
Thermal and Physical Ageing Properties of Poly(methyl methacrylate) Silica Nanocomposites

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Abstract: Poly(methyl methacrylate) (PMMA) nanoparticles were prepared by grafting methyl methacrylate from both aggregated silica and colloidally dispersed silica nanoparticles using atom-transfer radical polymerisation (ATRP). Cross-linking and macroscopic gelation were avoided using a miniemulsion system.

The thermal and physical ageing behavior of the nanocomposites have been examined by differential scanning calorimetry (DSC). The addition of silica nanoparticles to PMMA can influence its thermal and aging properties. Grafting PMMA-aggregated silica revealed considerable increase in the glass transition temperature, whereas colloidally silica nanoparticles showed only a marginal improvement. Additionally, while dispersing PMMA in colloidal and aggregated silica accelerated physical ageing, grafting to aggregated silica significantly reduced ageing rates.

Keywords— ATRP , Nanoparticles, glass transition temperature, Physical Aging, PMMA.

1. Introduction

The modification of polymer composites using sub-micrometer fillers with high surface-to-volume ratios is currently receiving a lot of interest in both academia and industry. However, homo-polymers often do not have the required properties for certain purposes. A technique that is commonly used in industry to adjust polymer properties is adding a filler material to the polymer, which can drastically affect

its performance. The nature of the reinforcement effect in polymer–filler composites has been extensively discussed in the literature. It is known that polymer–particle as well as particle–particle interactions play a very important role in determining the reinforcing ability of a composite. Particle pre-treatment is often a necessary step used to improve polymer–particle interactions.^{1, 2} At high filler concentration, particle–particle aggregation

may dominate the mechanical response with a consequent decrease in the level of improvement. Controlling the dispersion of fillers in a polymer matrix is crucial but not always straightforward: poorly bonded particles increase brittleness and lower the composite's resistance to crack growth.³ While some filler materials are quite cheap (e.g. carbon black, talc and silica), others such as glass fibres and carbon nanotubes are considerably more expensive.² Polymer–filler composites are often prepared by solution dispersion due to its simplicity which involves dispersing the particles in a polymer solution followed by evaporation the solvent.^{4,5} From a chemical point of view, silica particles are relatively easy to functionalise and modify. In particular, a suitable surface treatment makes silica hydrophilic or hydrophobic, and thus helps to improve the filler's compatibility with a surrounding polymer matrix. Several recent papers have demonstrated already that polymer chains can be grafted onto silica and alumina particles by controlled radical polymerisation.⁶⁻⁹ The most prominent method is atom-transfer radical polymerisation (ATRP), which has the added advantage that the functionalisation of silica particles with a suitable initiator is

straight forward and allows polymer chains to be grown from the silica surface in a narrow size distribution.

Fillers affect the mobility, and thus the T_g , of the polymer chains in the vicinity of the filler particle, and this effect is even more pronounced for the long term physical ageing properties of the polymer. The physical ageing of a material is an important issue to study, as it can lead to degradation of mechanical properties and strength, optical or transport properties which makes the materials much less useful for its intended application. While various characterisation

techniques such as DSC, creep, fluorescence, and dielectric have been used to investigate physical aging in amorphous polymers,^{10,11} very few studies have been reported on polymer-silica nanocomposites. Furthermore, most other groups have either chosen aggregated or non-aggregated silica nanoparticles, but never compared the effect of surface-grafted filler particles on the thermal and long-term ageing properties of nanocomposites made using both types of silica.¹²⁻¹⁴ Since the type of silica particles is known to significantly influence the properties of the polymer composites is instructive to carry out comparative studies.¹⁵ Reactive silica particles have

already been converted into PMMA composites. These studies were carried out by dispersing non-aggregating spherical silica nanoparticles, which were either untreated or surface modified, in methyl methacrylate monomer, followed by polymerisation using a free radical initiator.^{16,17} Although chemical bonds between organic and inorganic phase are likely to exist in such cases, the free radical polymerisation process also produces free polymer chains, unattached to the silica surface. This is therefore different from the grafting process described here. In this study, the effect of grafted PMMA chains from the surface of silica nanoparticles on the thermal and the physical ageing properties will be investigated. To be able to compare the properties of PMMA-grafted particles to those of more conventional PMMA/nanosilica composites, we prepared also a series of samples by dispersing silica nanoparticles in a tetrahydrofuran (THF) solution of PMMA and investigated their thermal and physical ageing behaviour using differential scanning calorimetry (DSC).

2. Experimental

2.1 Reagents

PMMA (M_n 100,000 g/mol, T_g 120 °C) was supplied by Dow Chemical Company and

methyl methacrylate, ascorbic acid, N,N,N',N'',N''' -

pentamethyldiethylenetriamine (PMDETA), and Brij 98 were purchased from Aldrich; Copper (II) chloride, tetrabutylammonium fluoride (TBAF), and triethylamine from Lancaster; 3 aminopropyltriethoxysilane and hexadecane from Fluka; and ethylenediaminetetraacetic acid disodium salt (EDTA) from Acros. Hydrophilic Cab-o-sil H5 silica particles with a specific surface area of 300 ± 30 m²/g and a diameter of 7 nm were obtained from Cabot and a 30% solution MEK-ST Colloidal silica, having a particle size between 10-15 nm from Nissan Chemical. Methyl methacrylate monomer was extracted with 0.1 M aqueous NaOH to remove inhibitor, then washed with water, dried over MgSO₄, filtered, and degassed.

2.2 Samples preparation

2.2.1 Preparation of PMMA-MEK-ST or Cab-sil H5 composites by dispersion

A 5% solution of PMMA in THF along with

the required amounts of dried filler particle were added to a beaker. The beaker was sealed with Nesco film to prevent evaporation of the solvent and stirred for 48 hours. The solvent was then allowed to evaporate at room temperature for 48 hours. Samples were dried in an oven at 160 °C for 24 hours to remove all solvent residues.

2.2.2 Preparation of 2,2,2-trichloroethyl carbamate initiator

A mixture of 3-aminopropyltriethoxysilane (13.6 mL, 12.9 g, 58.4 mmol), 2,2,2-trichloroethyl chloroformate (7.9 mL, 12 g, 58 mmol), and triethylamine (10.0 mL, 7.26 g, 71.7 mmol) in toluene (100 mL) was stirred at 40 °C for 4 hours. The reaction mixture was filtered to remove triethylammonium chloride. The filtrate was concentrated in vacuum to give a yellow-brown oil (20.6 g, 89%). For analysis, the crude product was further purified by vacuum distillation (Kugelrohr, 205 °C/0.4 mbar) to yield product as a colourless liquid. ¹H NMR (300 MHz, CDCl₃): δ 0.64 (t, *J* = 7.9 Hz, 2 H), 1.22 (t, *J* = 7.1 Hz, 9 H), 1.67 (tt, *J* = 7.9, 6.6 Hz, 2 H), 3.24 (q, *J* = 6.6 Hz, 2 H), 3.82 (q, *J* = 7.1 Hz, 6 H), 4.71 (s, 2 H), 5.38 (br. t, 1 H). ¹³C NMR (50 MHz, CDCl₃): δ 7.52 (CH₂), 18.16 (CH₃), 22.88 (CH₂), 43.47 (CH₂), 58.35 (CH₂), 74.29

(CH₂), 95.62 (C), 154.47 (C=O). IR (KBr, cm⁻¹): ν 3338 (bs), 2974 (s), 1733 (s), 1538 (s), 958 (s). MS (CI, NH₃): *m/z* 417, 415, 413 (1, 3, 3%), 352, 350 (9, 10), 265 (27), 222 (100), 208 (25), 176 (33). Exact mass calcd. for C₁₂H₂₄³⁵Cl₃NO₅Si + NH₄⁺ requires *m/z* 413.0828, found 413.0826 (CI, NH₃). Anal. Calcd. for C₁₂H₂₄Cl₃NO₅Si (396.8): C, 36.33; H, 6.10; N, 3.53. Found: C, 35.88; H, 5.72; N, 3.53.

2.2.3. Synthesis of trichloroethyl carbamate-functionalised silica nanoparticles

Silica nanoparticles were dried at 110 °C/0.03 mbar for 6 hours. A slurry of silica nanoparticles (5.1 g), trichloroethyl carbamate initiator (273 mg, 0.688 mmol), and toluene (90 mL) was heated to 110 °C for 12 hours. The solid was centrifuged (4000 rpm, 20 min) and the supernatant decanted. Centrifugation–decantation was repeated 3 times using THF as the extracting solvent. The gel layer was transferred into a pre-weighed beaker and dried in an oven at 60 °C overnight.

2.2.4 ATRP of MMA from trichloroethyl carbamate-functionalised silica nanoparticles in miniemulsion.

Copper (II) chloride (5.1 mg, 38 μmol), PMDETA (6.5 mg, 38 μL, 38 μmol), inhibitor-free methyl methacrylate (4.0 mL, 3.8 g, 38 mmol) and deionised water (3 mL) were continuously stirred in a Schlenk flask

at 50 °C for 15 minutes. The solution became blue due to the presence of a copper (II) amine complex. The solution was then cooled in an ice bath. A solution of Brij 98 (115 mg) in deionised water (17 mL), hexadecane (0.23 mL) and trichloroethyl carbamate-initiator functionlised silica nanoparticles (0.61 g) were added to the Schlenk flask. The solution was then sonicated for 7 minutes. The homogenized miniemulsion was then deoxygenated with nitrogen for 30 minutes before being heated to 70 °C in a poly(ethylene glycol) bath. An aqueous solution of ascorbic acid (4.0 mg, 23 μ mol, dissolved in 0.5 mL of deionised water) was added to initiate the polymerisation. The polymerisation was stopped after 90 min. An aqueous solution of EDTA (15.5 mg, dissolved in 3 mL of deionised water) was then added in order to extract the copper complex. The solid was collected by suction filtration and washed with methanol (20 mL). After suspension of the solid in deionised water (50 mL), this procedure was repeated once, and the crude

product further purified by Soxhlet extraction with THF (100 mL, 12 hours at 90 °C). The residual solid was dried for 24 hours in an oven at 160 °C. Yield: 2.96 g of a colourless solid.

2.3 Measurements

2.3.1 DSC

Differential scanning calorimetry (DSC) analyses were performed with a Thermal Advantage DSC 2010 at a heating rate of 20°C min⁻¹ under a constant nitrogen flow. Glass transition temperatures were taken as the mid-point of the transition.

2.3.2 NMR analyses

¹H NMR analyses were performed with a Bruker AC200 NMR spectrometer to confirm the absence of solvent or other plasticizing impurities as shown in **Figure 1**. NMR samples were prepared by dissolving 15–20 mg of sample in 1 mL of CDCl₃.

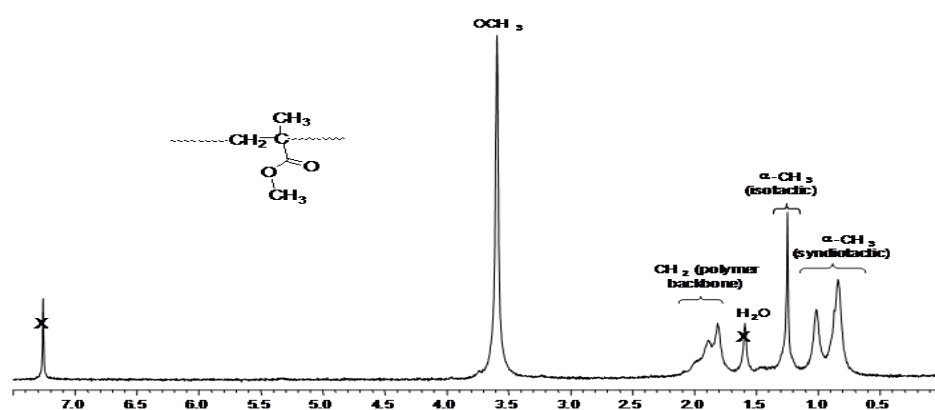


Figure. 1 ¹H NMR spectrum of PMMA–silica composite .

3. Results and discussion

3.1 Thermal properties – glass transition temperature

The glass transition temperature, T_g , is the temperature when the polymer softens on heating. Above T_g , the thermal energy enables the motion of polymer chains. Restricting the mobility of the polymer chains requires more thermal energy, and a higher T_g might be expected with an increasing concentration of filler nanoparticles. According to the DSC measurements (**Figure 2 and Table 1**), dispersed the silica (Cab-o-sil H5 and MEK-ST) in PMMA has no significant effect on the T_g of neither polymer, which is consistent with the results found in literature.¹⁸ The Cab-o-sil H5 composite appears to show a slightly lower T_g than MEK-ST sample. The difference is, however, small and may be due to moisture present acting as a plasticizer. The lack of changes in T_g could be attributed to the polymer not being absorbed onto the surface of the particles which restricted molecular motion of the polymer. Many researchers have studied the effect of the filler materials on T_g and have drawn different conclusions. Most of the researches reported an increase in the glass transition temperature as a

function of filler content¹⁹ however, decreases or no effect on the T_g of the polymer composites also have been found.^{5,20,21}

Figure 3 shows the synthetic scheme used to graft PMMA from the surface of silica nanoparticles. A literature procedure for ATRP in miniemulsion, introduced by Matyjaszewski *et al.*, was opted since this process was straight forward and had already been demonstrated to work successfully for grafting poly(butyl acrylate) from the surface of colloidal dispersed silica nanoparticles.⁸

As illustrated in **Figure 4 and Table 1**, the glass transition temperatures measured by DSC are usually higher for the grafted hybrid material compared to pure PMMA. This could be due to the strong adhesion between PMMA and silica nanofiller when linked together by a covalent bond,²¹ which restricts the mobility of the PMMA chains. Grafted PMMA Cab-o-sil H5 composite has a higher T_g than the grafted MEK-ST composite with closer silica content. This fact indicates that the T_g of the composites is also strongly dependent on the nature of the silica (*i.e.* aggregated or non-aggregated). This could be due to the decrease in the segmental mobility of grafted chains with aggregation of

nanoparticles.²²

Table 1. T_g of PMMA and nanocomposites

Polymer/Nanocomposite	DSC T_g / °C
Pure PMMA	120.0
Dispersed PMMA-MEK-ST (20 wt%)	120.6
Dispersed PMMA-Cab-soil H5 (20 wt%)	119.5
Grafted PMMA-MEK-ST (20 wt%) ¹	123.2
Grafted PMMA-Cab-soil H5 (22 wt%) ¹	128.3

1. measured by TGA

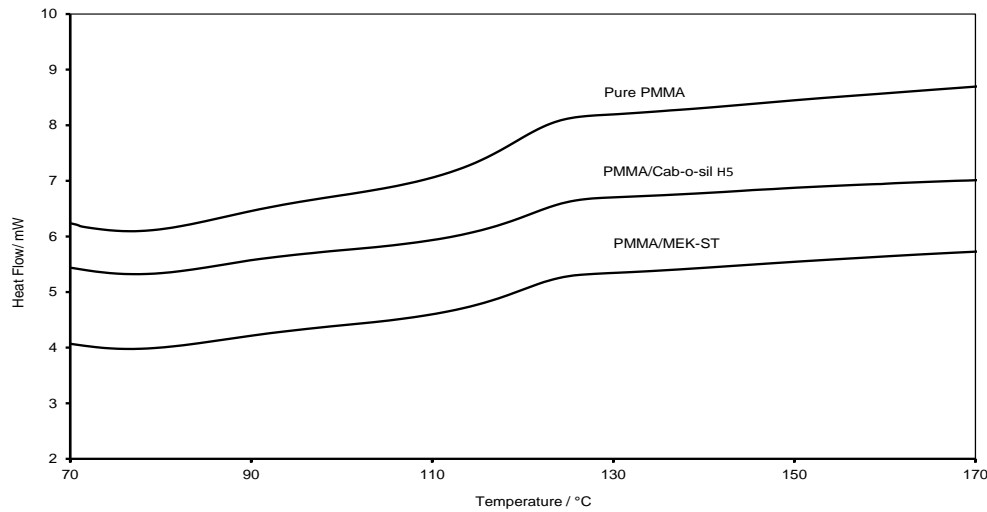


Figure 2. DSC traces of pure PMMA and dispersed PMMA-silica nanoparticles. The traces have been shifted vertically for clarity.

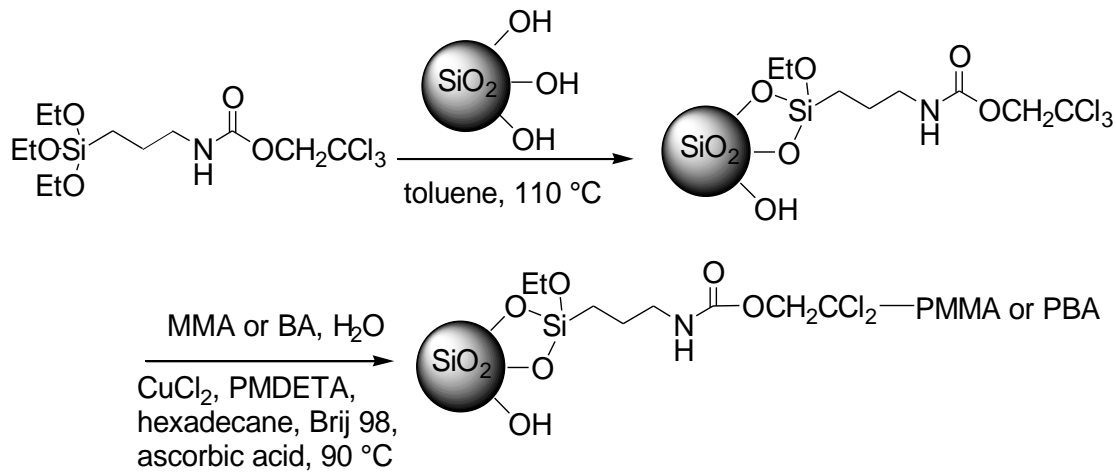


Figure 3. Synthetic scheme for the grafting of PMMA from silica nanoparticles using ATRP

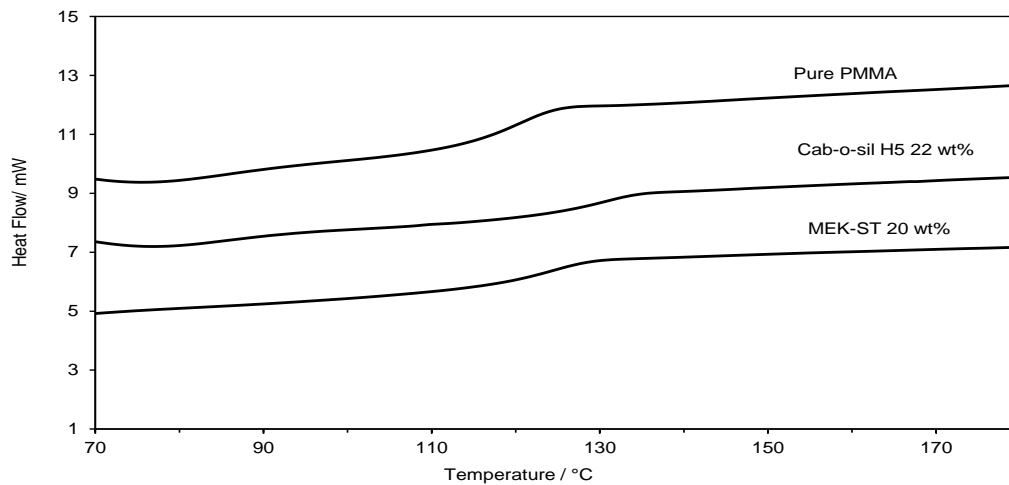


Figure 4. DSC traces of pure PMMA and grafted PMMA-silica nanoparticles. The traces have been shifted vertically for clarity

3.2 Enthalpy Relaxation

Enthalpy relaxation experiments are used to measure the effects of physical ageing on a polymer material. Physical ageing is a slow process of an amorphous material relaxing into its thermodynamic equilibrium state

when stored below the glass transition temperature (T_g).²³ This phenomenon is due to a series of small relaxation events taking place in the amorphous region of glassy polymers. Whilst the chemical structure of the polymer remains unchanged, the change in the packing of the polymer chains leads to

a loss of thermodynamic properties such as enthalpy and entropy²⁴ which typically results to decreased thermal and mechanical properties over time.

Several models have been proposed to analyse the experimental data collected by enthalpy relaxation experiments using differential scanning calorimetry (DSC).

A semi-empirical model proposed by Cowie and Ferguson^{25,26} (C-F) used in this paper to describe the physical ageing data of the polymer nanocomposites. At any ageing temperature (T_a) and ageing time (t_a), the enthalpy relaxed $\Delta H(T_a, t_a)$ is the integrated difference between the C_p curves for the aged and the unaged sample. According to CF, this is described by the following expression:

$$\Delta H(t_a, T_a) = \Delta H(\infty, T_a)[1 - \phi(t_a)] \quad (5)$$

where ΔH_∞ is the equilibrium excess enthalpy lost after an infinite ageing time and $\Phi(t_a)$ is the Kohlraush- Williams-Watt (KWW) function, as follows:

$$\phi(t_a) = \exp\left\{-\left(\frac{t}{t_c}\right)^\beta\right\} \quad (6)$$

where β is related to the width of the distribution of relaxation times and t_c may

be regarded as an ‘average’ relaxation time, i.e. both are kinetic parameters.

The C-F parameters of net PMMA and PMMA nanocomposites obtained from the fitted curves are listed in **Table 2**. The $\Delta H_\infty(T_a)$ data shows that the dispersed samples show a small decrease in the relaxed enthalpy at the plateau compared to pure PMMA. However, a significant decrease in relaxed enthalpy is shown in the grafted sample, as $\Delta H_\infty(T_a)$ is decreased almost by a factor of 2.

The β values give the distribution of relaxation times; a small value implies a larger distribution. In general, the grafted PMMA-Cab-o-sil H5 sample show lower β values than pure PMMA and the rest of the PMMA nanocomposites which could be due to a higher degree of interaction²⁷ between the particles and PMMA. **Figure 5** shows a comparison of fitted ageing curves for the different nanocomposites at $T_a = T_g - 15$. These curves clearly show the large decrease in ΔH_∞ values when comparing grafted polymers to dispersed polymers. It can also be seen that in PMMA grafted to aggregated Cab H5, the slope of the fitted curve is shallower compared to the dispersed samples and even pure PMMA, which suggests a decrease in the ageing rate.

This trend can be qualitatively assessed

by the $\log (\langle t_c \rangle / \text{min})$ value, which are calculated from the $\log (t_c / \text{min})$ and the β values obtained from the C-F model eq. (**Figure 6**). The dispersed and the grafted MEK-ST samples showed accelerated ageing, which is consistent with the previous results from Boucher *et al.*²⁷ This has previously been attributed to silica affecting the segmental dynamics of the polymer.

However, the grafted PMMA-Cab-o-sil H5 showed a reduced ageing rate compared

to bulk PMMA. This result is consistent with the thermal result that showed that only grafting to aggregated silica had a significant effect on the thermal properties. The formation of a 3-dimensional network of silica nanoparticles (with Cab-o-sil H5) could reduce the ageing rate by restricting segmental motion, unlike simply dispersing the particles which has been shown to have little effect on the segmental motion of the polymers.¹⁴

Table 2. CF Parameters for PMMA and PMMA silica nanocomposites

Polymer	T_a (K)	$T_g - T_a$ (K)	$\Delta H_\infty (T_a)$ (J g ⁻¹)	Log t_c (min)	β
PMMA	378	15	1.84	2.18	0.43
	384	9	1.67	1.99	0.32
	388	5	0.89	1.60	0.38
PMMA-dispersed Cab-O-Sil	374	15	1.80	2.44	0.42
	380	9	1.41	1.79	0.42
	384	5	0.95	1.52	0.40
PMMA-dispersed MEK-ST	378	15	1.61	2.23	0.46
	384	9	1.39	1.95	0.29
	388	5	0.88	1.51	0.39
PMMA-grafted Cab-O-Sil	386	15	1.02	1.92	0.37
	392	9	0.98	1.55	0.24
	396	5	0.51	1.87	0.34
PMMA-grafted MEK-ST	381	15	1.24	1.89	0.52
	387	9	1.03	1.69	0.42
	391	5	0.46	1.85	0.46

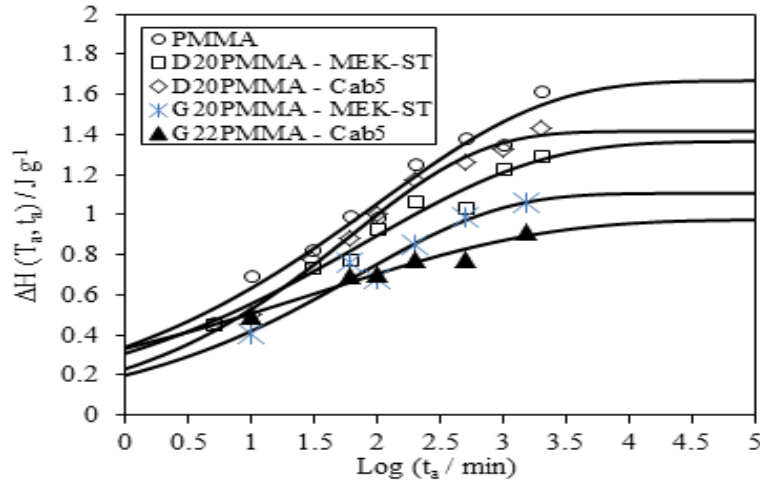


Figure 5. Comparison of PMMA and PMMA-silica nanocomposites at $T_a = T_g - 9$

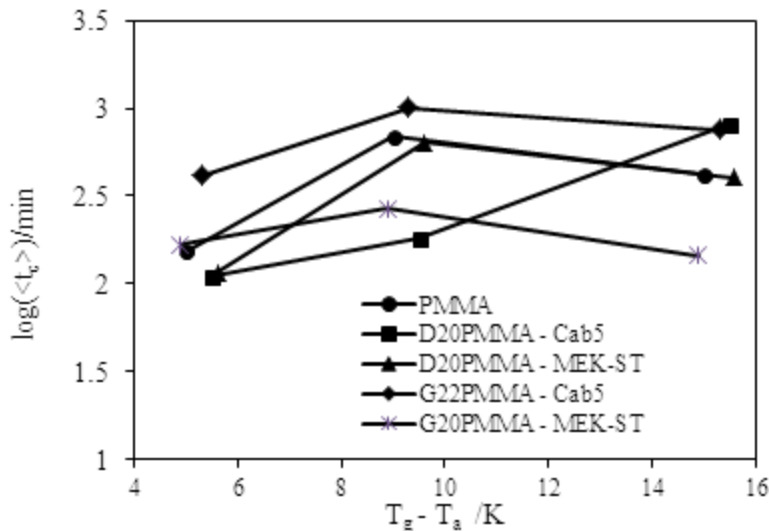


Figure 6. $\text{Log}(\langle t_c \rangle / \text{min})$ vs $T_g - T_a$ for PMMA and PMMA-silica nanocomposites

Conclusion

Using an ATRP in miniemulsion procedure, PMMA was successfully grafted from both non-aggregated and aggregated silica nanoparticles that possessed a high tendency to aggregate. Whilst simple dispersion silica nanoparticles in PMMA has a negligible or

little effect on the glass transition temperature, grafting the PMMA from the surface of the filler nanoparticles gives materials with higher T_g compared to the neat polymer. The largest effect is seen with the aggregated Cab-o-sil H5 particles. The physical ageing of PMMA nanocomposites

showed that dispersing the polymer in silica accelerated ageing, which is consistent with previous results obtained by Boucher *et al.*

However, grafting PMMA to aggregated silica reduced ageing rate.

الخواص الحرارية و العمر الفيزيائي للبولي (ميتايلمييتاكراليت)-نانوسليكا

موسى خليفة عبدالسلام يوسف مهدي المكي عبدالرحمن فرج

قسم الكيمياء – كلية العلوم – جامعة سبها

ملخص

بولي (ميتايل مييتاكراليت)-مرتبطة بجزئيات النانوسليكا تم تحضيرها من انتشار مونومر ميتايل مييتاكراليت من على سطح السليكا المتجمعة والمنفردة بواسطة البلورة عن طريق انتقال الشقوق الحرة. عملية البلورة تمت بعملية الجزئيات الدقيقة المعقدة لمنع أي تصلد أو تكلس للبوليمر الناتج. الخواص الحرارية والعمر الفيزيائي تم تعيينه بجهاز المسح التفاضلي. إضافة السليكا للبوليمر يؤثر على الخواص الحرارية والعمر الفيزيائي. تغطية بولي (ميتايل مييتاكراليت)-لسطح السليكا المتجمعة يزيد من درجة الحرارة الانتقالية أكثر من في حالة استخدام السليكا المنفردة. كلا من بولي (ميتايل مييتاكراليت)-المنشر بين جزئيات السليكا المنفردة والمتجمعة يودي الى استرخاء العمر الزمني اما تغطية بولي (ميتايل مييتاكراليت)-لسطح السليكا المتجمعة يودي الى انخفاض معدل العمر الزمني بدرجة ملحوظة.

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