%)			
	Maxwell–Eucken	Petersen–Herman	Cheng–Vachon	Nielsen
PP/Ag 0.43%	0.64	0.113	0.742	1.13
	(0.064)	(0.59)	(0.035)	(0.42)
PP/Ag 1.3%	0.56	1.07	0.035	2.05
	(1.56)	(3.2)	(2.2)	(0.71)
PP/Ag 2.4%	1.97	5.03	3.67	0.77
	(4.09)	(7.15)	(5.79)	(1.34)
PP/Ag 4.1%	4.91	10.22	8.52	0.14
	(7.73)	(13.05)	(11.35)	(2.97)
PP/Ag 5.6%	5.25	12.61	10.68	1.34
	(8.78)	(16.15)	(14.22)	(2.19)

The values in the parentheses are for PP/Ag treated composites.

filler contents (ϕ_F up to 0.013) with all the models, the deviation being within 3% (Table III). With further increase in filler content, the data were much higher than those of the Maxwell–Eucken, Petersen–Hermans, and Cheng–Vachon models, whereas the data showed the closest fit with Nielsen's equation, the deviation on an overall basis being within 1.1‰. This may be due to the elongated shape of the particles, which was taken into account in the Nielsen's equation. The data with treated Ag-filled composites were greater than other models tested but showed good fit with Nielsen's equation, the deviation being 1.5% on an overall basis.

Coefficient of Thermal Expansion

The variation of the coefficient of thermal expansion (α) of the composites is presented in Figure 6 as a function of ϕ_f. The standard deviation values were within ±3‰. The α values of PP/Ag (untreated) composites decreased with increasing Ag content. Thermal expansion is directly related to bonding forces between atoms in a solid material,[16] so that polymers, in general, have much higher α values than most rigid fillers,[27,28] the latter having higher bonding forces. In the presence of Ag filler, the free volume content in PP decreases, which leaves reduced room for expansion of the polymer. This, in turn, reduces the α values in PP/Ag composites. With increase in Ag content, the extent of free volume decreases, decreasing the α values.

PP/Ag treated composites also showed the decreasing trend of α values with increasing ϕ_f; the values were even lower than the PP/Ag untreated composites at corresponding compositions (Fig. 6).

The decrease in α values may arise due to a degree of increased adhesion between Ag powder and PP matrix brought about by the titanate coupling agent which also removes the water of hydration of the filler.[31]

The α values measured for PP and PP/Ag composites are low compared to published values (Table II). This may be due to early mobility of the lower molecular weight and amorphous fractions (MFI 10) in a relatively broader molecular weight distribution ($M_w/M_n = 5$) of the PP under influence of increased thermal input. Decrease in thermal expansion coefficient with increase in Ag content as well as with surface-treated Ag implies better dimensional stability of the composites, making them potential materials for machine parts at elevated temperatures.

Thermal Stability Studies

Thermogravimetric analysis (TGA) of the PP/Ag composites showed (Figs. 7 and 8) that weight loss of PP in nitrogen commences at around 668 K, and upon incorporation of Ag powder, this temperature is increased. Total degradation takes place at around 750 K and the residue increases with increase in Ag content (Table IV).

In the TGA studies, one way of estimating thermal stability of polymers is estimation and comparison of initial decomposition temperatures (IDT) values.[4] IDT values were obtained from the TGA traces and plotted against ϕ_f in Figure 9. In the PP/Ag (untreated) composites, the IDT values increased significantly up to $\phi_f \approx 1.25$ and then the increase was only marginal. A similar trend was observed with PP/Ag treated composites; the IDT
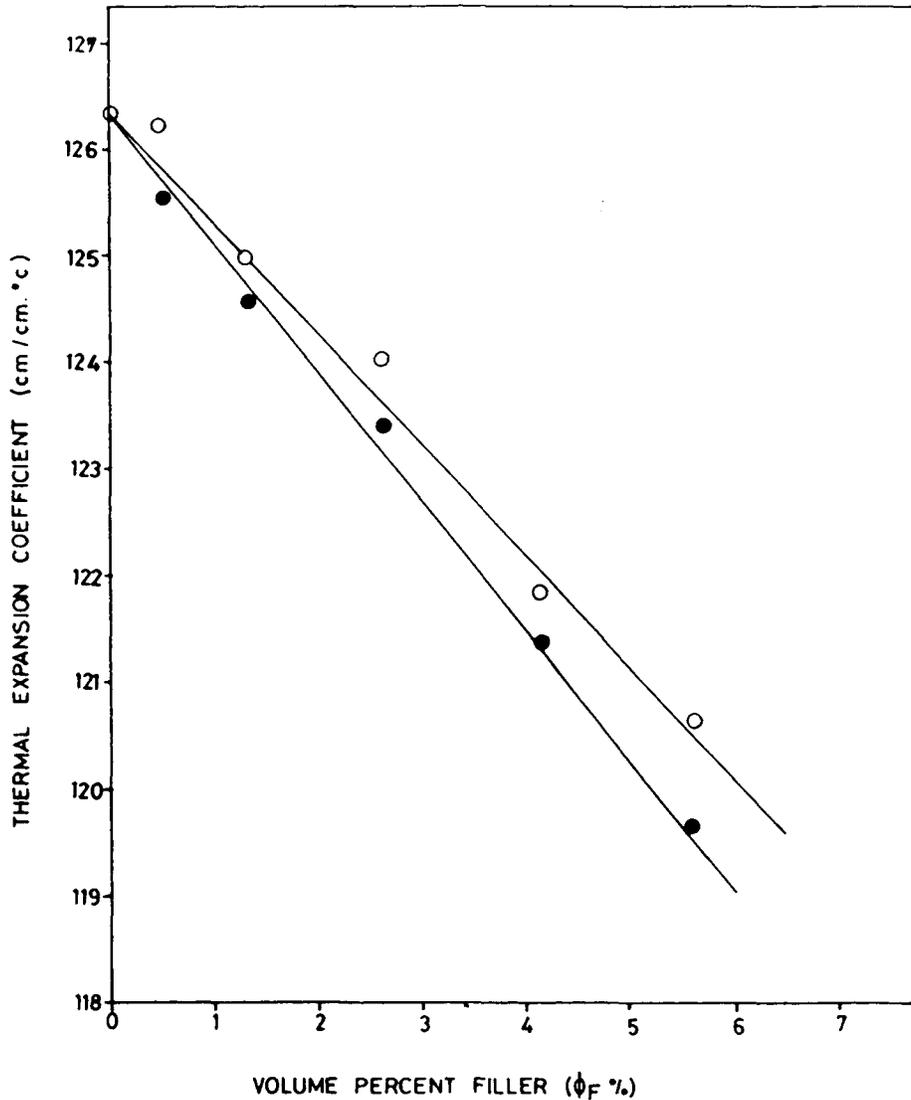
Figure 6   Variation of thermal expansion coefficient (α) against ϕ_f in PP/Ag (open symbols) untreated and (closed symbols) treated composites.

values were, however, lower by 10–20 K, in particular, beyond $\phi_f = 0.5\%o$. Early decomposition of the surfactant type of coupling agent may contribute to this.

To understand the enhancement in thermal stability, the activation energy of thermal decomposition of the composites was estimated according to the method described by Coats and Redfern.[34]

Using the equation

$$\log_{10}\left[-\frac{\log_{10}(1 - \alpha)}{T^2} \right]$$

$$= \log_{10} \frac{AR}{aE}\left[1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad (8)$$

where α is the fraction of compound decomposed at time t; a, the linear heating rate deg/min; A, the frequency factor; and E, the activation energy of the reaction, the plot of

$$\log_{10}\left[-\frac{\log_{10}(1 - \alpha)}{T^2} \right]$$

against $1/T$ should result in a straight line of slope $-E/2.3R$, from which activation energy for degradation can be calculated.

Such plots for PP/Ag untreated and treated composites are shown in Figures 10 and 11, respectively, and E values estimated from the slopes are presented in Table IV. The activation energy for
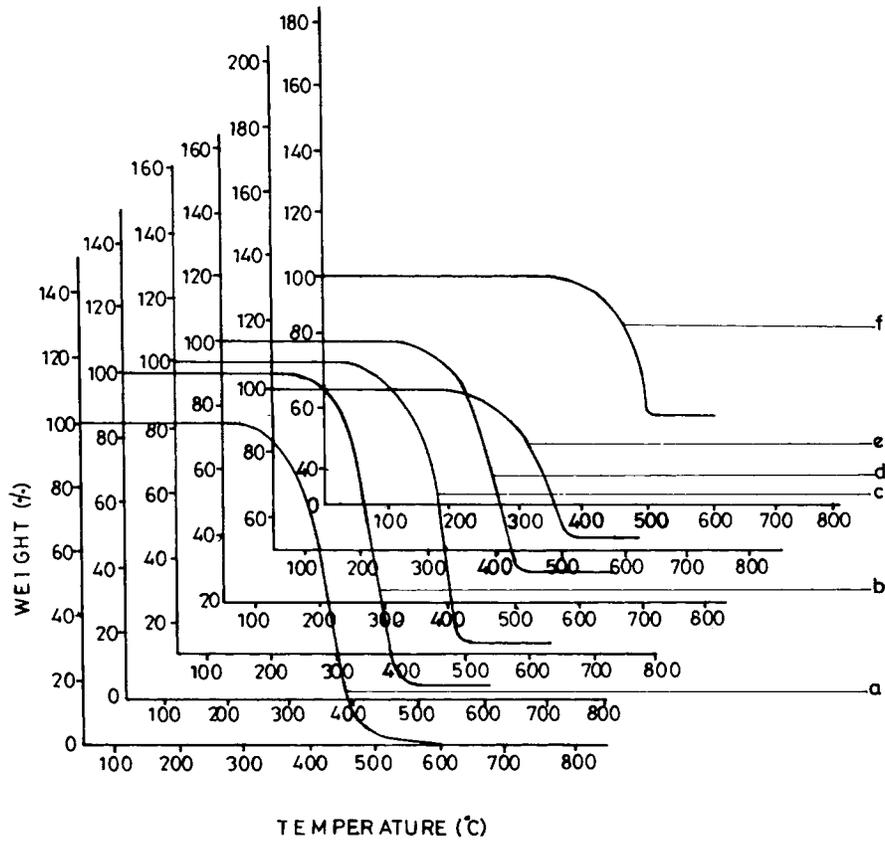
Figure 7 Thermogravimetric traces of PP/Ag untreated composites with varying Ag content (vol %): (a) 0.0; (b) 0.43; (c) 1.3; (d) 2.4; (e) 4.1; (f) 5.6.
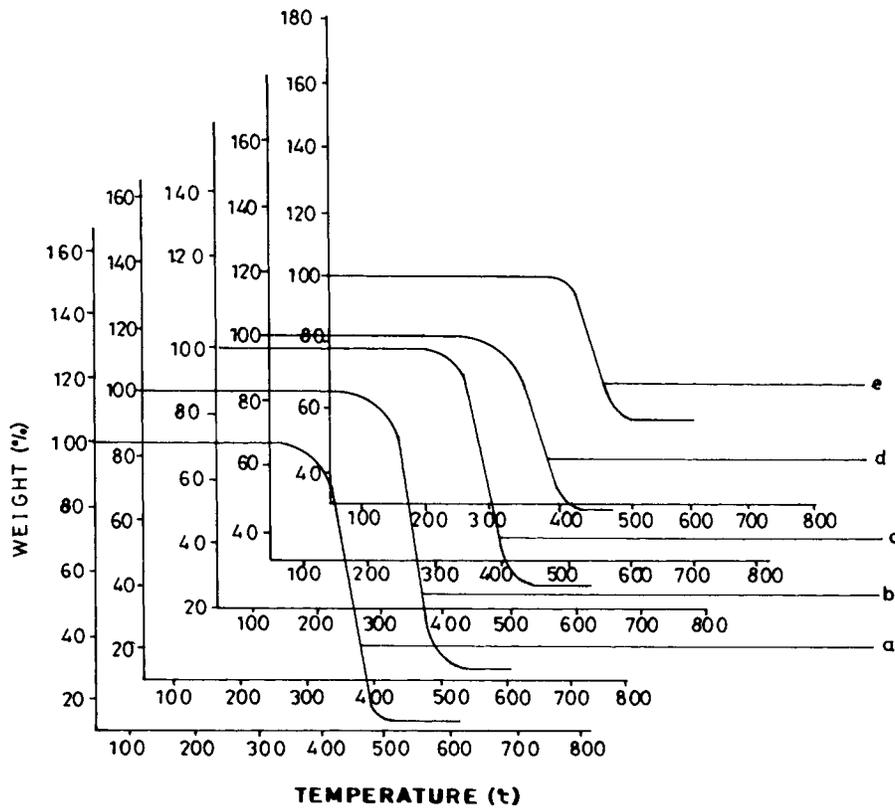
Figure 8 Thermogravimetric traces of PP/Ag treated composites with varying Ag content (vol %): (a) 0.43; (b) 1.3; (c) 2.4; (d) 4.1; (e) 4.6.

Table IV Activation Energy (ΔE) for Thermal Degradation and Residue (%) in PP/Ag Composites

Composition Vol % of Ag	Residue (%)	ΔE (kcal/mol)
0	0.13	30.68
0.43	4.5	34.50
	(3.91)	(40.48)
1.3	13.82	42.17
	(13.50)	(42.46)
2.4	30.67	41.40
	(28.33)	(50.18)
4.1	53.55	42.67
	(42.01)	(46.00)
5.6	60.29	54.63
	(52.69)	(46.00)

The values in the parentheses are for PP/Ag treated composites.

thermal degradation of PP/Ag untreated composites showed an increase up to ϕ_f = 1.3 and increases marginally beyond this ϕ_f. Thus, the activation energy increases may account for the increase in thermal stability of these composites. Increase in

thermal stability through increase in activation energy was shown in other work also.[35] Furthermore, metallic Ag almost always is enveloped with an oxide layer[2] that is not easily removable. The oxide may also be hydrated to a certain extent.[2] During heating of the sample, this water is expelled first, which takes away thermal energy in the form of latent heat of vaporization, thus aiding the thermal stability of PP, similar to other reports.[36] The increase in thermal stability may also arise in part from improved interfacial heat transfer. Better heat transfer due to enhanced thermal conductivity will reduce the chances of local overheating and formation of hot spots, delaying the thermal degradation of the polymer. Similar trends are observed for treated samples also.

CONCLUSIONS

The thermal properties—thermal conductivity, thermal stability, and thermal expansion coefficient—of PP/Ag composites have been studied. Thermal conductivity increased with Ag concentration although the increase was not dramatic. This
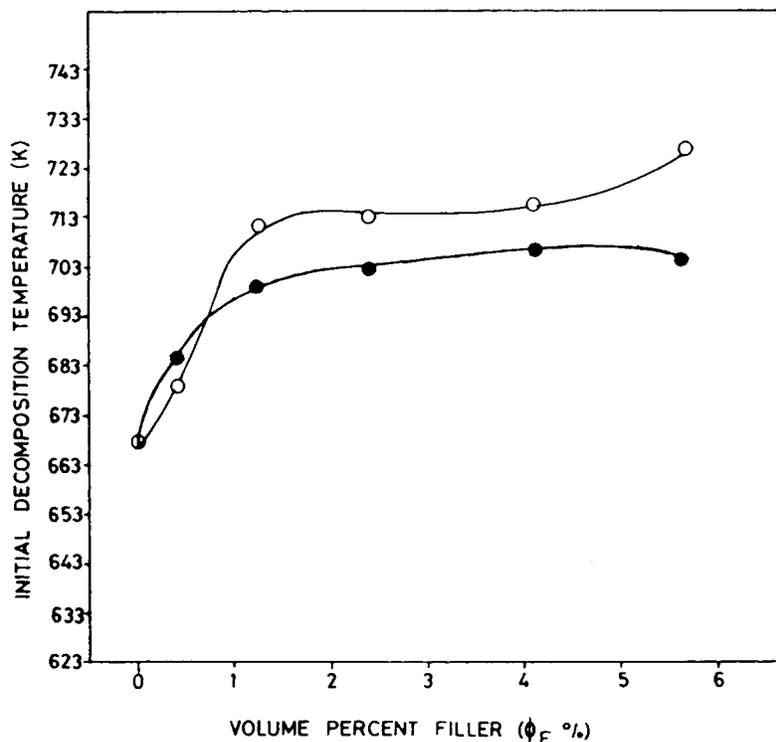
Figure 9 Plot of initial decomposition temperature (IDT) of PP/Ag (open symbols) untreated and (closed symbols) treated composites vs ϕ_f.
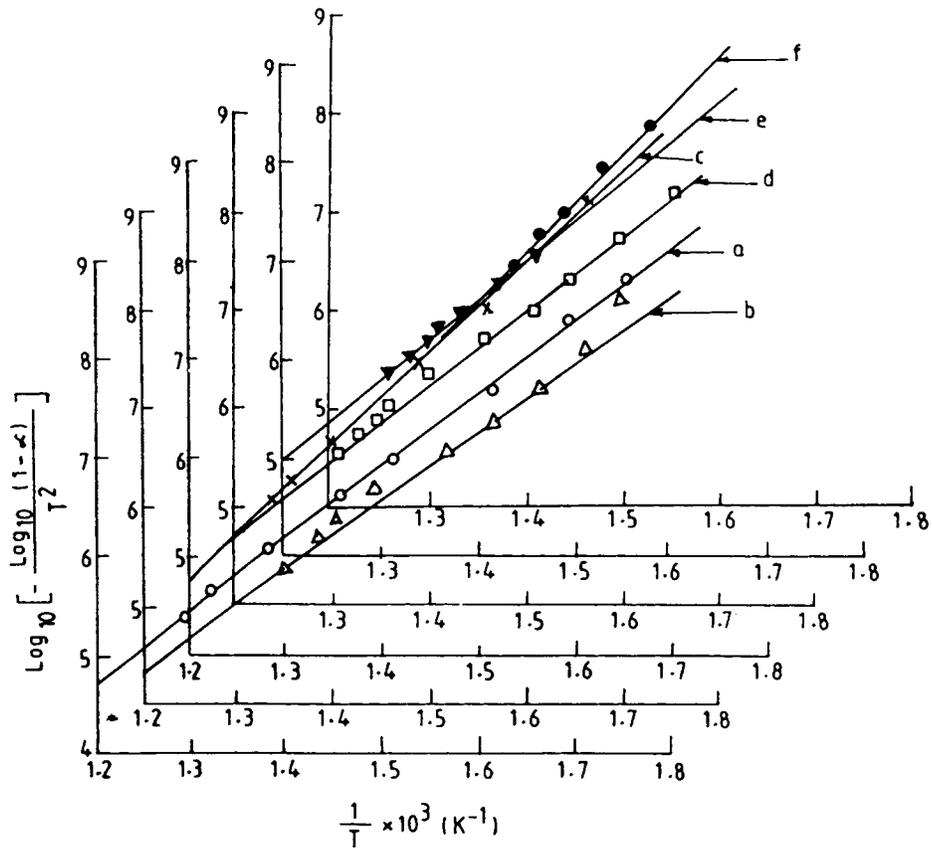
Figure 10 Evaluation of activation energy of thermal degradation of PP/Ag untreated composites at varying ϕ_f (%): (a) 0; (b) 0.43; (c) 1.3; (d) 2.4; (e) 4.1; (f) 5.6.
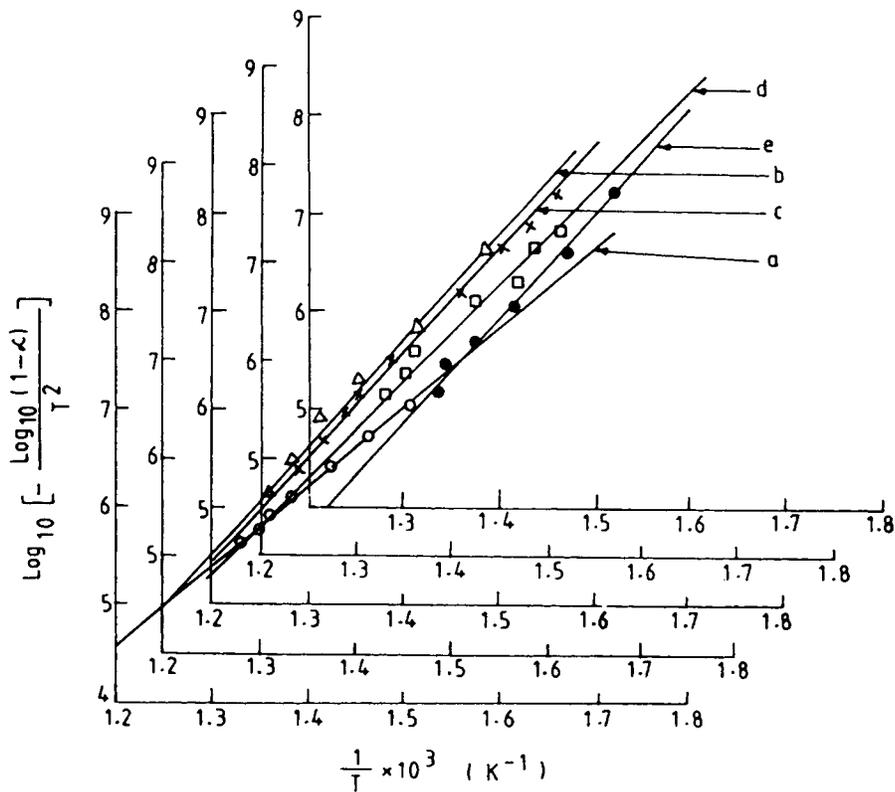
Figure 11 Evaluation of activation energy of thermal degradation of PP/Ag treated composites at varying ϕ_f (%): (a) 0.43; (b) 1.3; (c) 2.4; (d) 4.1; (e) 5.6.

is because thermal conductivity is a bulk property rather than a path-dependent property. The equation of Nielsen for thermal conductivity showed the closest fit with the data.

Thermal stability increased with Ag content. This has been attributed to an increase in the activation energy of thermal degradation in part as well as to an increase in thermal conductivity due to the presence of Ag.

Incorporation of Ag powder also decreased the value of the coefficient of thermal expansion, suggesting closer dimensional stability at elevated temperatures.

Surface modification of Ag with LICA 38 gives rise to a degree of improved adhesion of Ag with PP. This, in turn, contributed to marginally enhanced values of thermal conductivity and decreased thermal expansion coefficient. Thermal stability, however, is slightly decreased due probably to early degradation of the surfactant type of coupling agent.

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