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Effect of the interfacial structure on the thermal stability of poly(methyl methacrylate)–silica hybrids

Y.T. Wang [a], T.C. Chang [a,*], Y.S. Hong [a], H.B. Chen [b]

[a] *Department of Applied Chemistry, Chung Cheng Institute of Technology, National Defence University, Tahsi 335, Taoyuan, Taiwan, ROC*
[b] *Chemical Systems Research Division, Chung Shan Institute of Science and Technology, Lungtan 325, Taoyuan, Taiwan, ROC*

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Abstract

Poly(methyl methacrylate)–silica hybrid materials, P(MMA-MA5)–SiO_2 or P(MMA-GMA5)–SiO_2, were synthesized from the in situ reaction of the methyl methacrylate (MMA) with maleic anhydride (MA) or glycidyl methacrylate (GMA), then hydrolyzed with 3-aminopropyl methyl diethoxysilane (APrMDEOS) and tetraethoxysilane (TEOS) by a sol–gel process. The thermal stability and the apparent activation energies (E_a) of the PMMA moieties in the hybrids under air and nitrogen, evaluated by van Krevelen's method, were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). P(MMA-GMA5)–SiO_2 hybrids with the flexible chain of the coupling agent had the lower glass transition temperature (T_g) and E_a. Moreover, the structure of the coupling agent influences the thermal and thermo-oxidative degradation of the PMMA within the hybrids.

Keywords: Poly(methyl methacrylate); Silica; Hybrid; Degradation; Interfacial structure; Stability

1. Introduction

The mixture of a tetrafunctional silicon alkoxide and poly(methyl methacrylate) (PMMA) with the 3-(trimethoxysilyl)propyl methacrylate (MSMA) coupling agent, produces poly(methyl methacrylate)–silica, P(MMA-MSMA)–SiO_2, hybrid materials through variations of the sol–gel method [1–14]. The P(MMA-MSMA)–SiO_2 hybrids have been investigated focusing on the microstructure [8], morphology [9], mechanical properties [10], optical properties [11,12], and thermal stability [13,14]. In our previous work, the P(MMA-MSMA)–SiO_2hybrids were prepared by in situ polycondensation of alkoxysilanes in the presence of trialkoxysilane-functional PMMA, and the apparent activation energies (E_a) for the random scission of the PMMA segments in the hybrids were evaluated. It was found that SiO_2 greatly reduced the thermal stability of PMMA moieties, whereas that enhanced less the thermo-oxidative stability [15].

Recently, Xie et al. [16] condensed the poly(methyl methacrylate-maleic anhydride) copolymer with 3-aminopropyl trimethoxysilane coupling agent, and then hydrolyzed with tetraethoxysilane (TEOS) to prepare the transparent poly(methyl methacrylate-maleic anhydride)-silica hybrids, P(MMA-MA)–SiO_2, with amide bonds by a two-step process. They demonstrated the SiO_2 content had an influence on the mechanical properties of the hybrids. However, the imide-containing P(MMA-MA5)–SiO_2 (or amine-containing P(MMA-GMA5)–SiO_2) hybrids were

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[*] Corresponding author.
E-mail address: techuan@ccit.edu.tw (T.C. Chang).

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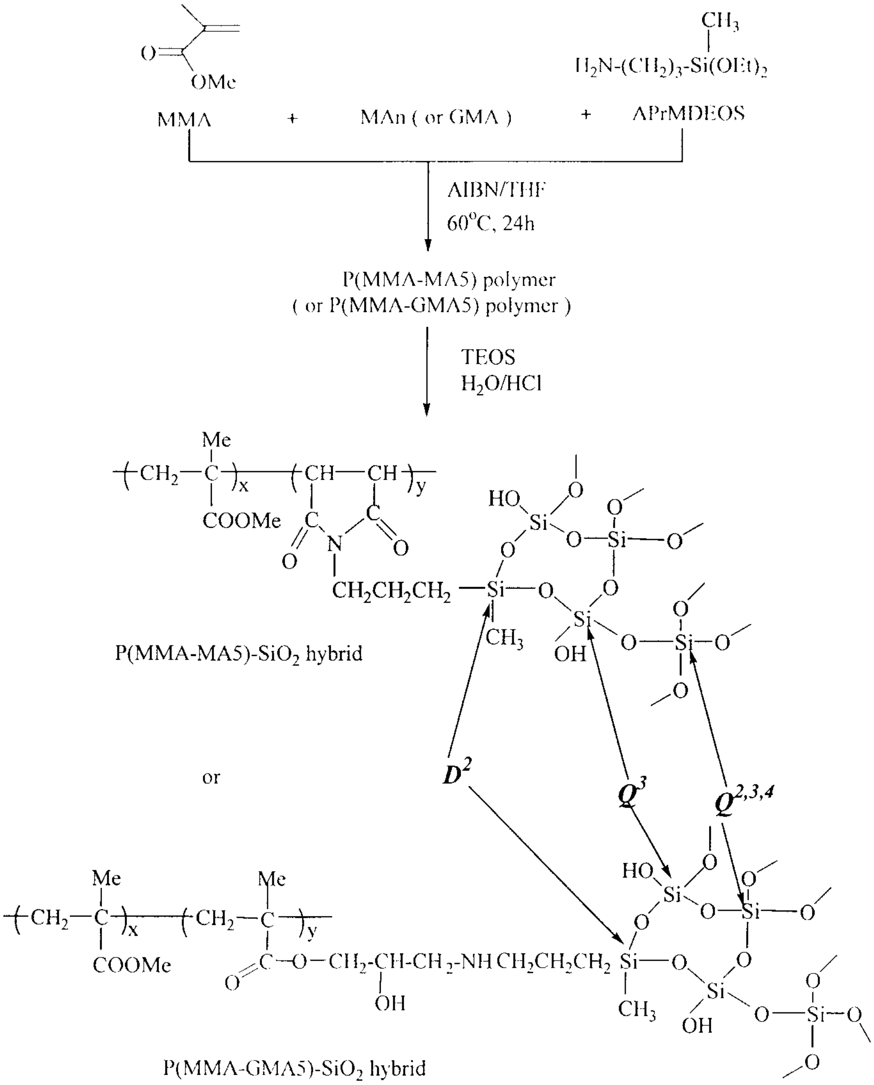
prepared by in situ additional polymerization of MMA, MA (or GMA), and condensation with 3-aminopropyl methyl diethoxysilane (APrMDEOS) coupling agent, then co-hydrolyzed with TEOS via the sol–gel technique. We found that the local segment dynamics and the average spin-diffusion path length of the hybrids were influenced by the interfacial (coupling agent) structure [17]. The effect of interfacial structure on the thermal property of the hybrids is further studied in this work by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The values of apparent activation energies (E_a) are evaluated by van Krevelen's method [18].

2. Experimental

2.1. Materials

The monomer methyl methacrylate (MMA; Janssen), was purified by distillation before use. Maleic anhydride (MA; Showa Chemical Inc.),



Scheme 1.

glycidyl methacrylate (GMA; TCI), tetraethoxysilane (TEOS, TCI), and 3-aminopropyl methyl diethoxysilane (APrMDEOS; Gelest Inc.) were used without purification. Azobisisobutyro nitrile (AIBN; BDH) was recrystallized from ethanol prior to use. Tetrahydrofuran (THF; Aldrich) was fractionally distilled in the presence of metallic sodium and benzophenone under a nitrogen atmosphere. Deionized water (18 MΩ) was used during the hydrolysis.

2.2. *Preparation of hybrids*

P(MMA-MA5)–SiO_2 and P(MMA-GMA5)–SiO_2 hybrids were prepared in situ by sequential synthesis, as shown in Scheme 1. In a typical example, a mixture of MMA (2.0 g), MA (0.1 g), APrMDEOS (0.2 g), AIBN (3.63×10^{-3} g), and THF (14 ml) was poured into a 250 ml round-bottom flask under nitrogen, and the solution stirred at 60 °C (24 h) to initiate the copolymerization of the methacrylic monomers. A desired amount of water (0.43 g), TEOS (1.24 g), and HCl with THF was added and then vigorously stirred for 10 min at room temperature. The resulting homogeneous mixture was poured onto a Teflon dish. After drying at room temperature for 24 h under atmospheric pressure, the film was heated for 3 h at 60 °C, 3 h at 100 °C, and finally 24 h at 150 °C under vacuum. Hybrid MA5-70 was obtained, where 70 donates that 70 wt.% of 95 mol% MMA with 5 mol% diethoxysilyl functional group condenses with 30 wt.% of TEOS based on the weight of monomer (MMA, MA, and APrMDEOS).

2.3. *Degradation of hybrids*

Differential scanning calorimetry (DSC) was conducted in a Perkin-Elmer 7 unit. The sample weight was 5 mg, and the scanning rate was 10 °C/min under nitrogen. The kinetics of degradation of the hybrids were measured using a Perkin-Elmer TGA-2 at a heating rate of 10 °C/min under air and nitrogen. The sample weight was about 10 mg, and the gas flow rate was kept at 100 ml/min.

3. Results and discussion

3.1. *DSC of hybrids*

The SiO_2 particles from the hydrolysis of TEOS decreases the free volume of the hybrids and makes the T_g increase. But the microparticles of SiO_2 fills in among the polymer molecules, making the interaction among the polymer molecules to decrease, therefore the T_g decrease [16]. The T_g of the P(MMA-MA5)–SiO_2 hybrids (∼124 °C) is independent of silica content (Table 1). The phenomenon is also observed in the P(MMA-MSMA)–SiO_2 hybrids (∼163 °C [15]; ∼150 °C [19]), revealing that the two effects are comparable in magnitude. On the other hand, the T_g of the P(MMA-GMA5)–SiO_2 hybrids decreases with increasing silica content. This dissimilar behavior, as observed from a comparison with the P(MMA-MA5)–SiO_2 hybrids, may be due to the uncondensed residual $Si(OH)_4$ [17] that

Table 1
The characteristic parameters of the degradation (10 °C/min) for hybrid materials

Hybrids	T_g (°C)	N_2/air			
		T_5 (°C)	T_m (°C)	Y_c (wt.%)	E_a (kJ/mol)
A: MA5-100	124	281/272	416/402	7.6/3.9 (4.0)	140/90
B: MA5- 90	123	309/291	412/395	13.6/8.0 (8.4)	122/82
C: MA5- 80	125	311/288	411/387	17.0/13.2 (12.2)	115/90
D: MA5- 70	123	309/290	410/374	23.2/18.5 (15.4)	97/111
E: GMA5-100	112	262/253	411/363	8.1/6.3 (2.9)	67/82
F: GMA5- 90	112	266/258	416/361	18.1/15.3 (7.7)	82/85
G: GMA5- 80	91	232/237	412/368	25.4/21.0 (11.8)	81/84
H: GMA5- 70	90	218/226	402/367	29.8/25.8 (15.3)	96/84

T_g: glass transition temperature; T_5: temperature of 5% weight loss; T_m: maximum rate temperature of weight loss; Y_c: char yield at 800 °C; E_a: activation energy for the degradation. The Y_c values in parentheses are evaluated by calculation method.

tends to create more free volume in the hybrid [20]. Moreover, the T_g value of hybrids is in the order P(MMA-GMA5)–SiO_2 < P(MMA-MA5)–SiO_2 < P(MMA-MSMA)–SiO_2 hybrid, suggesting that the structure of the coupling agent affects the flexibility of the PMMA in the hybrids.

3.2. Thermal degradation

Fig. 1 is the deconvoluted derivative thermogravimetry (DTG) curve of the MA5-70 hybrid under nitrogen. The broader peak at 360 °C refers to the scission of inherently weak head-to-head linkages [21,22] and vinylidene chain-end initiation [23], and the strong narrow component peaking at 416 °C originates from random positions by chain scission within the polymer [21,22]. Additionally, another shorter peak at 512 °C may be due to degradation of the SiO_2 network [15].

Fig. 2 shows the TGA and DTG curves of the P(MMA-MA5)–SiO_2 hybrids under nitrogen at a heating rate of 10 °C/min. Table 1 lists the characteristic data of the 5% weight loss temperatures (T_5), the maximum rate temperature of weight loss (T_m) and the char yield (Y_c) at 800 °C. The T_5 value of the P(MMA-MA5)–SiO_2 hybrids (∼309 °C) is larger than that in literature (∼260 °C) [16]. This suggests that interfacial structure in this study is imide bonding rather amide bonding. On the other hand, the T_m value of the P(MMA-MA5)–SiO_2 hybrids decreases with increasing silica content. The results reveal that SiO_2 retards the thermal scission of head-to-head linkage and vinylidene chain-end initiation, but enhances the random scission within the polymer chain. Moreover, the values of Y_c increase with increasing silica content, indicating that more three-dimensional silica network develops as the TEOS proportion increases.

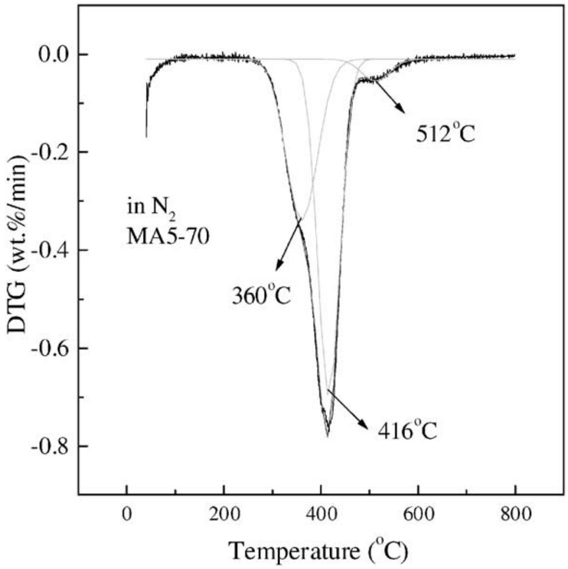


Fig. 1. The deconvoluted derivative thermogravimetry (DTG) curve of MA5-70 hybrid under nitrogen.

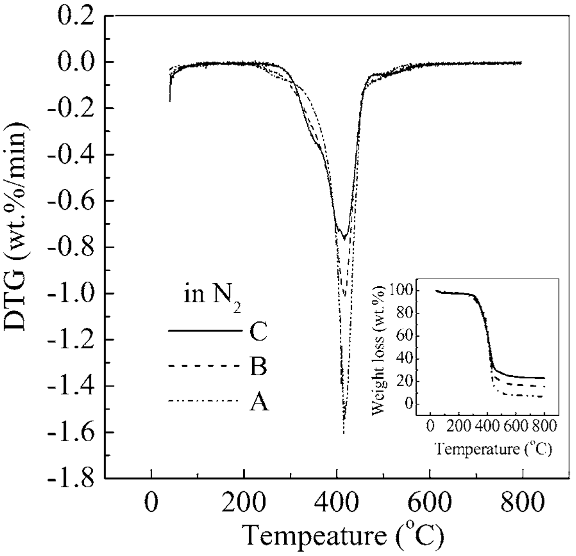


Fig. 2. TGA and DTG thermograms of hybrids (A) MA5-100; (B) MA5-85; (C) MA5-70 at the heating rate 10 °C/min under nitrogen.

The weight loss (TGA) and DTG curves of the P(MMA-GMA5)–SiO_2 hybrids under nitrogen display two main reaction steps (Fig. 3). The degradation at lower temperatures is due to scission of head-to-head and unsaturated chain ends of the polymer, while degradation at higher temperature is associated with random scission [24]. Interestingly, the value of T_5 of the P(MMA-GMA)–SiO_2 hybrids decreases with increasing silica content, while the value of T_m is around 411 °C. This indicates that SiO_2 enhances the initial thermal degradation of the PMMA segments containing amine bonds.

Fig. 4 shows the TGA and DTG curves of the MA5-70, GMA5-70 and MSMA5-70 hybrids under

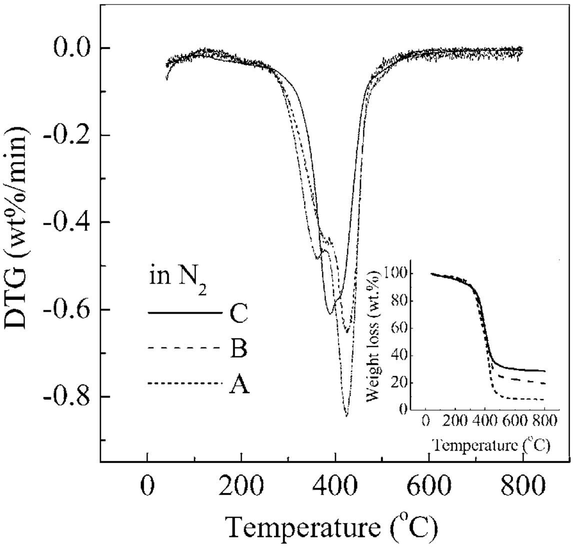


Fig. 3. TGA and DTG thermograms of hybrids (A) GMA5-100; (B) GMA5-85; (C) GMA5-70 at the heating rate 10 °C/min under nitrogen.

nitrogen. The T_5 value of hybrids is in the order MSMA5-70 < GMA5-70 < MA5-70. On the other hand, the T_m value of hybrids is in the order MSMA5-70 (402 °C) ≈ GMA5-70 (402 °C) < MA5-70 (410 °C) hybrid. This suggests that the structure of the coupling agent affects the thermal stability of the PMMA in the hybrids. The char yields (Y_c) are notably more than the calculated values (Table 1), and the difference between the calculated and experimental values is proportional to silica content. The results imply that other degradation products are produced. Moreover, the P(MMA-GMA5)–SiO_2 hybrids have the higher Y_c compared with P(MMA-MA5)–SiO_2 hybrids. This may be due to the contribution of amine interfacial structure that decreases the pyrolitic temperature, retards carbonization of PMMA, and increases pyrolysis residue.

3.3. *Thermo-oxidative degradation*

The deconvoluted DTG curve of MA5-70 hybrid under air is also fitted by three main reactions (Fig. 5). It can be seen that the temperature of maximum rate of weight loss (T_p) of each degradation step is about 360, 396 and 524 °C, respectively. The first stage is due to degradation of partially oxidized groups. These polymer chains are formed by oxygen trapping of the radicals that are generated from the weak linkages [21,22]. The second-step is an oxygen attack on the radicals that are generated by random scissions within

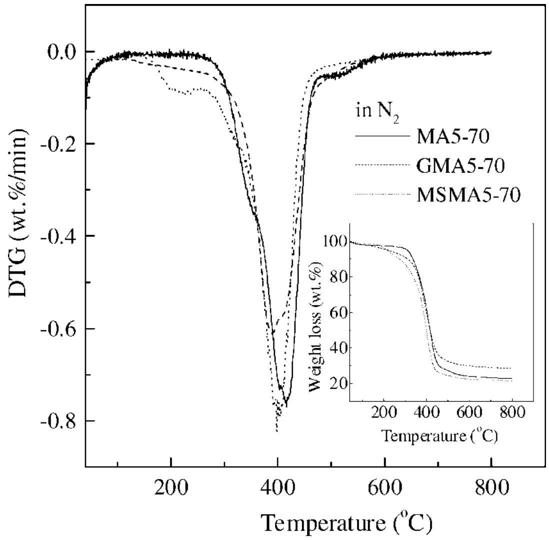


Fig. 4. TGA and DTG thermograms of hybrids (A) MA5-70; (B) GMA5-70; (C) MSMA5-70 at the heating rate 10 °C/min under nitrogen.

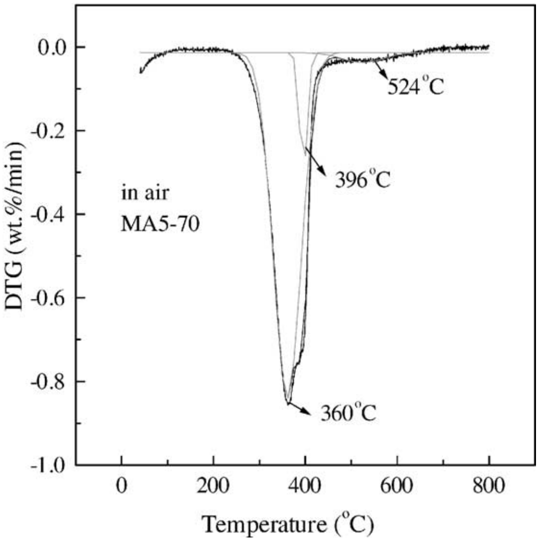


Fig. 5. The deconvoluted DTG curve of MA5-70 hybrid under air.

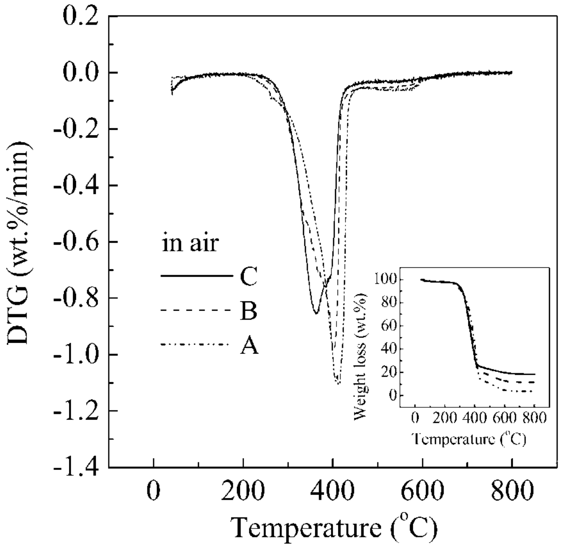


Fig. 6. TGA and DTG thermograms of hybrids (A) MA5-100; (B) MA5-85; (C) MA5-70 at the heating rate 10 °C/min under air.

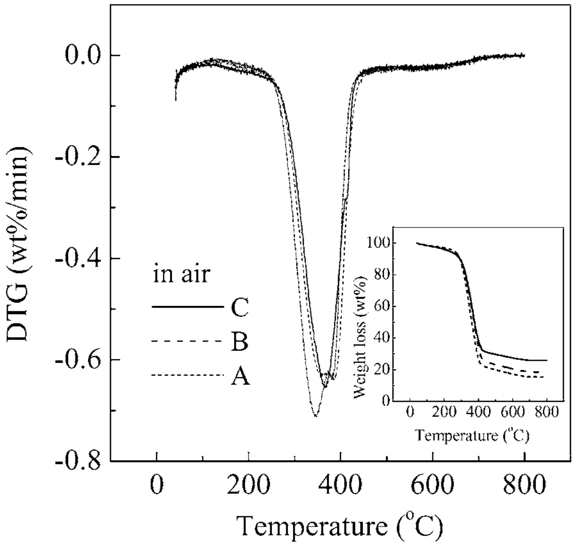


Fig. 7. TGA and DTG thermograms of hybrids (A) GMA5-100; (B) GMA5-85; (C) GMA5-70 at the heating rate 10 °C/min under air.

the polymer chains [21,22]. The third degradation step may be due to the SiO_2 network [15]. Fig. 6 shows that the T_5 of P(MMA-MA5)–SiO_2 hybrids (~290 °C) is larger than that of copolymer (272 °C), and the T_m of the hybrids decreases with increasing silica content. Therefore, SiO_2 retards the initial thermo-oxidative degradation of the PMMA segments, but it enhances the random scission.

The thermo-oxidative degradation of the P(MMA-GMA5)–SiO_2 hybrids (Fig. 7) is different from that of the P(MMA-MA5)–SiO_2 hybrids. The T_5 value of the P(MMA-GMA)–SiO_2 hybrids decreases with increasing silica content, while the value of T_m is around 365 °C. The results imply that SiO_2 enhances the degradation of the interfacial amine bond at initial stages.

Fig. 8 shows the TGA and DTG curves of the MA5-70, GMA5-70 and MSMA5-70 hybrids under air. The T_5 and T_m value of hybrids is in the order MSMA5-70 < GMA5-70 < MA5-70. The results reveal that the latter has the more stable interfacial structure. Thus, the apparent activation energy (E_a), evaluated by van Krevelen's method [18], for the hybrids in thermo-oxidative degradation may be in the order P(MMA-MSMA5)–SiO_2 < P(MMA-GMA5)–SiO_2 < P(MMA-MA5)–SiO_2.

3.4. Kinetic analysis

Figs. 9 and 10 represent the logarithmic plots for the degradation rate $g(\alpha)$ of the PMMA segments

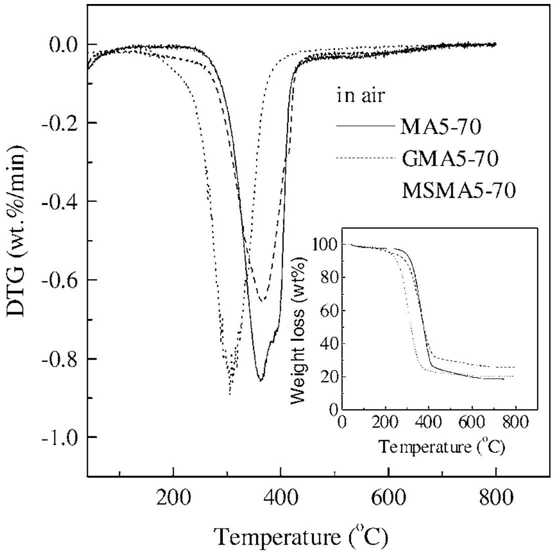


Fig. 8. TGA and DTG thermograms of hybrids (A) MA5-70; (B) GMA5-70; (C) MSMA5-70 at the heating rate 10 °C/min under air.

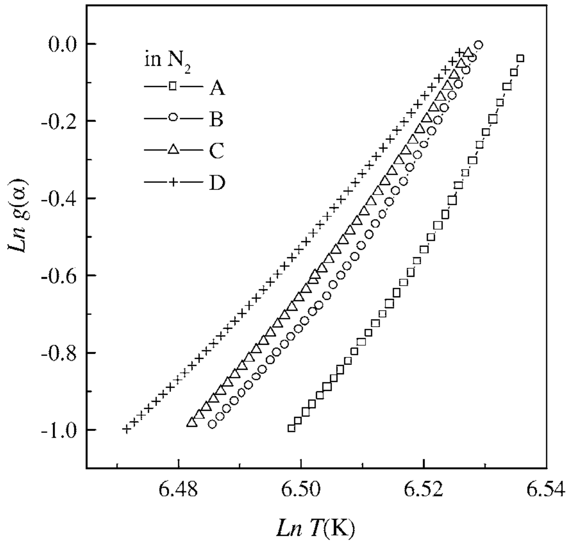


Fig. 9. Plot of $\ln g(\alpha)$ vs. $\ln T$ for thermal degradation of hybrids (A) MA5-100; (B) MA5-90; (C) MA5-80; (D) MA5-70 at heating rate10 °C/min under nitrogen.

in the hybrids versus temperature under nitrogen. The E_a values of random scission for PMMA segments in hybrids, evaluated from slopes in a plot of $\ln g(\alpha)$ versus $\ln T$, are listed in Table 1. The E_a value of the P(MMA-MA5)–SiO_2 hybrids under nitrogen decreases with increasing silica content, whereas that under air increases. However, the E_a values of random scission in the homopolymer are around 230 kJ/mol under nitrogen and 70 kJ/mol under air [25]. This indicates that the reduction in E_a by nitrogen is very large, whereas the enlargement by air is very small. This large difference reveals that chain scission of the PMMA segments in hybrids may be more complex than in the homopolymer. At present, the reduction in E_a may be associated with the higher thermal conductivity of SiO_2 (5 mcal/cm s °C) compared to that of PMMA (0.5 mcal/cm s °C) [26]. However, the reason for enlarged E_a value in the degradation under air is not clear at present. On the other hand, the E_a value of the P(MMA-GMA5)–SiO_2 hybrids is independent of the silica content under nitrogen (∼86 kJ/mol) and air (∼84 kJ/mol). The E_a value of the PMMA moieties in hybrids is in the order P(MMA-MSMA5)–SiO_2 < P(MMA-GMA5)–SiO_2 < P(MMA-MA5)–SiO_2 hybrid, as compared with the P(MMA-MSMA)–SiO_2 hybrids [15]. The result reveals that the stable interfacial structure, even only small amount (5% molar ratio), has the more thermal and thermo-oxidative stability of the PMMA.

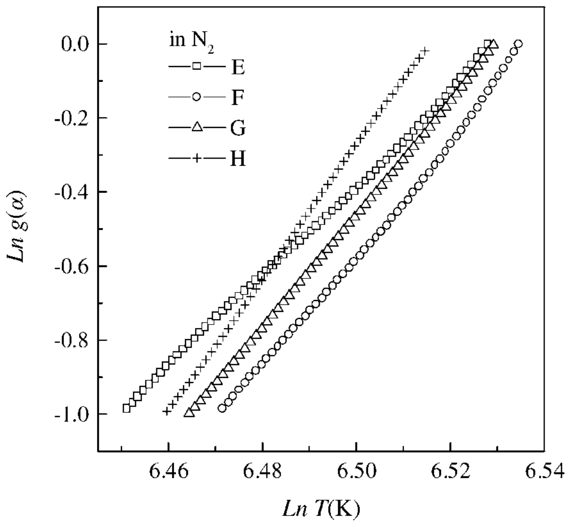


Fig. 10. Plot of $\ln g(\alpha)$ vs. $\ln T$ for thermal degradation of hybrids (E) GMA5-100; (F) GMA5-90; (G) GMA5-80; (H) GMA5-70 at heating rate10 °C/min under nitrogen.

4. Conclusions

MA and GMA, two coupling agents, were used to bond the PMMA and SiO_2. The effect of the SiO_2 content and interfacial structure on the flexibility and stability of the PMMA–SiO_2 hybrids was characterized by DSC and TGA. However, the E_a value of the PMMA moieties in hybrids was in the order P(MMA-MSMA5)–SiO_2 < P(MMA-GMA5)–SiO_2 < P(MMA-MA5)–SiO_2 hybrid, as compared with the P(MMA-MSMA)–SiO_2 hybrids. The result indicated that the stable interfacial structure had the more thermal and thermo-oxidative stability of the PMMA.

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