

PMMA/Silica Nanocomposite Studies: Synthesis and Properties

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ABSTRACT: Polymethylmethacrylate (PMMA)/silica nanocomposites are prepared by solution polymerization in this project and the resulting materials are subjected to characterization to evaluate thermal, mechanical, and fire properties. IR results show that both (3-acryloxypropyl)methyldimethoxysilane (APMDMOS) and (3-acryloxypropyl)trimethoxysilane (APTAMOS) can serve as reagents for the surface modification of silica, while APTAMOS performed better than APMDMOS for the modification of the silica surface. Mechanical properties of

PMMA/silica nanocomposites prepared by solution blending showed decreased tensile strength and elongation at break, while materials from solution polymerization performed better than PMMA itself. Moreover, all prepared samples have shown improved thermal stabilities versus PMMA. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3844–3850, 2004

Key words: nanocomposite; surface modification; PMMA; silica; flammability

INTRODUCTION

Organic/inorganic nanocomposites have received extensive attention in recent years. Unlike micronscale fillers, nanoscale fillers can offer excellent properties to a polymer matrix without decreasing mechanical properties. In recent years, several research groups have reported their own composites achieved by different strategies, including addition of a modified silicate to a polymerization reaction (*in situ* method),^{1–3} to a solvent-swollen polymer (solution blending),⁴ or to a polymer melt (melt blending).^{5,6} However, most of the work in this field has focused on clay/polymer materials, and very few contributions can be found for additives other than clay.

In general, most clay additives belong to the layered silicate family. These layered clays can be considered as the combination of a batch of plates, and the thickness of each plate is several nanometers. Essentially, they are plate-type additives. Polymer-layered silicate nanocomposites have unique properties compared to conventional filled polymers. For example, the mechanical properties of a Nylon-6—layered silicate nanocomposite, with a silicate mass fraction of only 5%, showed excellent improvement over those of pure Nylon-6.⁷ The nanocomposite exhibited increases of 40% in tensile strength, 68% in tensile modulus, 60% in flexural strength, and 126% in flexural modulus. The heat distortion temperature (HDT) was also increased, from 65 to 152°C, and the impact strengths were low-

ered by 10%. The mechanical properties of aliphatic amine cured epoxy-layered silicate nanocomposites, reported recently by Wang and Pinnavaia,⁸ revealed an improvement of 400% or more in tensile modulus and tensile strength and a substantial increase in the strain-at-break. Decreased gas permeability and increased solvent resistance also accompanied the improved physical properties. Also, polymer-layered silicate nanocomposites often exhibit increased thermal stability and reduced flammability.^{9–13} On the other hand, limited results can be found on the behavior of spherical additives. In this paper, silica was selected as the nanoscale additives for organic/inorganic nanocomposites because of the shape of the particles and the similarity of chemical composition with layered silicate.

To date, three major methods have been reported for the preparation of polymer/silica nanocomposites: the Sol-Gel process, *in situ* polymerization, and direct solution blending. Among these three approaches, the *in situ* polymerization method has the advantages of ease of handling, is a relatively quick process, and usually offers better performance for the final products. The process of *in situ* polymerization involves three continuous steps. First, the nanoscale additives are pretreated with appropriate surface modifiers and then the modified additives are dispersed into monomer, followed by polymerization. Nanocomposites are formed *in situ* during the polymerization.

From the literature, less than 1% of the papers are about free radical type polymer/silica nanocomposites.¹⁴ This phenomenon is not because researchers are unattracted by these materials, but because of the extreme difficulty in preparation of these materials.

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The fact is, the presence of silica particles will terminate free radical reaction as reported by Percy and coworkers, which will result in only oily low-molecular-weight oligomers. To overcome this problem, the modification of the silica surface with an appropriate surface modifier is considered the best approach to solve this problem. Since the silica surface will be covered with modifier after treatment, it will not hurt the further polymerization of monomers. The results are discussed in this paper.

EXPERIMENTAL

Materials

Methyl methacrylate was purchased from Aldrich Chemical Co. Surface modifiers, (3-acryloxypropyl)methyldimethoxy-silane (APMDMOS) and (3-acryloxypropyl)trimethoxysilane (APTAMOS), were purchased from Gelest, Inc. Nanoscale silica samples were provided by Degussa Co. The silica used in this project are OX50, OX80, Aerosil 90, Aerosil 130, and Aerosil 300, and their particle sizes are 40, 30, 20, 16, and 7 nm, respectively.

Surface modification of silica nanoparticles

The modification of the silica surface was achieved by the following procedure. Fumed silica was first dispersed in ethanol, then a 2 M ratio of surface modifier and 0.1 N of HCl solution were added to the above solution according to the moles of silanol groups on the silica surface. The mixture was subjected to magnetic stirring at room temperature for 24 h. Both APMDMOS and APTAMOS were used as surface modifiers. Modified silicas are used for solution polymerization without further treatment.

Solution polymerization PMMA/silica nanocomposites

The procedure for the preparation of polymethylmethacrylate (PMMA)/silica nanocomposites by direct solution polymerization is summarized by the following steps. Pretreated silica solution and methyl methacrylate were mixed together with toluene as the reaction medium and BPO as the initiator for free radical polymerization. Solution polymerization was allowed to take place at 100°C under stirring for 24 h. The resulting solution was cast on a Teflon sheet followed by drying for 6 days and vacuum drying at 60°C for 1 day.

FT-IR analysis of silica surfaces

FT-IR testing was carried out to verify the efficacy of the silica surface modification. Silica powder with 20

nm average diameter size was surface treated with the surface modification method mentioned previously. The modified silica solution was filtered on a Büchner funnel and rinsed with ethanol. Modified silica samples were dried at 60°C under vacuum for 24 h before testing to eliminate moisture in the sample. The resulting silica powders obtained were subjected to IR analyses with a Magna-IR Spectrometer 550 FT-IR spectrometer from Nicolet Co. Unmodified silica was also analyzed for comparison.

Tensile testing

A Chatillon LTCM-6 Tensile Tester was used to assess tensile strength, modulus, and elongation at break for all the materials obtained from the solution polymerization according to ASTM 638 standard. The testing rate was 0.05 in./min.

Thermal stability of PMMA/silica nanocomposites

All the materials were tested with a Hi-Res TGA 2950 thermogravimetric analyzer from Thermal Analysis Co. to evaluate thermal stability. Materials were preheated to 100°C and held for 5 min to eliminate solvent and moisture in the sample before testing. The temperature ramp rate was 20°C/min and temperature scan range was 100~550°C, respectively. All tests were performed under a nitrogen atmosphere.

Molecular weight measurement

A Cannon-Fenske capillary viscometer was used to measure the viscosity of PMMA, and the viscosity average molecular weight of PMMA was determined by the equation $[\eta] = KMv\alpha$, which was developed by Mark et al.. K and α are 0.55×10^{-4} and 0.76, respectively, when benzene is used as solvent.

Flammability evaluation

Oxygen index tests were performed on all samples according to ASTM 2863 to evaluate the flammability of PMMA/silica nanocomposites. Horizontal burning tests were also conducted to investigate the burning flame spread rate of the nanocomposites according to ASTM D635.

RESULTS AND DISCUSSION

Surface modifier effects on silica surface modification

Silica modification is one of the most important steps for the preparation of PMMA/silica nanocomposites. In this section, surface modifier effects are

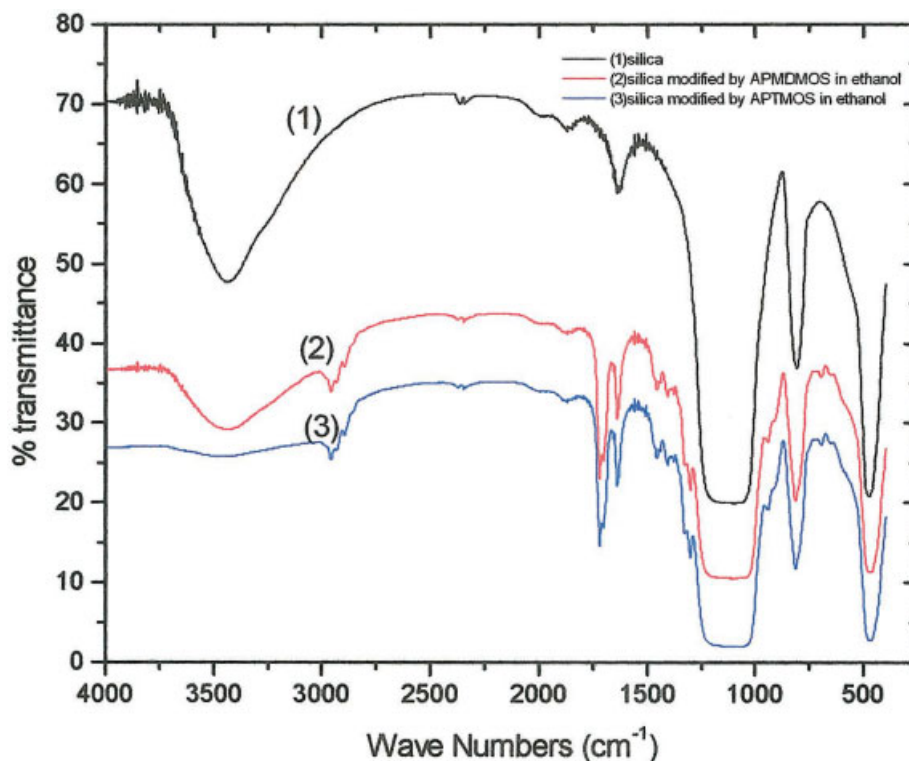


Figure 1 Surface modifier effects on the surface modification of silica (20 nm).

discussed based on the FT-IR test results as shown in Figure 1.

In Figure 1, three kinds of silica samples are shown. Sample 1 is silica, sample 2 is silica pretreated with $\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{SiCH}_3(\text{OCH}_3)_2$ (APMDMOS) and 0.1 N HCl solution in ethanol, and sample 3 is silica pretreated with $\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ (APTAMOS) and 0.1 N HCl solution in ethanol. Compared with silica, both sample 2 and 3 have new peaks appearing at 2966.7 ($\text{sp}^3\text{C-H}$), 1719.045 (O=C), 1643.9 (C=C), 1301.6 (acryl ethers), which indicates chemical bonding between surface modifiers and silica. However, the peak height of sample 3 is much higher than those of sample 2, and the silanol peak has totally disappeared in sample 3 but still is present in sample 2 in Figure 1. This suggests that the modification of silica in ethanol for both surface modifiers has succeeded, while APTMOS is more efficient than APMDMOS. Considering the structural similarity of the modifiers, which differ only at one methoxy substitution on the silicon atom, which will lead to the better approach of surface modifier to the silica surface after hydrolysis, the results are to be expected. After surface modification, the silica surface is chemically covered by unreacted 3-acryloxypropyl functional groups, which can undergo further chain polymerization.

Formation of PMMA/silica nanocomposites by solution polymerization

As shown in Table I, PMMA/silica nanocomposites were successfully prepared using solution polymerization with ethanol as the silica modification solvent. Because of the successful treatment of silica in ethanol, the silica surface is covered with surface modifier, which will protect the silica underneath from contact with the free radicals in the solution, therefore allowing the polymerization to progress. Moreover, the vinyl group on silica surface, introduced by surface modification, can undergo free radical polymerization with the free radicals in solution, and the resulting PMMA polymer chain will chemically attach to the silica surface and prevent phase separation between silica and the polymer matrix, and that is the reason why some of the resulting materials are not soluble in toluene.

The modifier effect can be discussed based on silica with 20 nm average diameter nanocomposites. With APMDMOS as surface modifier, both 5 and 10% nanocomposites are soluble in toluene, while only the 5% nanocomposite is soluble in toluene if one uses APTMOS as the silica surface modifier. As discussed in the silica surface modification section, APTMOS performs better than APMDMOS as a surface modifier. Therefore, the degree of crosslinking between

TABLE I
PMMA/Silica Nanocomposites
from Solution Polymerization

Sample*	Solubility	Silanol Group Amount (mmol/30 g nanocomposite)
<i>Solution Polymerization (APMDMOS)</i>		
PMMA-2-20-5-M1	Yes	0.68
PMMA-2-20-10-M1	Yes	1.4
<i>Solution Polymerization (APTAMOS)</i>		
PMMA-2-40-5-M2	Yes	0.36
PMMA-2-40-10-M2	Yes	0.72
PMMA-2-40-15-M2	No	1.1
PMMA-2-30-5-M2	Yes	0.45
PMMA-2-30-10-M2	Yes	0.90
PMMA-2-30-15-M2	No	1.4
PMMA-2-20-5-M2	Yes	0.68
PMMA-2-20-10-M2	No	1.4
PMMA-2-20-15-M2	No	2.0
PMMA-2-16-5-M2	No	0.90
PMMA-2-16-10-M2	No	1.8
PMMA-2-16-15-M2	No	2.7
PMMA-2-7-5-M2	No	1.8
PMMA-2-7-10-M2	No	3.6
PMMA-2-7-15-M2	No	5.4

* The code system can be explained by the following example: PMMA-16-10. The first element is the polymer matrix, which is PMMA in this case. The second element is the silica size in nanometers and the third element is the concentration of silica in the whole material while the last element is the surface modifier type that used, where M1 is APMDMOS and M2 is APTAMOS.

silica and PMMA of APTAMOS composite is higher than that of the APMDMOS composite.

The solubility testing results shows good correspondence with silanol group concentration. Gel point is a concept for multiple functional group (more than 2) monomer systems. It is used for the determination of the crosslinking propensity of materials. Although monomers with more than two functional groups have the possibility to form thermosetting polymers, the resulting polymer will not be thermosetting if the average number of functional groups per monomer is below the gel point. Because silica is chemically bonded with PMMA, this means that, if the concentration of crosslinking is higher than the gel point, the nanocomposite will change from a thermoplastic into

a thermoset. The data listed in Table I suggest that the gel point of PMMA/silica nanocomposite is 0.9~1.08 mmol of silanol groups per 30 g of nanocomposite, which can be used to explain the solubility behavior of different types of silica nanocomposites.

Mechanical properties of PMMA/silica nanocomposites

The mechanical properties of the materials from solution polymerization show a significant increase over PMMA. In general, the mechanical performance of polymer composites is associated with the interface strength between the inorganic phase and the organic phase. In most cases, the inorganic additives show much better mechanical properties than the organic polymer. If the interface between the inorganic phase and the polymer matrix is strong enough, the external force will transfer from the polymer matrix to the inorganic phase through the interface, and therefore reinforce the mechanical properties of the whole material. In contrast, if the interface is not strong enough, the interface will break down first and the inorganic domains become the weak points in composites, and further deteriorate the mechanical properties. The same rule also can be applied to nanocomposites, which works well to explain the results in Table II. As mentioned in the previous discussion, silica particles are chemically bonded with the PMMA polymer chain by solution polymerization. Chemical bonding is a very strong connection compared with physical entanglement, so the interface between silica and the PMMA matrix is strong enough for transportation of external stress to silica particles, which will lead to a significant increase in mechanical properties. Because of the better silica surface treatment when using APTAMOS, there is more contribution to the interfacial interaction from chemical bonding in APTAMOS as modifier than APMDMOS. It explains the high tensile strength of APTAMOS systems over that of APMDMOS.

Particle size plays a very important role in polymer reinforcement. For the same composition with different particle size, the resulting composites can have

TABLE II
Method Effect on Mechanical Properties of PMMA/Silica Nanocomposites (Average of 5 Tests)

Sample Code	Tensile Strength ($\times 10^3$ psi)	Modulus ($\times 10^3$ psi)	Elongation at Break (%)
PMMA	0.98	18.7	15.4
<i>Solution polymerization (APMDMOS)</i>			
PMMA-2-20-5-M1	1.35	22.7	19.7
PMMA-2-20-10-M1	1.83	35.6	17.9
<i>Solution polymerization (APTAMOS)</i>			
PMMA-2-20-5-M2	1.45	—	9.46

TABLE III
Mechanical Properties of PMMA/Silica Nanocomposites from Solution Polymerization (Average of 5 Tests)

Sample Code	Tensile Strength (kpsi)	Modulus (kpsi)	Elongation at Break (%)
PMMA	0.98	18.7	15.4
PMMA-2-40-5-M2	1.01	—	8.56
PMMA-2-40-10-M2	1.46	—	9.12
PMMA-2-30-5-M2	1.11	—	11.0
PMMA-2-30-10-M2	1.50	—	11.2
PMMA-2-20-5-M2	1.45	—	9.46

quite different properties. In Table III, the mechanical properties of different types of silica are presented.

The tensile strength of the nanocomposites from solution polymerization shows a large increase over PMMA. The general trend shows clearly that, with a decrease of silica particle size, the tensile strength of the resulting nanocomposite increases. It also indicates that, with an increase of silica content in the nanocomposite, the tensile strength also increases. Considering that the only difference between those materials in Table III is the particle size, the following rational can be made to explain the mechanical behavior. The smaller the particle size, the more particles in the same weight of silica, which means more reinforcement sites in the nanocomposite.

Viscosity average molecular weight of the PMMA prepared by solution polymerization is 208,000 as determined by viscosity of this sample.

Unlike the work done by Ash et al.,¹⁵ which was with a PMMA/alumina nanocomposite, the results reported in this paper show increased tensile strength with 5 wt % additives. The differences between these two kinds of materials are not only that different additives were employed, but also the interface interaction between the additive and PMMA matrix was different. In this paper, the silica and PMMA formed a pseudocrosslink bonding, which provides strong linkage between them, while Ash et al.¹⁵ reported a weak physical interface system. However, instead of obtaining brittle strong materials for strong binding interface systems, the elongation at break of PMMA/silica nanocomposites obtained increased over PMMA. The extra toughness of the nanocomposites is coming from the flexibility of the surface modifier, which imports both extra free volume and lower conformation energy to the material. This approach offers an alternative way for researchers to achieve tougher materials without sacrificing the stress of the materials.

Thermal stability of PMMA/silica nanocomposites

Thermal stability is another important property that determines the usage of materials. Thermal properties provide the engineer with an idea about the processing temperature of plastics and the highest tempera-

tures at which the material can be used. To improve the thermal stability of polymeric materials, it is necessary for researchers to understand the decomposition process for each individual polymer. For PMMA, it has been shown that the degradation of the polymer can be divided into two steps. First, the polymer chain will break down into small segments and then the segments will further decompose into monomer, which is methyl methacrylate. Therefore, the polymer will retain significant weight after the first step, although the average molecular weight decreases dramatically. In the following sections, the relationship between surface modifier, particle size, and thermal stability of nanocomposites are discussed.

Surface modifier effect on thermal stability can be discussed based on Table IV. Basically, APTMOS performs better than APMDMOS for the surface modification of silica. The interfacial interaction between silica and the polymer matrix is much stronger for APTMOS than that of the APMDMOS-modified nanocomposite because of the stronger chemical bonding between silica and polymer chains as discussed previously, which can explain the higher 10 wt % loss

TABLE IV
Weight Loss Temperatures (10 and 50%) of PMMA/Silica Nanocomposites

Sample	Temperature at 10% Weight Loss (°C)	Temperature at 50% Weight Loss (°C)
PMMA	190	326
<i>Solution Polymerization (APMDMOS)</i>		
PMMA-2-20-5-M1	225	372
PMMA-2-20-10-M1	252	378
<i>Solution Polymerization (APT MOS)</i>		
PMMA-2-40-5-M2	206	369
PMMA-2-40-10-M2	209	363
PMMA-2-40-15-M2	245	385
PMMA-2-30-5-M2	235	355
PMMA-2-30-10-M2	247	375
PMMA-2-30-15-M2	263	391
PMMA-2-20-5-M2	233	368
PMMA-2-16-10-M2	268	358
PMMA-2-16-15-M2	306	398
PMMA-2-7-5-M2	254	381
PMMA-2-7-10-M2	280	377
PMMA-2-7-15-M2	310	398

TABLE V
Oxygen Indices of PMMA/Silica Nanocomposites
Solution Polymerization

Sample Code	Oxygen Index
PMMA	17.3
<i>Solution Polymerization (APMDMOS)</i>	
PMMA-2-20-5-M1	18.4
PMMA-2-20-10-M1	18.4
<i>Solution Polymerization (APT MOS)</i>	
PMMA-2-40-5-M2	18.4
PMMA-2-40-10-M2	18.4
PMMA-2-40-15-M2	18.9
PMMA-2-30-5-M2	17.8
PMMA-2-30-10-M2	17.8
PMMA-2-30-15-M2	18.9
PMMA-2-16-5-M2	18.4
PMMA-2-16-10-M2	18.4
PMMA-2-16-15-M2	19.8
PMMA-2-7-5-M2	18.4
PMMA-2-7-10-M2	19.4
PMMA-2-7-15-M2	20.8

temperature of PMMA-2-20-5-M2 (APT MOS) over PMMA-2-20-5-M1 (APMDMOS).

Table IV also provides an indication that thermal stabilities of nanocomposites increase with particle size decrease. Consider the fact that there are more

particles per weight for smaller size silica than larger size silica. It will offer more restriction sites for the polymer chain, and the scission of polymer chains will become more difficult, therefore moving the first step of decomposition of PMMA to higher temperatures.

With an increase of silica content, the interfacial interaction between silica and polymer matrix also increase, which leads to more restriction of the polymer chain movement and further improves the thermal stabilities of the whole material, as shown in Table IV.

Flammability of PMMA/silica nanocomposites

Oxygen index is a common test used for evaluation of the ease of extinction of plastics. The minimum percentage of oxygen in an oxygen/nitrogen mixture to just sustain the combustion of a top ignited specimen is measured. It is a general method to evaluate the flammability of plastics. Table V lists the oxygen indices of PMMA/silica nanocomposites via solution polymerization. Although oxygen indices of nanocomposites from solution polymerization show very little improvement, it shows negative results for these materials as flame retardant materials, because real flame retardancy will be achieved only when the oxygen

TABLE VI
Horizontal Burning Testing of PMMA/Silica Nanocomposites

Sample	t_1 (s) ^a	t (s) ^b	Burning rate (cm/min) ^c	ATB(s) ^d
PMMA	16	79	7.14	52.00
	15.8	81	6.90	
	15.8	86	6.41	
PMMA-2-20-5-M1	10	44	13.24	11.67
	6	39	13.64	
	9	42	13.64	
PMMA-2-20-10-M1	8	42	13.24	11.33
	8	41	13.64	
	7	41	13.24	
PMMA-2-40-5-M2	12	54	10.71	24.33
	12	54	10.71	
	12	55	10.46	
PMMA-2-40-10-M2	12	34	20.45	9.67
	15	48	13.63	
	14	37	19.56	
PMMA-2-30-5-M2	11	36	18.00	5.67
	8	34	17.31	
	10	37	16.6	
PMMA-2-30-10-M2	7	34	16.67	3.00
	9	31	20.45	
	8	34	17.31	
PMMA-2-20-5-M2	11	35	18.75	6.00
	12	36	18.75	
	15	37	20.45	

^a Burning time from the beginning to 25 mm.

^b Burning time from the beginning to 100 mm.

^c Burning rate = $450/(t - t_1)$

^d Average time of burning = $\Sigma(t - 30 \text{ s})/\text{number of specimens}$

index of the material reaches 25~28. Below this number, materials are easy ignited, and not easy extinguished once ignited.

The horizontal burning test is a test to evaluate the fire spread rate of materials. It will give fire travel information on the horizontal surface including fire-spread rate, burning behavior, and ease of extinction if the material burns without dripping. The nanocomposites listed on Table VI are not flame retardant materials. They all exhibit substantially higher burning rates and lower average times of burning compared to PMMA. In other words, they burn faster. However, all the nanocomposites burn without dripping, which is very different from PMMA, which drips badly during the test. The phenomenon can be explained by the "wick effect." For some organic/inorganic composites, fire will burn out the organic phase and leave the inorganic phase intact, which will lead to a faster burning rate of the composite.

CONCLUSION

PMMA/silica nanocomposites were successfully prepared by solution polymerization. The characterization of pretreated silica and untreated silica indicate that APTMOS as surface modifier performs better than APMDMOS for the surface modification of silica surface. Mechanical properties of PMMA/silica nanocomposites are improved. As the silica content increases, and/or the silica size decreases, the final materials exhibit better mechanical properties. Nanocomposites also show better mechanical properties when the silica surface is treated with APTMOS versus APMDMOS.

The addition of silica results in better thermal stability of the final products. Silica size and modification method effects follow the same trends found for mechanical properties.

PMMA/silica nanocomposites are not flame retardant materials. They are easier to ignite, burn faster, and are harder to extinguish but do not drip. The loss of dripping may lead to the other observation that the heat is not carried away in the molten flow.

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