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Polymer 43 (2002) 4123–4136

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Organic–inorganic hybrids derived from 2-hydroxyethylmethacrylate and (3-methacryloyloxypropyl)trimethoxysilane

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Received 25 June 2001; received in revised form 21 January 2002; accepted 14 March 2002

Abstract

Composites based on (3-methacryloyloxypropyl)trimethoxysilane and 2-hydroxyethylmethacrylate have been prepared and their properties are studied. Chemical structure of the materials made by a range of synthetic approaches was defined using nuclear magnetic resonance spectroscopy and gel permeation chromatography. Thermal properties such as glass transition temperature of the systems were determined. The inorganic phase content was measured after the samples were decomposed at high temperatures in the furnace. The small angle X-ray scattering technique was used in an attempt to describe the possible morphologies of the systems. Density was measured using a Helium Pycnometer and hardness was determined using a Vickers hardness tester. Resistance of the surface to an abrasive material was studied by following weight and transmission loss during erosion testing. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Organic–inorganic composites; Glass transition temperature; Morphology

1. Introduction

Sol–gel chemistry has been studied extensively for over the last two decades [1–4]. Initially, sol–gel technology was used as a method of fabrication of high quality ceramics and mono- and multicomponent glasses of high homogeneity and purity which could be made into bulk, fibre and coating geometries at considerably lower temperatures than used in conventional techniques [5–8].

The great potential of the sol–gel method has been explored further to produce organically modified sol–gel materials [9–11]. A range of different compositions of hybrid materials, ORMOSILs (organically modified silicates), ORMOCERS (organically modified ceramics) or CERAMERs (ceramic polymers) have been prepared and their properties studied [12–17]. A great number of polymers (polyacrylates [18,19], poly(vinylalcohol) [20], poly(vinylacetate) [21]) and methods have been utilized to prepare organic–inorganic hybrid materials with no covalent bond between the components. These polymers exhibit affinity for inorganic oxides through interactions such as, for example, hydrogen bonding [22] which allows them to form homogeneous systems.

There has been an extensive investigation that has led to advanced materials for use in the optical industry as well as in electronics, communication, energy and high technology fields as hard or protective coatings. The majority of abrasion resistant coatings used are based on organosiloxanes, such as methyl trimethoxysilane, phenyl trimethoxysilane and glycidoxypropyltrimethoxysilane or organoheterosiloxanes which can be hydrolysed in the presence of colloidal silica [23]. Mercaptopropyltrimethoxysilane and methacryloxypropyltrimethoxysilane can be used in order to improve abrasion resistance of the polymer substrates.

In this study, a synthetic approach based on (3-methacryloyloxypropyl)trimethoxysilane (MPTS) and 2-hydroxyethylmethacrylate (HEMA) was investigated. The latter was used as a monomer (HEMA) or a polymer (PHEMA). MPTS was introduced either as a monomer, or in its hydrolysed form, where we refer to it as pMPTS. Note that pMPTS stands for an inorganically polymerized system containing Si–O–Si units, prior to radical polymerization of the pendant double bonds. Radical polymerization of the system produced materials with a range of optical and mechanical properties. Variations of the synthetic approach using the two component system are presented. Previously

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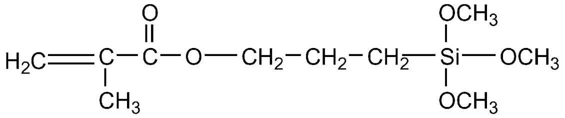
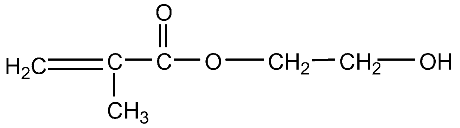
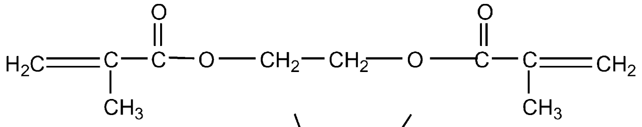
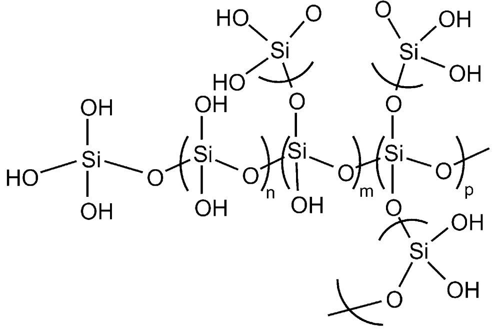
PII: S0032-3861(02)00209-4

Table 1
Chemical formulae of the materials used in the synthesis of the MPTS/HEMA composites or were referred to in the paper

Abbreviations	Name	Formula
MPTS	(3-Methacryloyloxypropyl)trimethoxysilane	 $H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}CH_2{-}Si(OCH_3)_3$
HEMA	2-Hydroxyethylmethacrylate	 $H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}OH$
EGDMA	Ethylene glycol dimethacrylate	 $H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}O{-}C({=}O){-}C(CH_3){=}CH_2$
PSA	Poly(silicic acid)	

studied organic–inorganic composites based on poly(silicic acid) (PSA) and HEMA [24,25] contained up to 10 wt% silica with the possibility to vary the amount of inorganics by changing the molar ratio of the reaction components. However, the properties (mechanical and optical) as well as the overall appearance of the PSA/HEMA composites were negatively affected when the inorganic content increased. We reported in an earlier work [24] that covalent bonds were not formed between PSA and HEMA and their absence proved to be of great importance in regards to the mechanical performance of the material during erosion testing as shown in PSA/MPTS/HEMA systems [26]. Incorporation of MPTS is an easy way of increasing the amount of silica, with the simultaneous establishment of a Si–C linkage to the organic component of the composite.

There are several possibilities for routes to MPTS/HEMA composites with different structures and properties. HEMA can be combined with either MPTS or hydrolysed MPTS (pMPTS). Acidic hydrolysis of MPTS can be undertaken to produce an oligomeric inorganic network (pMPTS) prior to combination with HEMA or the hydrolysis can be performed in situ with the radical polymerization. The extent of the step growth polymerization of MPTS either carried out as prepolymerization or in the presence of HEMA will influence the size of the inorganic network and final structure of the hybrids.

2. Experimental work

2.1. Materials

HEMA (97%) and ethylene glycol dimethacrylate (EGDMA, 98% pure) were purchased from Aldrich, benzoyl peroxide (BPO) from Ajax, tetrahydrofuran (THF) and hydrochloric acid (HCl) from Merck and MPTS from Lancaster. THF was dried over lithium aluminium hydride, distilled and stored over sodium wire. It was distilled from sodium and benzophenone prior use. All other chemicals were used as received. Table 1 lists the chemical formulae of the materials that were used in the synthesis and are referred to in this paper.

2.2. Characterization techniques

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded at 200 MHz with a Bruker AC-200 spectrometer for deuterochloroform ($CDCl_3$) solutions with tetramethylsilane as the internal standard (δ 0.00 ppm).

Gel permeation chromatography (GPC) was performed on a Waters GPC system (Waters 6000A solvent delivery pump, Waters U6K injector and Waters R-401 detector). Columns were packed with Plgel Mix B 10u Linear (7.5 mm × 60 cm) and μstyragel 100 Å (7.8 mm × 30 cm). The samples were run at 1 ml/min with THF as the eluant.

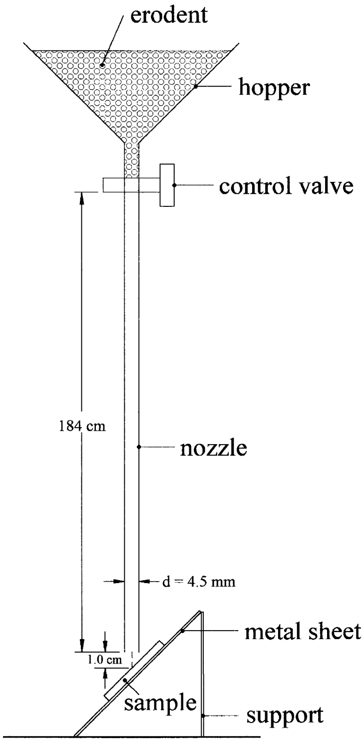


Fig. 1. Schematic representation of the laboratory erosion tester.

Monodisperse polystyrene standards were used for molecular weight calibration.

Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer and are of thin films of liquids between sodium chloride discs.

Samples were decomposed in a furnace at 900 °C for 6 h, cooled and the residue/ash was weighed as inorganic content.

Dynamic mechanical thermal analysis (DMTA) was performed on a Perkin Elmer DMA 7 (penetration probe mode). Samples of 18 mm × 4 mm × 2 mm (width × depth × height) were tested in the temperature range 90–150 °C at a heating rate of 2 °C/min and at 1.00 Hz frequency. The sample chamber was purged with helium during the run. Pure indium and *n*-octane were used for calibration.

Small angle X-ray scattering (SAXS) measurements were performed on a Rigaku SAXS System with a Kratky camera. The wavelength of the Cu Kα X-ray was 1.5419 Å. The Rigaku X-ray generator was utilized. The operating voltage was 30 kV with a current of 30 mA. Continuous data collection in a scattering angle range of -1 to $+1°$, 2θ with steps of 0.002° at a scattering rate 0.04 °/min were performed at ambient temperature. Background collection was performed under the same conditions as the sample data collection prior the data collection. The background was scaled and removed from the scattering beam data.

Density was measured using a Micromeritics AccuPyc 1330 Helium Pycnometer. The device works by using pressure of helium to accurately determine the volume of a sample of known mass. Hardness tests were measured using a Matsuzawa Microhardness Tester (Vickers) with a load of 100 g up to 1 kg.

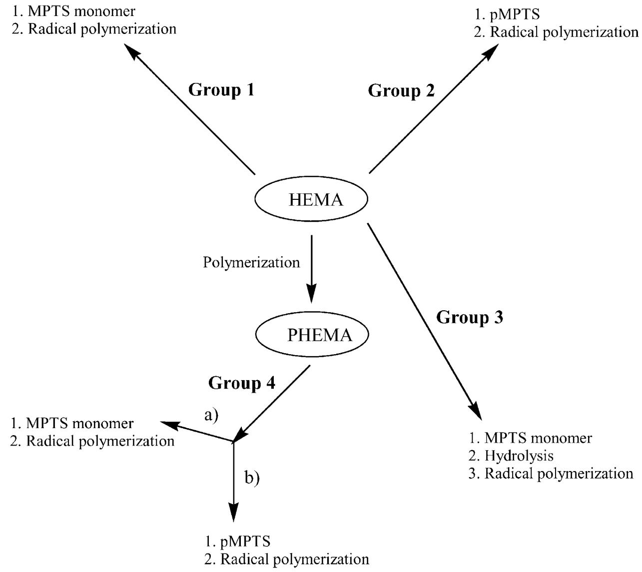


Fig. 2. Schematic representation of the synthetic pathways to the MPTS/HEMA composites.

Erosion testing was performed using a laboratory scale instrument, schematically shown in more detail in Fig. 1, consisting of a hopper from which accurately weighed amounts of erodent (SiC of mesh size 36/70) were introduced onto the flat surface of the composite material through the nozzle at an average velocity of 5.85 m/s, the sample placed in a metal holder causing an impact angle of 45°. The weight loss and transmission loss after incremental increase of mass of the erodent (by 200 g up to 1 kg) was used to assess the degree of erosion resistance of the material. The initial and final mass loss were determined using a Sartorius analytical laboratory balance. The initial transmission and transmission loss were recorded using a Cary 3 UV–Vis spectrophotometer at wavelengths between 400 and 850 nm (with 50 nm steps).

3. Preparation of composites

The target composite material was prepared using four possible synthetic pathways which depend on the form of MPTS (monomer or hydrolysed) and HEMA (monomer or polymerized) used. A summary of the various pathways is shown in Fig. 2.

Group 1. MPTS (19 ml, 80 mmol) in THF (10 ml) was stirred under nitrogen and HEMA (10 ml, 80 mmol) was slowly added dropwise at ambient temperature and the mixture stirred for 3 h. The solvent was removed in vacuo to yield a colourless liquid. A crosslinking agent EGDMA (2 wt%) and BPO (2 wt%) were added, the latter to initiate

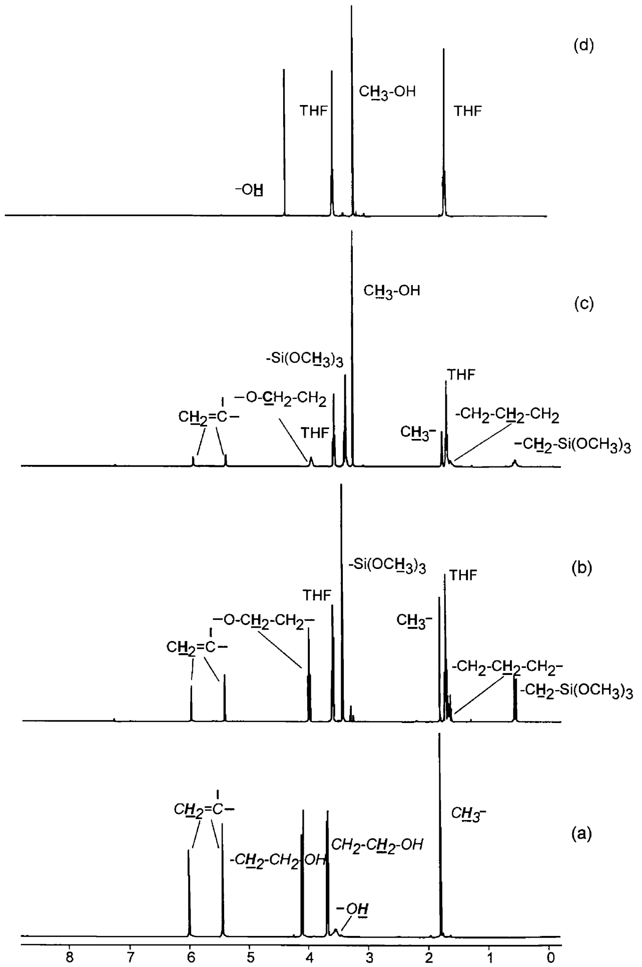


Fig. 3. ^{1}H NMR spectra of (a) HEMA, (b) MPTS monomer in THF, (c) pMPTS in THF, and (d) solvent removed after hydrolysis of MPTS.

polymerization. The reaction mixture was poured into a Teflon mould or plastic vials and radical polymerization of the monomers (MPTS, HEMA and EGDMA) carried out at 60 °C for 3 h, 80 °C for 24 h and the system postcured at 90 °C.

Group 2. MPTS in THF was stirred under nitrogen, hydrolysed using HCl (0.7 ml) and stirred for half an hour. HEMA was added slowly (quantities of the reactants were the same as used for the Group 1 composites). The mixture was stirred for 3 h at ambient temperature, followed by the removal of the solvent. A crosslinker (EGDMA) and an initiator (BPO) were added and the mixture cured under conditions described for Group 1 composites. The acidic hydrolysis (the first basic step of the sol–gel process) of the alkoxysilanes (such as TMOS, TEOS, etc.) has been described previously in a number of publications [1–3]. It initiates formation of the inorganic network by hydrolysing methoxy groups in alkoxysilanes, followed by the condensation reaction to form a Si–O–Si polymeric network.

Group 3. MPTS and HEMA were stirred in THF (the same quantities as for Group 1) at ambient temperature under nitrogen and HCl was added dropwise to initiate the inorganic network formation. The mixture was stirred for 3 h and the solvent removed prior addition of a crosslinker (EGDMA) and an initiator (BPO). The system was cured as described for the Group 1 system. In this case, the inorganic network growth initiated by the addition of HCl takes place in the presence of the organic HEMA monomer, i.e. in a more dilute environment than in Group 2 system.

Group 4. HEMA in THF was radically polymerized using BPO at 60 °C under nitrogen and either MPTS (Group 4a) or hydrolysed MPTS (pMPTS) (Group 4b) was added dropwise. The mixture was stirred for 3 h, solvent was removed in vacuo and a crosslinking agent (EGDMA) and an initiator (BPO) were added. The system was cured as described for Group 1. The larger organic HEMA polymers were combined with the smaller MPTS monomer molecules, or were allowed to interact with the hydrolysed MPTS-containing Si–O–Si network which contained pendant organic groups.

Curing of the systems as described earlier led to the formation of composite samples of different thickness (bulk samples 0.5–1 cm, layers 0.2–0.3 cm) and different mechanical, thermal, physical and optical properties.

4. Results and discussion

4.1. Chemical nature of the system

It has been shown previously [24–26] that HEMA does not chemically link with the inorganic component of sol–gel composites based on PSA or PSA/MPTS. The co-existence of HEMA with MPTS monomer (mutual miscibility) or HEMA with hydrolysed pMPTS was investigated in this study. MPTS may be incorporated with HEMA, either as MPTS monomer (Groups 1, 3 and 4a) or incorporated as the hydrolysed MPTS form (pMPTS) (Groups 2 and 4b) as shown in Fig. 2. The acidic hydrolysis can be carried out prior to any interactions with HEMA (Groups 1 and 4a) or at the same time (Group 3). Furthermore, HEMA could be incorporated as a monomer (Groups 1–3) or a radically polymerized HEMA (PHEMA) (Group 4). The form of the components and the order of chemical operations will influence the size (molecular weights) of the phases within the final composite, resulting in different degrees of mutual interactions and miscibility and thus, in the variety of resultant morphologies. Changes in the reaction mixtures were monitored by NMR and FTIR spectroscopy and GPC.

^{1}H NMR spectra of HEMA, MPTS monomer and pMPTS as well as the solvent removed from pMPTS (after acidic hydrolysis) prior to radical polymerization are shown and peaks assigned in some detail in Fig. 3(a)–(d). It can be seen that there are no major shifts in protons in pMPTS compared to MPTS (Fig. 3(b) and (c)). However, broadness of the proton peaks due to the step-growth polymerization of the Si–O–Si chain is evident (Fig. 3(c)). Also, the ratio of the methoxy protons (OCH_3) to terminal double bond

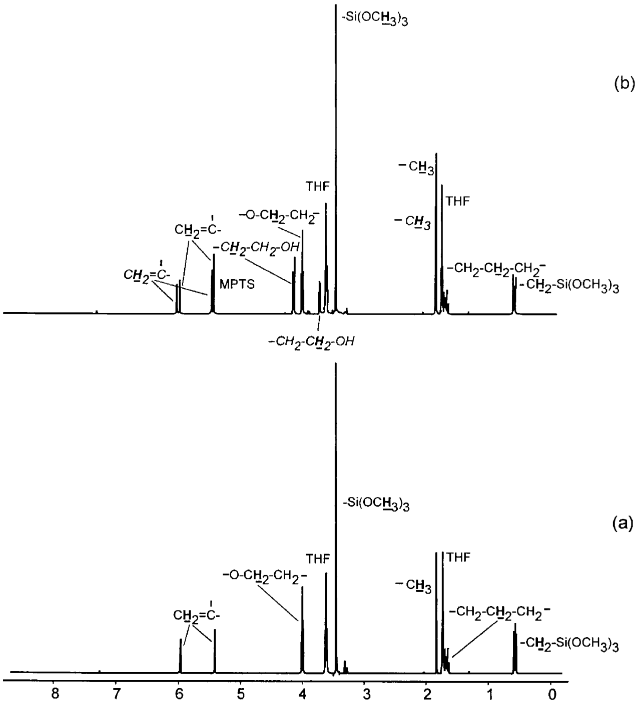


Fig. 4. ^{1}H NMR spectra of (a) MPTS monomer in THF and (b) a mixture of HEMA and MPTS monomer in THF.

protons (CH_2) in MPTS is ~4.3 in MPTS monomer (Fig. 3(b)) and decreases to ~2.2 in pMPTS (Fig. 3(c)). It was observed that solvent removed from pMPTS (Fig. 3(d)) prior to curing contained released methanol, confirming that hydrolysis and condensation (sol–gel reaction) took place (Fig. 2). The inorganic Si–O–Si polymeric network was formed with the organic part of the MPTS molecule connected via Si–C bonds.

Initially, the interactions of MPTS and HEMA monomers were studied (Group 1 composites) (Fig. 2). It was observed that there was no change in proton or carbon shifts of MPTS and HEMA in the final product (Fig. 4) compared to those in neat monomers (Fig. 3(a)). The ratio of the methoxy protons (OCH_3) to terminal double bond protons (CH_2) in MPTS was unchanged and thus no reaction, such as substitution of OCH_3 with HEMA, occurred. It appeared that there was no phase separation of the two monomers and a high degree of miscibility led to well intermixed blends capable of yielding transparent composites.

It was observed that changes in ^{1}H NMR spectra of Group 2 composites based on pMPTS and HEMA were the same as changes for the single component system (i.e. changes in the proton ratio and broadness of the peaks) due to the hydrolysis of MPTS, with no chemical shifts in protons. A clear solution was produced, possibly due to the high degree of miscibility resulting from the presence of the hydroxyl group functionalities in both components.

The Group 3 system (Fig. 2) initially involved the study of the two MPTS and HEMA monomers that were stirred for a short period of time (up to 3 h), as well as for prolonged lengths of time (several days) under the conditions described in Section 2. It was observed that there was no change in the ^{1}H NMR spectra compared to those of the starting materials (monomers) with the ratio of the methoxy protons (OCH_3) to terminal double bond protons (CH_2) in MPTS being constant (Fig. 5(a)). After addition of HCl to the system, MPTS was hydrolysed immediately with proton peaks becoming broader and the ratio of the OCH_3 to double bond protons decreased to 1 (after 3 h), decreasing further with prolonged time (24 h) to 0.43 (Fig. 5(b)). There was no change in the shifts of the protons of the organic component of HEMA, supporting the observation described previously for the PSA/HEMA and PSA/MPTS/HEMA systems [24,26] that the HEMA component does not chemically link with MPTS due to a substitution reaction of methoxy groups with HEMA.

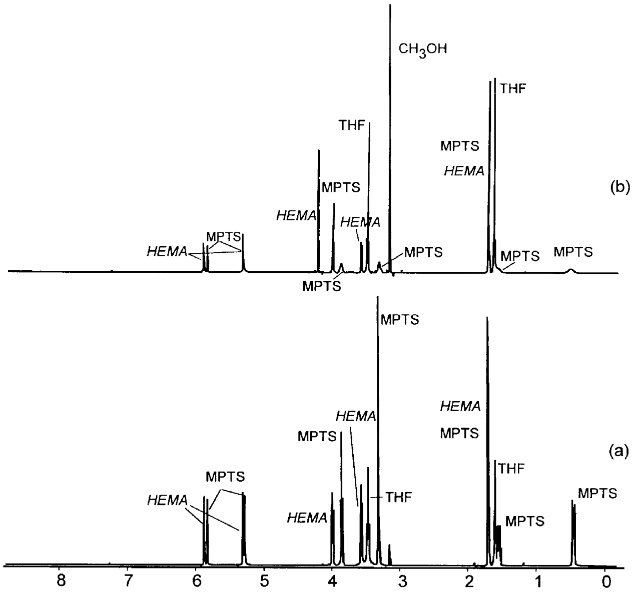


Fig. 5. ^{1}H NMR spectra of (a) MPTS monomer and HEMA after prolonged time of mixing and (b) MPTS/HEMA system hydrolysed.

GPC was used to determine molecular weights (MW) of the products for all groups. The molecular weight of MPTS monomer is 170 and was increased after being hydrolysed with HCl (up to 552) to produce an inorganic oligomeric network (pMPTS) with pendant double bonds. In any of the reaction sequences involving HEMA addition to either MPTS or pMPTS (Fig. 2, Groups 1–3), there was no change in MW of the final products compared to the initial values of MPTS monomer or pMPTS. For example, it can be clearly seen in Group 2 chromatographs, that apart from a pMPTS peak (MW 500), the peak at the low MW due to monomeric HEMA species was also present, suggesting no reaction between the components, and thus no coupling.

It was found that the MW of polymerized HEMA (PHEMA) species was 2227. In Group 4 systems, PHEMA was mixed with MPTS monomer (Group 4a) or pMPTS (Group 4b). No new peaks were observed in chromatographs after the components were mixed together.

Table 2
FTIR assignments of absorption bands of functional groups in organic silicon compounds [27] (m, medium; s, strong; vs, very strong; w, weak)

Functional group	Region (cm^{-1})	Intensity	Comments
Silanols			
Si–OH	3700–3200	m	broad O–H (s)
	955–835	s	Si–O strong, for condensed-phase samples a b, m–w band occurs near 1030 cm^{-1} due to SiOH def
Silyl esters and ethers			
Si–O–R	1110–1000	vs	Asym Si–O–C (s) and Si–O–Si absorbs in this region
Si–O–CH_2–	1190–1140	s	
	1100–1070	vs	Asym Si–O–C (s), usually a doublet
	990–945	s–m	Sym Si–O–C (s)
Si–O–Si and Si–O–C	1090–1020	vs	Si–O (s), two bands of almost equal intensity, siloxane absorbs near 1085 and 1020 cm^{-1} increasing in intensity with increase in chain length
Siloxanes			
$-(\text{SiO})_n-$	1100–1000	s	
	$\sim$800	m	

Likewise, no change in the MW of the final products was observed, confirming that there was no reaction or linkage occurred in this system, as observed for Groups 1–3. Polydispersity (PDI), defined as the ratio of the weight-average molecular weight M_w and number-average molecular weight M_n, is a measure of the heterogeneity of the system with $M_w/M_n = 1$ representing a perfectly monodisperse system. PDI was found to be quite low for the whole range of composites. It was between 1.26 and 2.1 for all groups of MPTS/HEMA composites with 1.06 for MPTS monomer and 1.64 for pMPTS.

FTIR studies (Table 2) were used to assign significant features of the starting material and to analyse the reaction products. The dominant features of all spectra were C=O and OH bands for HEMA, Si–O–C band for MPTS monomer and Si–O–Si and OH bands for pMPTS. All features were observed in the spectra of the products. However, comparison of FTIR spectra of initial materials (HEMA, MPTS monomer or pMPTS) and the final products (Groups 1–4) showed no significant differences between each spectra, suggesting that this technique might not be sufficiently sensitive to allow a complete understanding of the system.

4.2. Appearance of the samples

Radically polymerized MPTS and pMPTS (produced by similar conditions described in Section 2 for the composites) were found to be brittle (SiO_2 content $\sim$26 wt%) (Table 3) and yellow to light brown in colour. The appearance of the

Table 3
Glass transition temperature (T_g) and silica content of PHEMA, PMPTS, PpMPTS and the composite samples (T_gs (tan δ) values in the brackets show the 'shoulders' of the α-relaxations; $W_{1/2}$ is the width of the peak at half-height; the relaxation strength is determined from the height of the tan δ peak)

Group	Sample composition (molar ratio)	T_g (°C)	Relaxation strength (°C)	$W_{1/2}$ (°C)	SiO_2 content calculated (%)	SiO_2 content (wt%)
	PHEMA	111	1.30	42	–	–
	PMPTS	9	0.90	34	24.0	27.5
	PpMPTS	31	0.15	116	24.1	26.4
1	MPTS/HEMA (1:1)	(12), 68	0.17, 0.12	85	15.9	15.5
	MPTS/HEMA (1:2)	71	0.60	40	11.8	10.9
2	pMPTS/HEMA (1:1)	48	0.15	31, 139	15.9	16.5
	pMPTS/HEMA (1:2)	(44), 109	(0.18), 0.19	169	11.8	11.3
3	(MPTS/HEMA)/H^+ (1:1)	–	–	–	15.9	16.7
	(MPTS/HEMA)/H^+ (1:2)	–	–	–	11.8	13.0
4	pMPTS/PHEMA (1:1)	43	0.08	148	15.9	17.5
	MPTS/PHEMA (1:1)	19	0.29	75	15.9	17.3
	pMPTS/PHEMA (1:2)	133	0.12	108	11.8	12.0
	MPTS/PHEMA (1:2)	10, 104	0.08, 0.26	63	11.8	8.8
	pMPTS/PHEMA (2:1)	0	0.36	70	19.1	23.1
	MPTS/PHEMA (2:1)	83	0.25	72	19.1	11.7

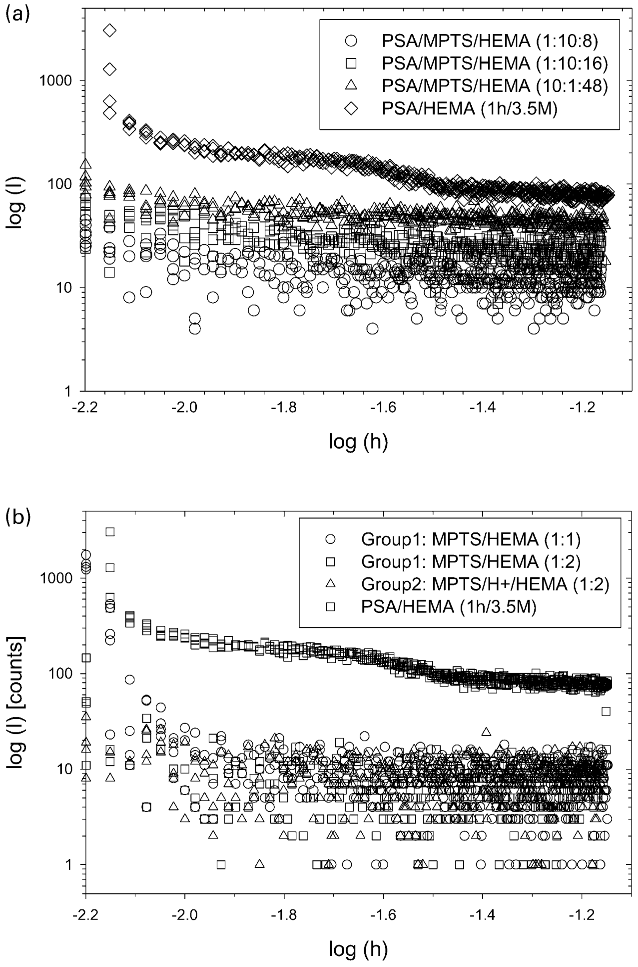


Fig. 6. Double logarithmic plots of SAXS intensities for (a) PSA/MPTS/HEMA and PSA/HEMA, and (b) MPTS/HEMA composites.

MPTS/HEMA composites (Groups 1–4) was found to be highly dependent on whether MPTS or pMPTS was incorporated. In almost all cases, when MPTS was used (Group 1), the cured samples were colourless and transparent, with a smooth surface. On the other hand, the majority of the samples with incorporated pMPTS (Group 2) appeared to be brittle, cracked throughout the whole sample volume and were a yellow to light brown colour. The samples with MPTS hydrolysed in the presence of HEMA (Group 3) appeared to be very brittle and with a white, snow-like appearance. The appearance of composite samples based on PHEMA (Group 4) was again dependent on the form of MPTS being combined with the polymer. Those with MPTS monomer (Group 4a) appeared to be solid samples with a regular surface. Samples containing pMPTS (Group 4b) were of a yellow colour and quite brittle, with many cracks. Overall, the inorganic content in the whole range of composites varied between ~9 and ~23 wt% (Table 3).

4.3. Inorganic phase content

The content of inorganic phase in the composite materials was determined after thermal decomposition of the samples in a furnace that was gradually heated to 900 °C and held for 6 h (Table 3). It can be seen that the values of the inorganic phase content obtained after decomposition of the organic component were very close to the calculated values in the majority of cases. However, it was not easy to explain some irregularities (approx. ±6 wt%) in the Group 4 composites, where PHEMA was incorporated in the system. It was also not possible to obtain decomposition profiles of any of the MPTS/HEMA composites using TGA as they decomposed explosively, in either air or nitrogen flow, for unknown reasons possibly related to internal stresses generated during the heating. It could, however, be predicted by analogy with the previously described PSA/HEMA, PSA/MPTS and PSA/MPTS/HEMA organic–inorganic hybrid materials [24,26], that there would be one major weight loss at elevated temperature (about 270 °C for PHEMA), followed by the loss of the organic part of the MPTS at slightly higher temperatures (~320 °C) due to obstruction of the decomposing organic gases by the remaining inorganic silicate phase.

4.4. Morphology of the systems

It has been shown previously [19,28] that the SAX technique can be an important tool to determine the degree of miscibility between organic and inorganic phases due to the chemical differences between segments resulting in fluctuations in electron densities (inorganic rich SiO_2 vs. lower electron densities of polymer matrix). The SAXS intensity reflects the relative electron density difference between phases and may show differences in the phase behaviour (miscibility) in the composites. It was shown in our previous publication which reported PSA/HEMA composite materials [25], that scattering intensities and power laws vary with the changes in reaction conditions used for the PSA preparation, reflective of formation of different morphologies. In those materials, morphologies were manipulated by varying reaction conditions (reaction time and concentration of acid) during hydrolysis of starting material (sodium metasilicate) and production of the PSA material. This influenced the shape of the inorganic phase (assigned by Q values) [25] and thus the eventual miscibility between this component and the organic HEMA phase. It was shown that no definite phase separation resulted, with an inorganic phase (up to ~10 wt% of inorganic content) remaining finely dispersed (~low nm range scale) within the organic matrix.

Overall, scattering intensity and power laws within our previously reported PSA-based system (either PSA/HEMA [25] or PSAMPTS/HEMA [26]) were quite low (Fig. 6(a)) and even lower compared to the previously described organic–inorganic sol–gel materials based on TEOS and HEA by other authors [19,28]. The SAXS log I vs. log h plots of our PSA/MPTS/HEMA composites (with inorganic content between ~10 and 21 wt% as examples) [26] revealed that the scattering intensity was much lower than

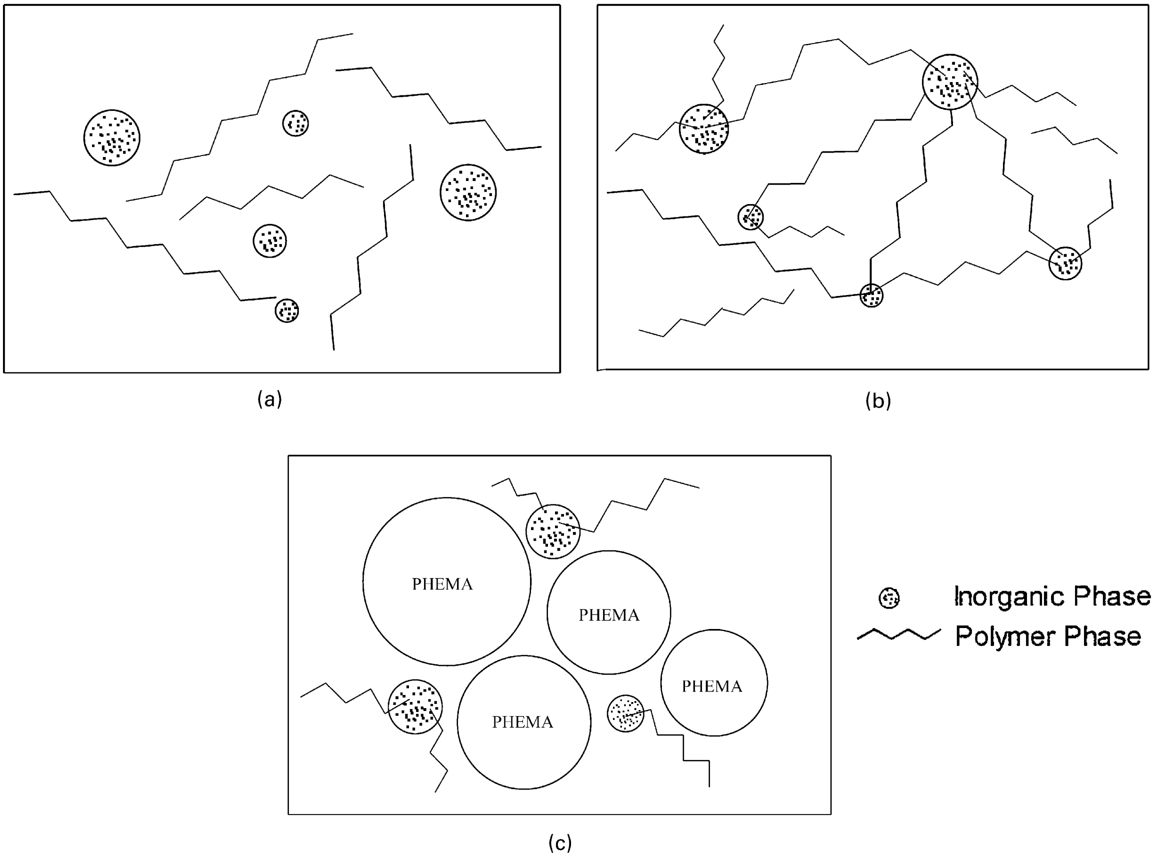


Fig. 7. Schematic representation of the composite materials with (a) no chemical bond (as, for example, PSA/HEMA composites and MPTS/HEMA Groups 1–3), (b) chemical bonding between phases (as for PSA and MPTS) and (c) MPTS/HEMA—Group 4 composites.

for the PSA/HEMA system (with inorganic content up to ~10 wt%) and thus covalent bonding in PSA/MPTS/HEMA composites leads to greater miscibility. It was expected that PSA/MPTS/HEMA systems with higher silica content (for example, ~21 wt% for molar ratio PSA/MPTS/HEMA 1:10:8, Fig. 6(a)) with more centres of different electron densities present, would result in higher scattering intensities. That was not the case, with the scattering intensity being lower than for PSA/HEMA, in a range that does not allow definitive conclusions as the measurement is within experimental error. This is most likely due to the aforementioned higher miscibility of chemically similar components.

It has been shown previously [19,28] that scattering intensities of the composite systems are indicative of the degree of phase mixing and also of the size/shape of the phases within the overall morphology. Higher values (near −3 or −4 for TEOS and HEA-based composites) indicated that the differences in electron densities between phases are larger and thus the presence of well-defined, sharp, three-dimensional structural features were present within the composite morphology. For systems with lower values of power law exponents (~ − 1), the difference in electron densities of both phases was less and the possibility of a finer morphology was more likely. For power law values approaching zero, mixtures which are miscible on some level are likely, with no distinct phases present.

Only a limited number of SAX data were collected for the MPTS/HEMA composites in this study, due to the quality of the bulk samples. However, from the available data, it could be seen that the scattering intensity and power law (slope) of each of the samples was very low (Fig. 6(b)), even slightly lower than those in the PSA/MPTS/HEMA system [26]. As previously suggested, the organic part of the MPTS molecule is very chemically similar to the organic phase of HEMA, offering a high degree of miscibility resulting in such low scattering intensities.

It was reported previously [24,25] for the PSA/HEMA composites, that there was no chemical bond formed between the two phases (PSA and HEMA) and a proposed morphology was schematically presented as in Fig. 7(a). On the other hand, Fig. 7(b) represents the possible morphology in the previous PSA/MPTS/HEMA [26], where chemical bonding between the inorganic PSA and MPTS phase was achieved.

In summary, it is quite difficult to distinguish between the morphologies for the MPTS/HEMA composites for each group in this study due to the limited number of the

SAXS data available and the low scattering intensity observed. However, the thermal and physical properties shown later, as well as physical appearance, do indicate that the morphologies differ from each other as a result of the alternative synthetic approaches. Group 1 composites were based on monomeric HEMA and MPTS species. As has been shown by NMR and GPC, they were not coupled and existed as two separate phases that were radically polymerized in the final curing step. Their morphology may thus be very close to that outlined for the PSA/HEMA composites (Fig. 7(a)). Group 2 composites based on pMPTS, produced by prior addition of HEMA monomer, contain larger inorganic centres with the organic portion of the molecule pendant from the inorganic matrix, allowing both phases to be well intermixed. Morphology of this system might also be similar to that shown in Fig. 7(a), albeit with larger inorganic centres. The morphology of the Group 3 composites containing MPTS that was hydrolysed in the presence of HEMA monomer appears to differ from the morphology of Group 2 composites. The inorganic centres formed might be smaller than in Group 2 due to the dilution of the organic phase which would restrict the growth of the Si–O–Si chain. The white colour of the resultant composites suggest that phase separation has occurred. The size of the organic centres in Group 4 composites was enhanced by the polymerization of HEMA prior the addition of MPTS, as shown in Fig. 7(c). The size of the inorganic centres depends on the form of MPTS, which was mixed with PHEMA, with smaller centres formed using MPTS monomer, and larger ones following hydrolysis of MPTS. One would predict that the miscibility of both components would decrease due to the increase in MW of PHEMA. However, it appeared that the miscibility was still sufficient to produce non-phase-separated systems.

4.5. Thermal behaviour of the systems

The glass transition temperatures of PHEMA (radically polymerized HEMA monomer) PMPTS (radically polymerized MPTS monomer), PpMPTS (radically polymerized hydrolysed MPTS) and the composites were determined using DMTA. In Fig. 8(A)–(E), tan δ measurements are presented for a number of systems, and the maxima of tan δ peaks, width at half-height ($W_{1/2}$) of peaks and relaxation strength, summarized in Table 3. PHEMA showed a strong glass transition at ~110 °C (Fig. 8(A)). A relaxation for PMPTS was located at ~9 °C and for PpMPTS at ~31 °C and its strength decreased, possibly due to increased crosslinking of the Si–O–Si network. It can be seen that the shapes and positions of the α-relaxations of the composites are quite different from the PHEMA, PMPTS or PpMPTS and vary according to overall composition and thus, presumably, to the overall degree of mixing and morphology. The width of the DMTA peaks for the majority of the composites was broader than those for the neat polymers. Broadness of the tan δ peaks and the relaxation strength (the height of the tan δ peak) [29] has been shown previously to be quite sensitive to changes in morphology.

As can be seen in Fig. 8(B), Group 1 composites based on MPTS monomer and HEMA, show a clear T_g, that is located closer to the transition of neat PHEMA than to PMPTS, in the composite with molar ratio of the components 1:2 (~71 °C). MPTS/HEMA composite with a molar ratio 1:1 showed one broad transition (~68 °C) with a shoulder at slightly lower temperatures (~12 °C) that appeared to be suppressed compared to the neat polymer transitions. The T_g transitions of the Group 2 composites based on pMPTS and HEMA are shown in Fig. 8(C). The relaxations of any organic component in the presence of pMPTS (or in neat PpMPTS) were significantly suppressed and were dependent on the overall composition. There are no data shown for the Group 3 composites, as these were quite brittle with irregular surfaces and thus not suitable for measurement. Similarly, composites based on PHEMA and MPTS monomer (Group 4a, Fig. 8(D)) showed clear transitions, which were suppressed if pMPTS was incorporated (Group 4b, Fig. 8(E)). As for the Groups 1 and 2 composites, glass transition temperatures in Group 4 were dependent on the overall composition of the composites.

In all groups of MPTS/HEMA composites, it appeared that the glass transition temperature was different from that of neat polymers (PHEMA, PMPTS or PpMPTS) and was dependent on the molar ratio of the components. Transitions for the composites based on pMPTS (Group 2, Fig. 8(C) and Group 4b, Fig. 8(B)) were much broader and weaker than those in comparable composites (with the same molar ratio) based on the MPTS monomer (Group 1, Fig. 8(B) and Group 4a, Fig. 8(D)). This possibly results from a higher degree of miscibility of the components resulting in a broader range of mutual interactions.

4.6. Density of the MPTS/HEMA composites

Density of each component as well as of the composite materials were measured using a He-gas pycnometer and are summarized in Table 4 and shown in Fig. 9. The composite samples consist of an inorganic phase which is incorporated with the organic part of the MPTS molecule via Si–C bonds, and the organic phase of HEMA. The densities of PHEMA, PMPTS and PpMPTS were taken as limiting values. It appeared that hydrolysed and subsequently radically polymerized MPTS (PpMPTS) is slightly more dense than that of unhydrolysed and radically polymerized PMPTS, possibly due to the formation of a more compact silicate network. It was expected that the densities of composites would be between those of PHEMA and PMPTS or PpMPTS, and dependent on the composition as well as the morphology. Densities of Groups 2 and 3 composites were indeed between the extremes of the neat polymers. The rest of the samples, i.e. Groups 1, 4a and 4b are out of range of densities of neat polymers, with Group 1 (composites based on

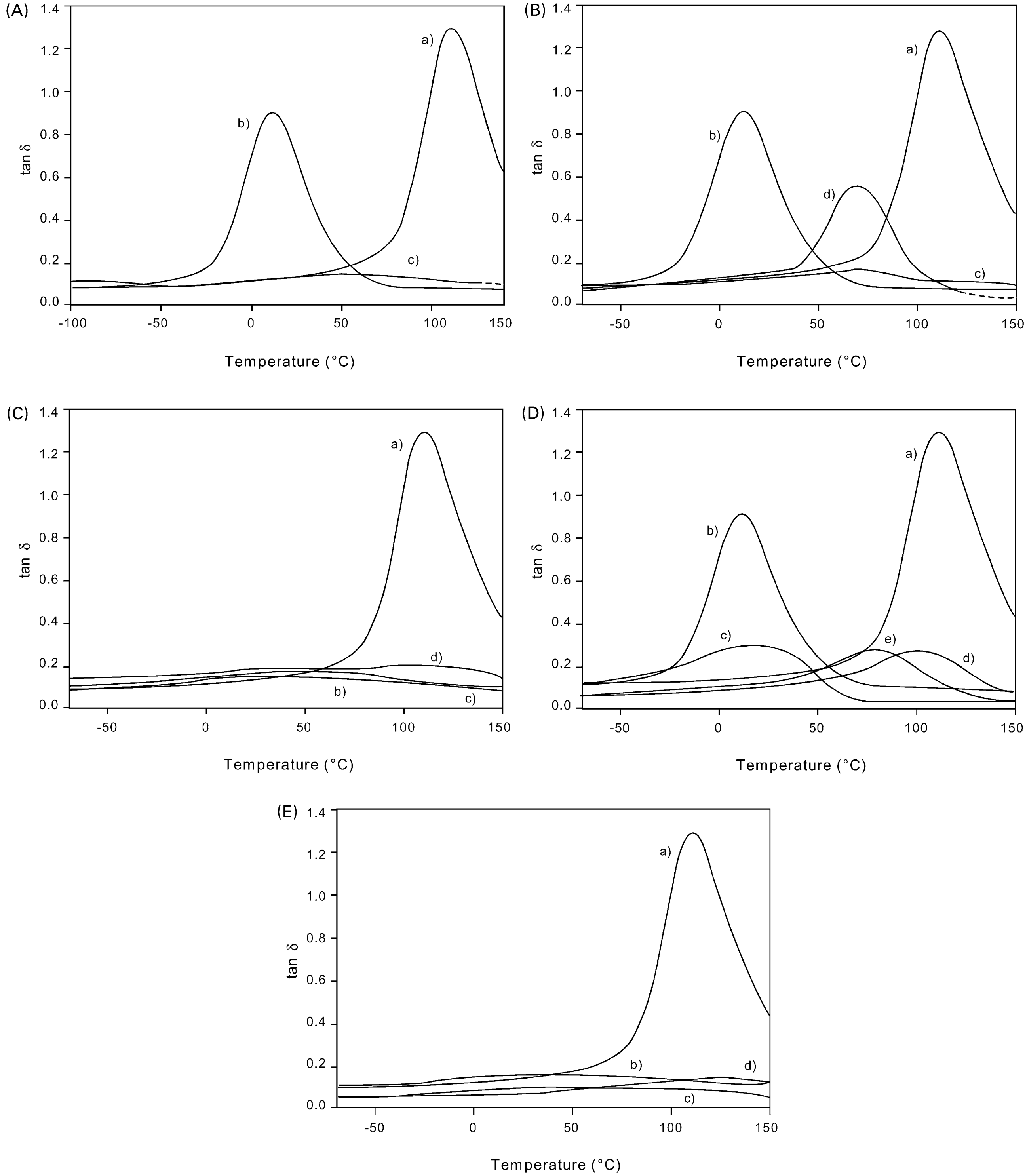


Fig. 8. tan δ vs temperature of (A) (a) PHEMA, (b) PMPTS and (c) PpMPTS; (B) (a) PHEMA, (b) PMPTS and Group 1 MPTS/HEMA composites, (c) 1:1 and (d) 1:2; (C) (a) PHEMA, (b) PpMPTS and Group 2 pMPTS/HEMA composites (c) 1:1 and (d) 1:2; (D) (a) PHEMA, (b) PMPTS and Group 4a MPTS/PHEMA composites, (c) 1:1, (d) 1:2 and (e) 2:1; (E) (a) PHEMA, (b) PpMPTS and Group 4b pMPTS/HEMA composites, (c) 1:1 and (d) 1:2.

HEMA and MPTS monomer) and Group 4a (composites based on PHEMA and MPTS) densities being below the density of PMPTS, and Group 4b composites (based on pMPTS and PHEMA) being above the values of PHEMA.

Slightly higher densities were found for composites where the hydrolysed form of MPTS (pMPTS) was incorporated with HEMA. The formation of Si–O–Si network during hydrolysis of MPTS leads to tighter structures, resulting in greater values of density. The presence of

Table 4
Density of PHEMA, PMPTS, PpMPTS and composites as a function of SiO_2 content

Group	Sample composition (molar ratio)	SiO_2 content (%)	Measured density (g/cm^3)	Calculated density 'rule of mixtures' (g/cm^3)[a]	Deviation +ve or −ve[b]
	PHEMA	–	1.2730 ± 0.0003	–	
	PMPTS	27.5	1.2331 ± 0.0013	–	
	PpMPTS	26.4	1.2363 ± 0.0018	–	
1	MPTS/HEMA (1:1)	15.5	1.2223 ± 0.0017	1.2460	−
	MPTS/HEMA (1:2)	10.9	1.2264 ± 0.0020	1.2529	−
2	pMPTS/HEMA (1:1)	16.5	1.2482 ± 0.0014	1.2485	−
	pMPTS/HEMA (1:2)	11.3	1.2461 ± 0.0013	1.2548	−
3	(MPTS/HEMA)/H^+ (1:1)	16.7	1.2578 ± 0.0009	1.2460	+
	(MPTS/HEMA)/H^+ (1:2)	13.0	1.2549 ± 0.0004	1.2529	+
4	pMPTS/PHEMA (1:1)	17.5	1.2820 ± 0.0014	1.2485	+
	MPTS/PHEMA (1:1)	17.3	1.2018 ± 0.0019	1.2460	−
	pMPTS/PHEMA (1:2)	12.0	1.2852 ± 0.0007	1.2548	+
	MPTS/PHEMA (1:2)	8.8	1.2134 ± 0.0003	1.2529	−
	pMPTS/PHEMA (2:1)	23.1	1.2925 ± 0.0003	1.2437	+
	MPTS/PHEMA (2:1)	11.7	1.2035 ± 0.0003	1.2412	−

[a] Density was calculated using values of corresponding PMPTS or PpMPTS that were incorporated in composites.

[b] Deviation of measured values from calculated.

MPTS monomer can result in more interfaces when combined with HEMA, leading to lower densities if there is poor packing and free volume at the interfaces.

Table 4 summarizes the calculated (based on fraction volumes calculations) and measured densities and deviations (positive or negative) of the measured values from those calculated from the rule of mixtures. There is a positive deviation for Groups 3 and 4b composites, suggesting that there are close interactions within this system, resulting in well-packed composites. Conversely, deviations of measured densities from those calculated for Groups 1 and 4a composites based on initially monomeric species are negative deviation, suggesting fewer interactions and poor interfaces compared to the hydrolysed systems.

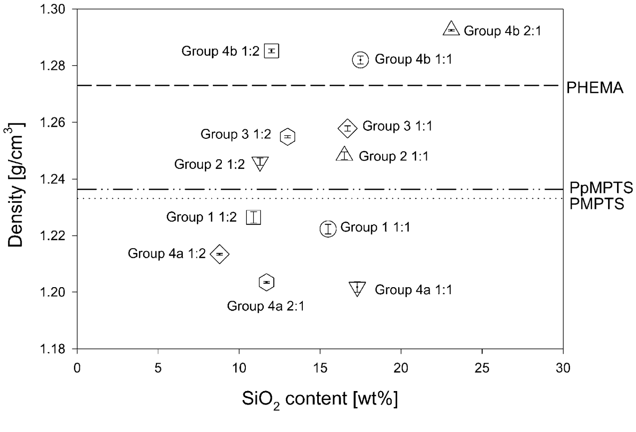


Fig. 9. Density of the PHEMA, PMPTS, PpMPTS and MPTS/HEMA composites as a function of silica content.

4.7. Hardness of the systems

Hardness measurements in ceramics are important and have been previously discussed in detail by us [26]. Vickers hardness testing was used to assess hardness of the MPTS/HEMA composite materials and typical values of some of the composites are shown in Table 5 and Fig. 10. A load of 1 kg was applied for 15 s. The size of the indent was measured in diagonals, averaged and the Vickers hardness number (VHN) assigned from the VHN tables at the applied load.

There was a limited range of hardness data of the MPTS/HEMA composites collected due to the fast recovery (non-permanent flow) of the surface (Table 5). Only Group 4 composites allowed a reliable and consistent study of the

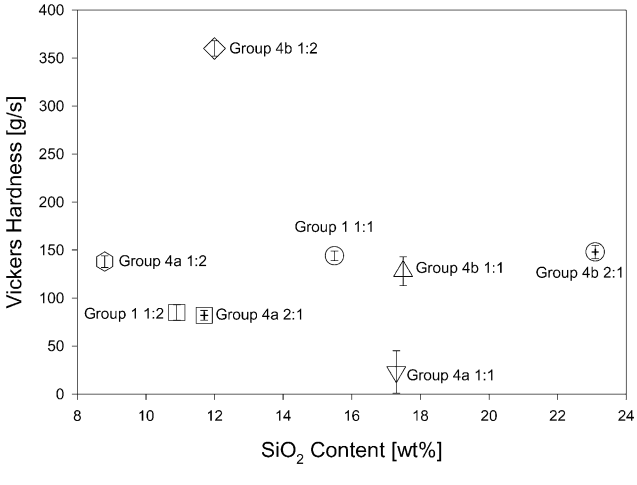


Fig. 10. Representation of VHN for the MPTS/HEMA composites.

Table 5
Vickers hardness of MPTS/HEMA composites

Group	Composition	SiO_2 content furnace (wt%)	Hardness load 1 kg/15 s
1	MPTS/HEMA (1:1)	15.5	144 ± 5
	MPTS/HEMA (1:2)	10.9	85 ± 8
4	pMPTS/PHEMA (1:1)	17.5	128 ± 15
	MPTS/PHEMA (1:1)	17.3	23 ± 22
	pMPTS/PHEMA (1:2)	12.0	360 ± 8
	MPTS/PHEMA (1:2)	8.8	138 ± 6
	pMPTS/PHEMA (2:1)	23.1	148 ± 7
	MPTS/PHEMA (2:1)	11.7	82 ± 5

Vickers hardness. Generally, it was observed that hardness values were lower than the previously described PSA/HEMA and PSA/MPTS/HEMA systems [25,26] which incorporate unattached or attached pre-formed PSA molecules in an organic matrix. The highest hardness value of ~360 was measured for the system based on pMPTS and PHEMA (molar ratio 1:2), followed by the system of similar composition with the molar ratio 1:1. Overall, it can be seen that the hardness values of the comparable systems when MPTS monomer was incorporated to PHEMA are less than those with hydrolysed MPTS (pMPTS) suggesting better interactions between components, and thus better packed systems. This correlates well with the density values. It was found that better packed systems with fewer interfaces formed when pMPTS was incorporated, leading to denser and harder materials.

Fig. 10 also shows that all composite samples which could be measured were of very similar hardness, regardless of silica content. Thus, with silica contents up to ~24 wt% morphology is a more important determinant of hardness

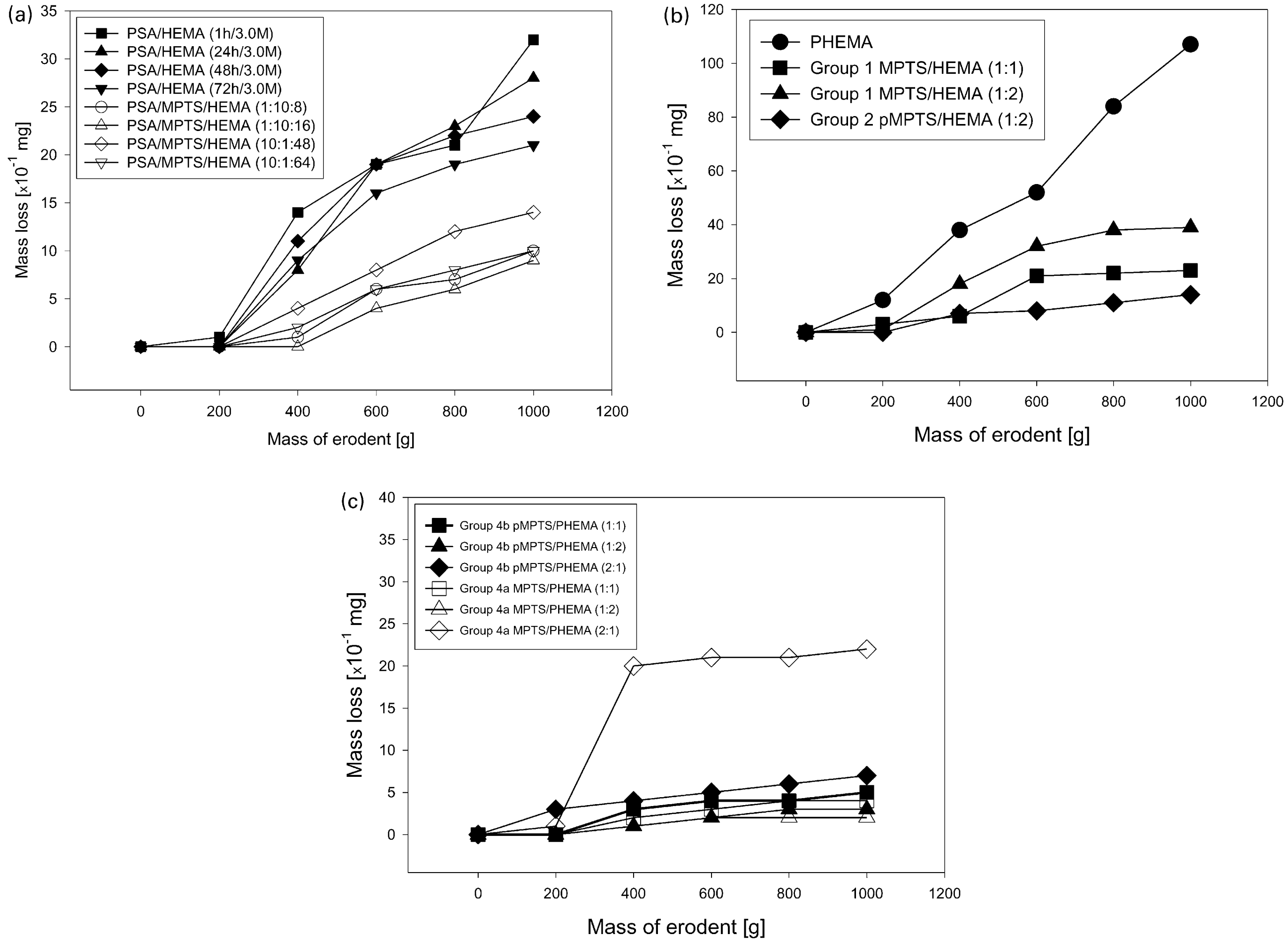


Fig. 11. Assessment of mass loss as a function of mass of erodent for (a) PSA/HEMA and PSA/MPTS/HEMA composites, (b) PHEMA and Groups 1 and 2 MPTS/HEMA composites and (c) MPTS/HEMA composites.

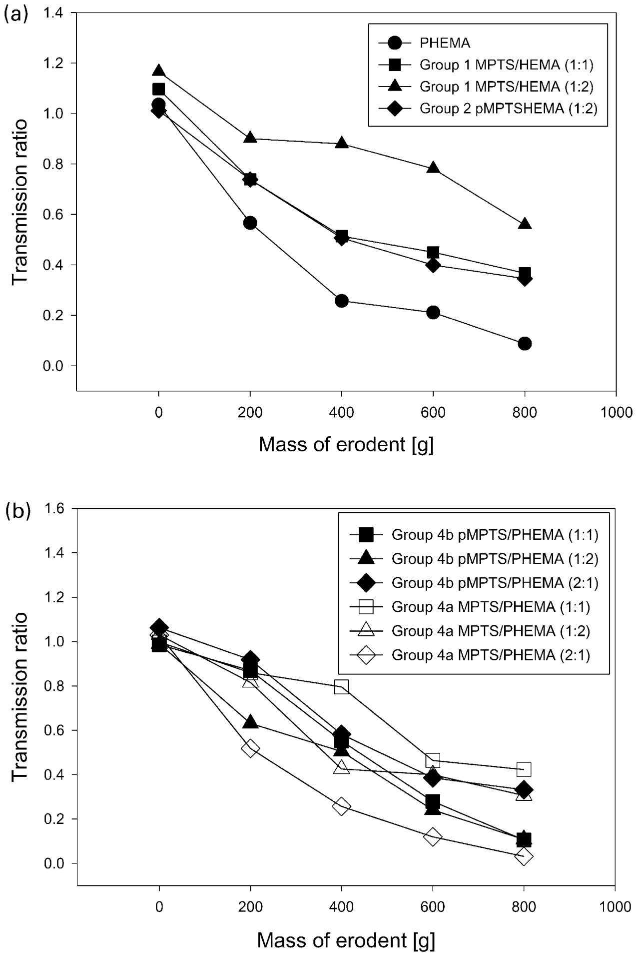


Fig. 12. Assessment of transmission loss as a function of mass of erodent for (a) PHEMA and Groups 1 and 2 MPTS/HEMA composites and (b) Group 4 MPTS/HEMA composites.

than the silica content, contrary to results reported previously for composites based on PEOX/SiO_2 [30].

4.8. Erosion test

The importance of erosion tests, as well as a detailed description of instrumentation has been discussed previously [26]. Fig. 11(a)–(c) represents mass loss as a function of mass of erodent for a range of composites. Previously reported PSA/HEMA and PSA/MPTS/HEMA composites [26] (Fig. 11(a)) showed that the PSA/MPTS/HEMA composites containing chemically linked organic and inorganic phases proved to be more resistant to abrasion than non-linked PSA/HEMA materials. Their level of resistance proved to be dominated by the morphology rather than total silica content.

Performance of the composite samples in erosion testing was only compared with the performance of PHEMA, as the erosion test was not performed with PMPTS and PpMPTS samples due to the surface irregularities. PHEMA was rapidly eroded, losing the most from its original weight in the early stages of erosion (Fig. 11(b)). The Groups 1 and 2 MPTS/HEMA composite materials were eroded much less easily than PHEMA. Group 2 composites based on pMPTS were most resistant to erosion through the whole process (SiO_2 content ~11 wt%) and more resistant than the Group 1 composites of the same composition (molar ratio 1:2, ~11 wt% SiO_2). Fig. 11(c) represents performance of Group 4 composites during erosion. Composites based on PHEMA and pMPTS or MPTS monomer showed similar erosion resistance, with only MPTS/PHEMA (2:1) composite less resistant (close to that of Group 1 (1:1) composite, Fig. 11(b)). The best performance was shown by the Group 4b (1:2) composite based on pMPTS and PHEMA (SiO_2 content ~12 wt%).

The level of erosion resistance is due not only to the overall inorganic phase content but is also significantly influenced by the chemical nature of the components, miscibility of the components and thus, overall morphology of the system. The Group 4 composites based on PHEMA and/or MPTS monomer or its hydrolysed form (pMPTS) with chemically linked organic and a part of an organic phase (in MPTS via Si–C bond) proved to be most abrasion resistant of all MPTS/HEMA systems, as well as previously presented PSA/MPTS/HEMA and non-linked PSA/HEMA system [26]. Only one composite of Group 4a (based on MPTS monomer and PHEMA, 2:1) was not as good, and was comparable to the lower performance of non-bonded PSA/HEMA systems. The second highest level of erosion resistance was that of Group 2 composites (based on pMPTS and HEMA, 1:2), followed by the Group 1 composites (based on MPTS monomer and HEMA).

The effect of erosion was also monitored by optical transmission ratio (Fig. 12(a) and (b)), defined as a ratio of the transmission as a function of gram of erodent used and initial transmission vs. mass of erodent. Neat PHEMA (Fig. 12(a)) was strongly affected, losing most of its transmission during erosion. Composites were also affected by the erodent. The least affected was Group 1 (1:2) (Fig. 12(a)). The Group 4a (2:1) lost most transmission. The composite losing most mass during erosion testing (Group 4a, 2:1) also had the greatest reduction in transmission and became the most hazy.

5. Conclusions

A range of composite materials based on MPTS and HEMA were prepared in order to be produced mechanically useful sol–gel materials. The chemical nature of the composites was studied using NMR and FTIR spectroscopy and GPC. There was no chemical bonding between HEMA and MPTS prior to radical polymerization.

The glass transitions of the range of composites were located at different temperatures than those of neat polymers PHEMA, PMPTS and PpMPTS. The magnitude of the shifts, as well as the strength and broadness of the peaks, depended on the composition, degree of mixing and morphology. The T_g for the composites based on pMPTS (hydrolysed MPTS) were broader and weaker than for the composites of the same composition with MPTS monomer.

The SAX intensities for the whole range of MPTS/HEMA composites were lower than for previously reported systems [25,26], possibly as a result of a high degree of miscibility of the chemically similar components. Densities varied among samples according to the composition. Composites based on pMPTS were denser than unhydrolysed systems due to better packing of the components within the system. VHN was quite high (360) in the system based on pMPTS, which should improve the strength due to the presence of more inorganic silicates than in the MPTS monomer. The composites resisted erosion much better than the neat polymers. The most resistant composites were those based on PHEMA and either MPTS or pMPTS, and they were more resistant to the erodent than previously reported PSA/HEMA and PSA/MPTS/HEMA systems [26].

Acknowledgements

Financial support from the Australian Government via a SPIRT grant and SOLA International Holdings Ltd is highly appreciated.

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