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Thermochimica Acta 412 (2004) 139–147
thermochimica acta
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Thermal stability of epoxy-silica hybrid materials by thermogravimetric analysis

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Received 17 July 2003; received in revised form 14 September 2003; accepted 16 September 2003

Abstract

The thermal degradation behavior and thermal stability of epoxy-silica nanocomposites were studied with thermogravimetric analysis (TGA). Detailed and precise factors on the thermal stability based on the initial decomposition temperature (IDT), temperature of maximum rate of weight loss ($T_{\max}$), integral procedure decomposition temperature (IPDT), decomposition temperature range, and activation energy (E_a) of the decomposition reactions were studied. Introduction of nanoscale silica into epoxy resins certainly improved their thermal stability and reduced their weight loss rates, and the improvement can be further enhanced with using a phosphorous compound as the curing agent. The activation energies of the thermal degradation reactions of the nanocomposites were calculated from various methods, and the results from the Ozawa method provided reliable data. It was shown that the presence of nanoscale silica leveled up the values of the activation energies of the degradation reactions, and phosphorus group depressed the values of E_a.

Keywords: Epoxy; Silica; Thermal stability; Thermogravimetric analysis

1. Introduction

For compensating the thermal, mechanical, and other properties of the organic polymeric materials, inorganic fillers are added into the polymer formulations to form organic–inorganic composites. The property of a composite material, certainly, is depending on the properties of the individual components. On the other hand, the phase morphology and interfacial properties of the composites also significantly influence the properties of the composite materials [1,2]. Recently, using nanoscale fillers in formation of nanocomposites is highly interested in, owing to the formed nanocomposites exhibited high interfacial areas and exceptional properties [3–5]. Nanoscale spherical particles [6–10], nanotubes [8,11], and layered clay [5,12–14] are major fillers in preparation of nanocomposites.

Nanoscale colloidal silica (CS) is commercially available in both aqueous and organic solution types [15]. Direct blending the nanoscale silica and polymer solution provides a convenient route to form polymer-silica hybrid materials [8,9]. This method is relatively cheap and easy in operation due to without using alkoxysilane compounds and sol–gel process [6,7,16,17]. Poly(methylmethacrylate)-silica hybrid materials prepared form the above-mentioned approach showed reduced mass loss rate and heat release rate under heating [8].

Our work is interesting in the studies of epoxy-silica nanocomposites [6,18], due to the wide applications of epoxy resins as structural matrixes and adhesives in electronic/electrical products and other industrials. The nanoscale colloidal silica was found being capable of forming epoxy-silica nanocomposites with high silica loading and good miscibility [6]. In this paper, the thermal stability of the epoxy-silica nanocomposites was investigated with thermogravimetric analysis. Detailed and precise factors on the thermal stability based on the initial decomposition temperature (IDT), temperature of maximum rate of weight loss ($T_{\max}$), integral procedure decomposition temperature (IPDT), decomposition temperature range, and activation energy (E_a) of the decomposition reactions were studied [19–22].

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doi:10.1016/j.tca.2003.09.004

2. Experimental

2.1. Materials

Diglycidylether of bisphenol-A (DGEBA) was purchased from Chang Chun Plastics Co., Taiwan, with a commercial product code of BE188 (epoxy equivalent weight (EEW) = 185–190 g/mol). 4,4′-Diaminodiphenylmethane (DDM) and diethylphosphite (DEP) from Aldrich were used as received. Nanoscale colloidal silica was from Nissan Chemical Industries, Ltd. with a commercial product code of MIBK-ST (30 wt.% colloidal silica in methylisobutylketone (MIBK)).

2.2. Instruments

Thermogravimetric analysis was performed with a thermal analysis (TA) TGA 2050 thermogravimetric analyzer under nitrogen or air atmosphere. Heating scans carried out with various heating rates and isothermal scans at various temperatures were performed.

2.3. Preparation of epoxy-silica hybrid materials

Certain amount of BE188, curing agent (DDM or DEP), and MIBK (Table 1) were mixed together. After the solutes were completely dissolved, the desired amount of colloidal silica solution was added into the epoxy/curing solution. The mixture was stirred at room temperature for 3 h to obtain a homogeneous solution. The solvent was removed under vacuum and the residual was cured in an oven. The curing conditions for DDM and DEP curing compositions were 135 °C (1 h), 160 °C (1 h), 200 °C (2 h) and 150 °C (1 h), 180 °C (1 h), 230 °C (2 h).

2.4. Calculation of activation energies of degradation reactions

The degradation reaction of a polymeric material can be expressed as

$$\beta\left(\frac{d\alpha}{dT}\right) = k(T)\,f(\alpha), \qquad (1)$$

Table 1
Preparation of epoxy-silica hybrid materials

Sample	BE188 (g)	DDM (g)	DEP (g)	MIBK-ST (g)
DDM–CS0	10	2.5	–	0
DDM–CS5	10	2.5	–	2.1
DDM–CS10	10	2.5	–	4.2
DDM–CS20	10	2.5	–	8.4
DDM–CS30	10	2.5	–	12.6
DEP–CS0	10	–	3.7	0
DEP–CS5	10	–	3.7	2.3
DEP–CS10	10	–	3.7	4.6
DEP–CS20	10	–	3.7	9.2
DEP–CS30	10	–	3.7	13.8

where β is the heating rate (°C/min), α the conversion, $k(T)$ the rate constant function of temperature, and T the temperature (K). Applying a n order reaction for the degradation reaction to obtain

$$f(\alpha) = (1-\alpha)^n. \qquad (2)$$

Combining Eqs. (1) and (2) to result in

$$\frac{d\alpha}{(1-\alpha)^n} = \left[\frac{A\exp(-E_a/RT)}{\beta}\right] dT, \qquad (3)$$

where A is the preexponential factor and E_a the activation energy of the reaction. Eq. (3) is the basic analytical equation for thermogravimetric data. Based on this equation three approaches based on differential mode [23,24] and integral mode [25–28] were applied for calculation of the activation energies of the degradation reactions of the hybrid materials.

The Kissinger's method [23] involved the maximum temperature (T_m) of the first derivative weight loss curve. Therefore, Eq. (3) was differentiated with respect to T and the resulting expression set to zero. With some rearrangement the expression

$$\frac{-d[\ln(\beta/T_m^2)]}{d(1/T_m)} = \frac{E_a}{R} \qquad (4)$$

was derived. The activation energy (E_a) can be determined from a plot of $\ln(b/T_m^2)$ against $1/T_m$.

The Ozawa's method [24] involved the TGA data obtained at different heating rates and to give the values of activation energies at various conversions. With variable separation and integration of Eq. (3), the resulting Ozawa equation is

$$\log\beta = \frac{-0.4567E_a}{RT} + \left[\log\left(\frac{AE_a}{R}\right) - \log f(\alpha) - 2.315\right]. \qquad (5)$$

Therefore, the activation energy can be obtained from a plot of $\log\beta$ against $1/T$ at a constant α, where T is the temperature at conversion α.

3. Results and discussion

3.1. TGA analysis

The thermal stability of the epoxy-silica hybrid materials was measured with TGA (Figs. 1–4). The patterns of the thermogravimetric curves of the epoxy resins hybrid with silica were similar to the patterns of the silica-free resins, either under nitrogen or air atmosphere. This is reasonable since the thermal weight loss of the hybrid resins was coming from the organic epoxy resin part. On the other hand, the temperatures of maximum weight loss (T_{max}) of the DDM cured silica hybrid resins shifted toward high temperature region, as observed for other inorganic-modified resins [19]. The enhancement on the resins' thermal stability was especially significant for samples heated in air at

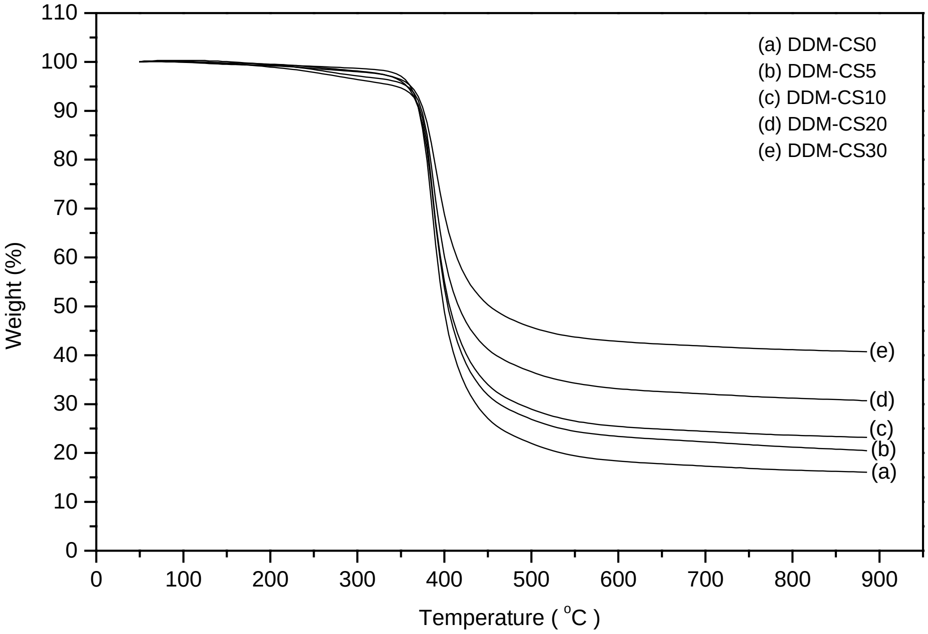

Fig. 1. TGA thermograms of DDM-cured epoxy-silica hybrid materials in N_2.

high temperature region (see Table 2, column T_{max} (Air-2) for DDM–CS series samples). The second stage of weight loss of an epoxy resin under air was referred to the oxidation of the residual formed from thermal decomposition of the resin at 200–400 °C [25]. Two points of inference can be read from the above experimental results. One is the silica particles can function as thermal insulating materials to the residual, and the other is only at high temperatures the thermal insulation effect of the silica can act effectively [26]. On the other hand, the low IDT and T_{max} of the DEP cured resins should be coming from the low bond energy of P–O bond to result in relatively poor thermal stability of the DEP–CS samples, as it can be seen in other phosphorus-containing polymers [27–29]. While heating in air, the epoxy hybrid materials cured with DEP showed higher T_{max} of the second stage of weight loss than did the DDM cured hybrid materials, to imply the residual of the DEP-cured resins having good oxidative thermal-stability since this stage of weight loss was from the oxidation of residual. On the other hand, the char yields of the hybrid resins increased with increasing

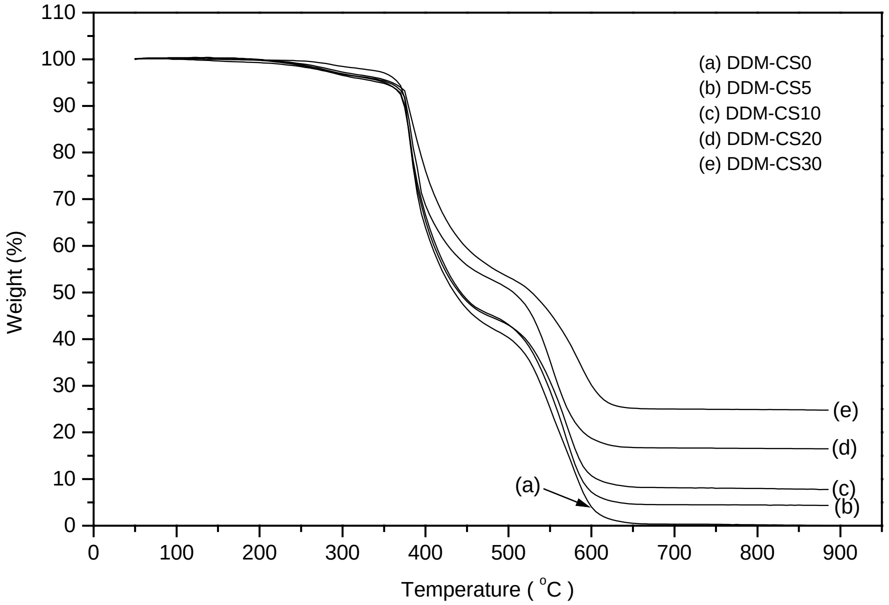

Fig. 2. TGA thermograms of DDM-cured epoxy-silica hybrid materials in air.

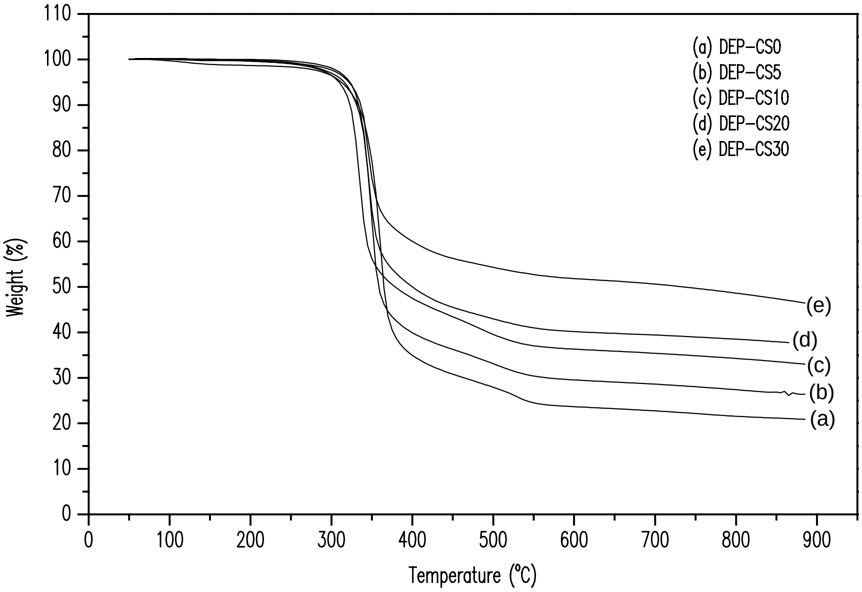

Fig. 3. TGA thermograms of DEP-cured epoxy-silica hybrid materials in N_2.

their silica contents. Using DEP as the curing agent also results in hybrid resins exhibiting high char yields. The residuals of the resins at high temperature mainly came from the inorganic silica part and the phosphorus-rich carbonaceous char [30]. The high char yields of the DEP cured hybrid resins also denoted that relatively less amounts of volatile small molecules were released under thermal decomposition, i.e. the hybrid materials possessing less volatile parts. The integral procedure decomposition temperature proposed by Doyle [21] has been correlated the volatile parts of polymeric materials and used for estimate the inherent thermal stability of polymeric materials [19–22]. The IPDT of the epoxy-silica hybrid materials were calculated from the TGA analysis curves and the results were collected in Table 2. First of all, all of the DEP cured hybrid resins showed higher IPDT's than did the DDM-cured hybrid resins, either in nitrogen or air atmosphere. An organophosphorus group in polymeric materials induced a series reactions of dehydration and carbonization to form thermally-stable char, and therefore to reduce releasing of volatiles [31]. On the other hand, the IPDT's increased with increasing the silica contents of the hybrid materials [22]. Increasing silicon contents

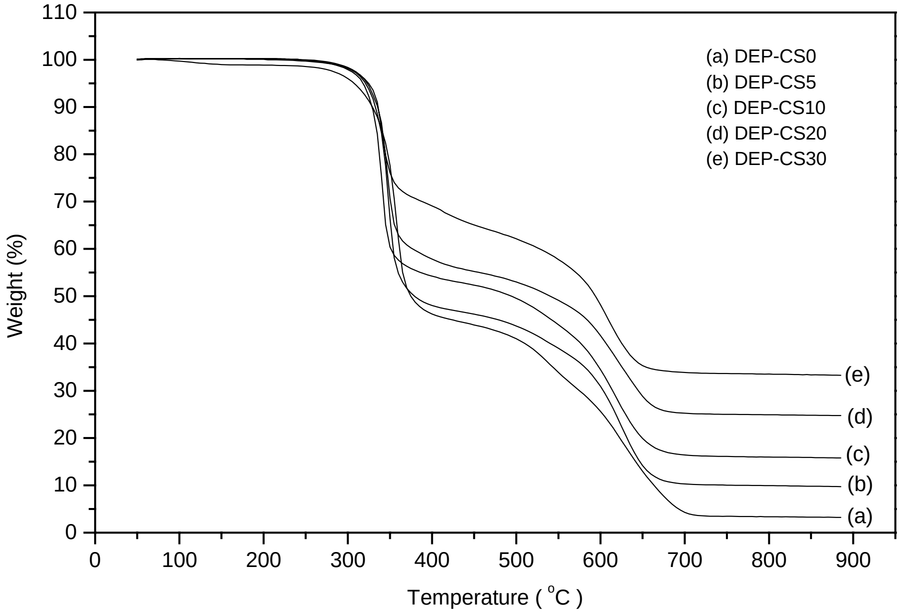

Fig. 4. TGA thermograms of DEP-cured epoxy-silica hybrid materials in air.

Table 2
Thermal stability data of the epoxy-silica hybrid materials from TGA

Sample	IDT (°C)		$T_{\max}$ (°C)			Char yield at 700 °C (%)		IPDT (°C)	
	N_2	Air	N_2	Air-1[a]	Air-2[a]	N_2	Air	N_2	Air
DDM–CS0	358	369	386	379	550	17.3	0.0	668	467
DDM–CS5	360	369	387	380	569	22.3	4.5	769	519
DDM–CS10	366	370	386	381	572	24.1	8.1	793	568
DDM–CS20	368	372	387	382	573	32.1	16.7	977	710
DDM–CS30	362	372	391	380	586	41.8	25.0	1420	888
DEP–CS0	310	309	360	358	626	22.7	4.3	757	495
DEP–CS5	313	317	350	348	626	28.6	10.3	904	582
DEP–CS10	313	317	341	341	621	35.4	16.4	1151	682
DEP–CS20	319	318	345	347	630	39.4	25.3	1327	877
DEP–CS30	316	319	345	340	607	50.6	33.9	1740	1132

[a] The first (Air-1) and second (Air-2) stage weight loss.

in the hybrid materials reduce their volatile fractions. Meanwhile, the good thermal stability and heat-resistant property of silica particles, which retarded the thermal degradation rate of the organic part of the hybrid materials, also contributed to level up the IPDT's of the hybrid materials. The high IPDT's of the hybrid materials further demonstrated their excellent thermal stability relative to the conventional epoxy resins.

The thermal stability of the epoxy-silica hybrid materials was also evaluated with TGA isothermal tests. Fig. 5 showed the TGA thermograms of some of the epoxy-silica hybrid materials heated under air at 300 and 400 °C. From the figure, it can be read out that the thermal stability of the epoxy resins were notably enhanced with loading colloidal silica. For DDM–CS30 and DEP–CS30, the weight loss at 300 °C was less than 10% in the long period of time (500 min). While heated at 400 °C, a rapid weight loss was observed at the beginning of the heating period. The results were coincident with the heating scan of TG analysis. Loading silica into the epoxy resins also showed great enhancement on improving the thermal stability of the epoxy resins. On the other hand, the different weight loss patterns of the hybrid materials from different curing agents were noteworthy. The hybrid materials using DEP as the curing agent exhibited a larger weight loss than the materials using DDM curing agent. This large weight loss could be correlated to the phosphorus group which possessing poor initial thermal stability. After the major weight loss, the weight loss curves of the DEP-based hybrid materials leveled off very soon and then followed with a very slow rate of weight loss. From the above results and discussion, it could be concluded that incorporation of colloidal silica into the epoxy resins significantly improved the resulting materials' thermal stability, especially under air atmosphere. Therefore, the colloidal silica could be considered as efficient oxidation-resistant filler. The improvement on the thermal stability of colloidal silica could also be further enhanced with incorporation of phosphorus into the compositions of the epoxy resins. That is, the colloidal silica and phosphorus showed a synergistic effect on improving the thermal stability of the epoxy-silica hybrid materials.

3.2. Kinetics of the thermal degradation

Both of the Kissinger's and Ozawa's methods involving TGA curves obtained at different heating rates were utilized in analyzing the kinetics of the thermal degradation reactions of the resins. Fig. 6 showed the examples of the plots for determining the activation energy of the hybrid materials' degradation reaction according to different methods. All of the data showed good coincidence with the proposed equations with the correlation factor square greater than 0.99. The activation energy data calculated from various methods were collected in Tables 3 and 4, and plots expressing the activation energies varying with degradation reaction conversions were also shown in Fig. 7. From the

Table 3
Activation energies (kJ/mol) of the degradation reactions of the epoxy-silica hybrid materials in nitrogen atmosphere

Sample	Kissinger's method	Ozawa method (at different conversion)						
		5%	10%	15%	20%	35%	50%	60%
DDM–CS0	194.5	108.6	155.7	168.2	175.0	177.6	191.9	258.4
DDM–CS30	185.6	178.7	174.0	177.3	179.1	180.0	–[a]	–[a]
DEP–CS0	139.0	112.8	138.8	150.2	153.9	154.7	159.2	–[a]
DEP–CS30	167.4	131.9	164.8	178.6	174.6	286.7	–[a]	–[a]

[a] Values could not be obtained owing to the high char yields of the samples.

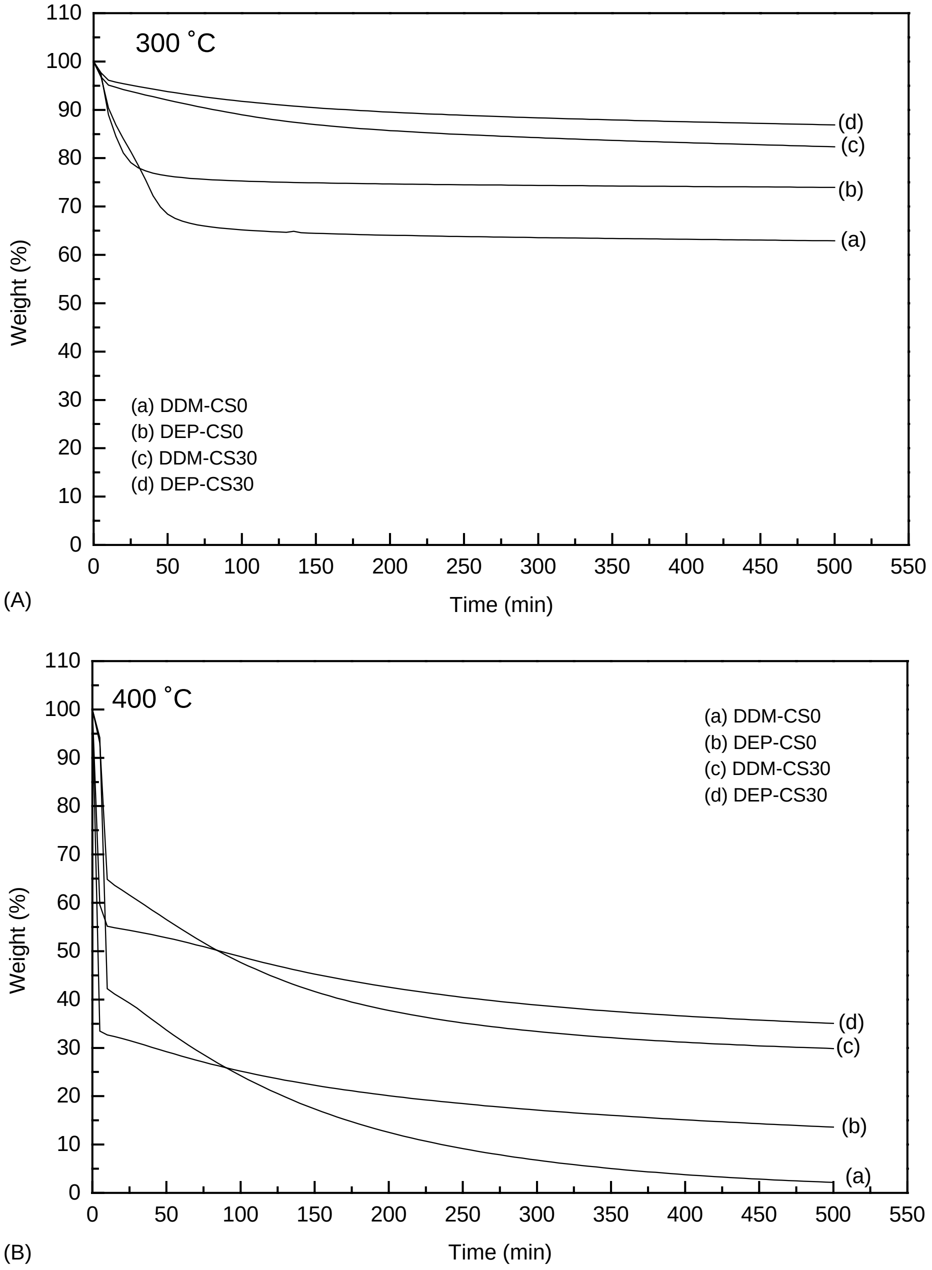

Fig. 5. Isothermal TGA thermograms of various hybrid resins at (A) 300 °C and (B) 400 °C.

Table 4
Activation energies (kJ/mol) of the degradation reactions of the epoxy-silica hybrid materials in air atmosphere

Sample	Kissinger's method		Ozawa method (at different conversion)											
	First stage	Second stage	5%	10%	15%	20%	35%	50%	60%	70%	80%	85%	90%	95%
DDM–CS0	178.7	188.8	113.5	130.6	144.1	151.2	155.6	–[a]	–[a]	399.0	207.2	154.0	130.3	140.5
DDM–CS30	144.4	184.1	165.5	191.3	202.0	202.3	215.6	–[a]	174.9	–[b]	–[b]	–[b]	–[b]	–[b]
DEP–CS0	222.3	294.6	189.6	191.9	192.7	194.5	288.3	–[a]	–[a]	199.9	178.3	162.6	143.9	125.3
DEP–CS30	134.0	115.7	124.7	148.6	153.8	168.0	–[a]	–[a]	133.9	–[b]	–[b]	–[b]	–[b]	–[b]

[a] Values missed owing to in the region an infinite slop was obtained from the plot of $\ln\beta$ vs. $1/T_m$.

[b] Values could not be obtained owing to the high char yields of the samples.

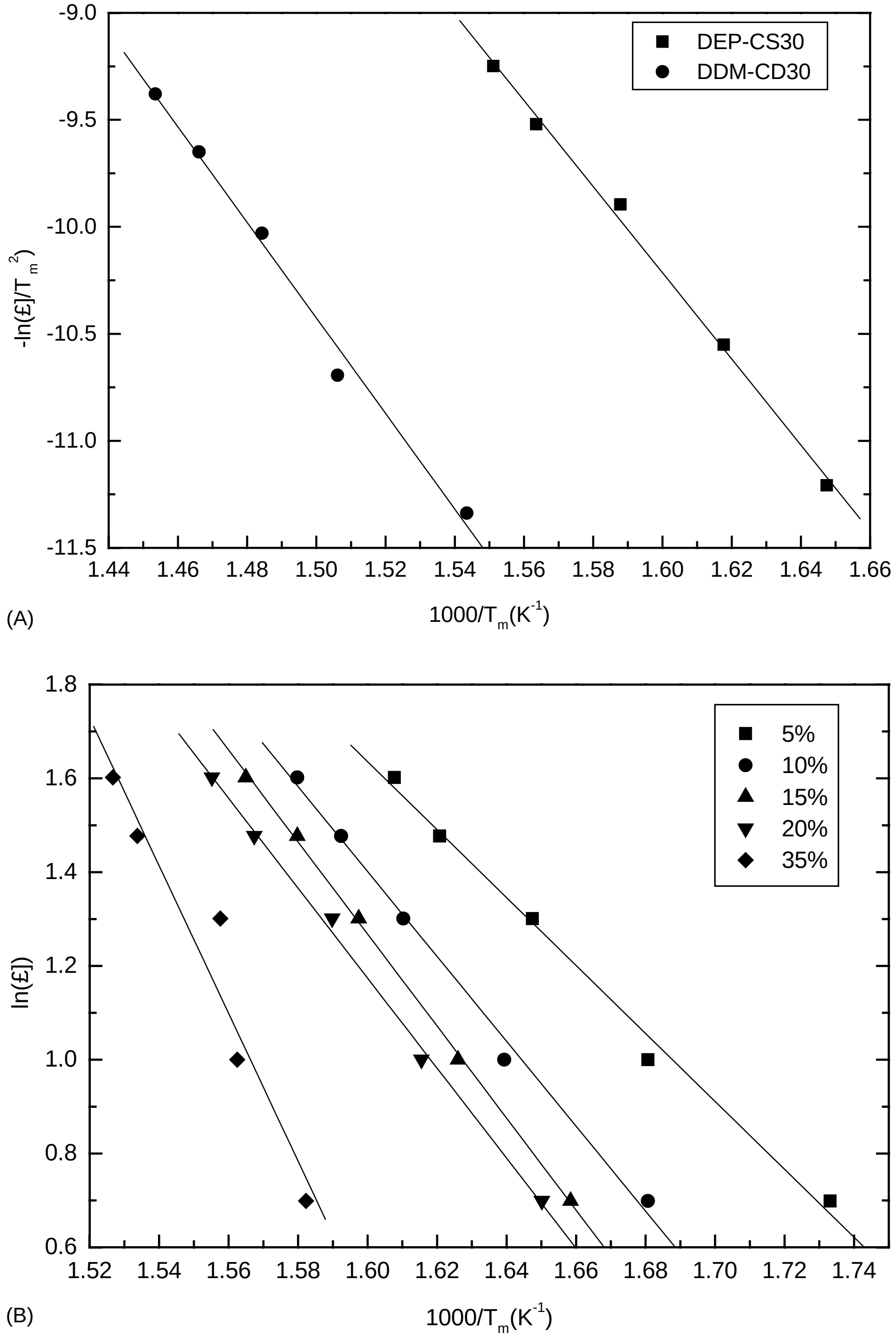

Fig. 6. The plots for determining activation energies of the degradation reactions of hybrid resins according to (A) the Kissinger's method (in N_2) and (B) the Ozawa method (DEP–CS30 in N_2).

TGA thermograms of the hybrid materials, it can be read that the thermal degradation of the materials was a complex process with multiple stages. Therefore, the apparent activation energies calculated from different mathematical approach might show wide variation in the analysis [32]. Based on the complicated degradation reaction mechanisms the data from Ozawa's method is considered more reliable, since The Ozawa's method is capable of providing activation energy data at all points on the TGA curves [33]. In the hybrid materials, both of the phosphorus group and silica might alter their thermal degradation process, being compared with the conventional epoxy resins (DDM–CS0). However, an opposite effect of phosphorus and silica on the activation energies was observed for the resins degrading in nitrogen. Introducing silica into the epoxy resin leveled up their activation energies of degradation and phosphorus depressed the activation energies. The enhancing effect of silica was understood with the thermal resistance of silica

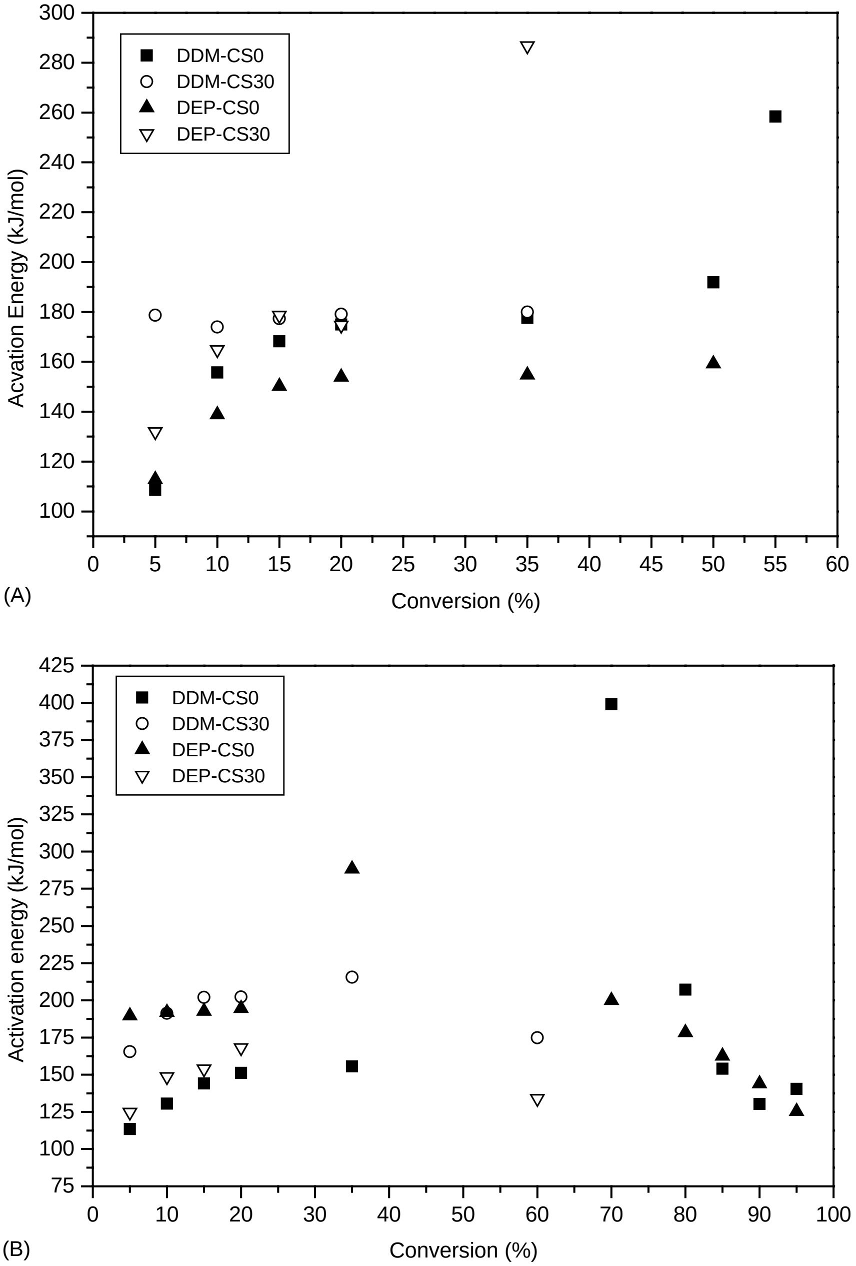

Fig. 7. The plots of activation energy (from Ozawa's method) against reaction conversions (A) in nitrogen and (B) in air.

that increased the energy demand for thermal degradation of organic resins. This effect would be certainly significant owing to the low potential energy of surface of silica, to result in the migration of silica to the surface of resins to form a heat-resistant layer. On the other hand, the low activation energy of the DEP cured resins was due to the weakness of the P–O bonds [34]. However, the values of activation energies for the DEP-cured resins heated in air showed different results. The high activation energy of DEP–CS0 in air might be owing to the formation of phosphorus-rich carbonaceous char, and this char has relatively thermal-oxidative stability. Moreover, DEP–CS30 showed a smaller value of activation energy than did DEP–CS0 for samples heated in air. This result is unusual if we just considered the activation energy as the parameter in analyzing degradation kinetics. However, for the complicated degradation mechanism of DEP–CS30, reaction model should also be included in the kinetics investigation [35]. Here we could not provide further comments, and this should be investigated in a future work through some other techniques, like GC/MS analysis on the TGA evolved gases and some other mathematical methods on analyzing the TGA degradation data, to dig out more information about the reaction mechanism and order of the degradation of DEP–CS resins.

4. Conclusions

The thermal stability and weight loss rates of epoxy resins were improved with introducing nanoscale colloidal silica to form epoxy-silica nanocomposites. The improvement can be further enhanced with using a phosphorous compound DEP as a curing agent. All of the organic–inorganic hybrid materials showed extremely high IPDT's with the synergistic effect of silica and phosphorus. The activation energies of the hybrid materials were calculated from Ozawa method with good reliance on the kinetic description of thermal degradation of the epoxy-silica hybrid materials.

Acknowledgements

Financial support on this work from the National Science Council of Taiwan, ROC (Grant no. NSC-89-2622-E-033-015) is highly appreciated.

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