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Alkoxysilane Functional Acrylic Latexes: Influence of Copolymer Composition on Self-Curing Behavior and Film Properties

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Summary: Reactive latexes based on acrylic polymers with trimethoxysilyl groups in the side chain were prepared by semi-continuous emulsion copolymerization. The properties of the latex film related to the polymer network structure and their evolution upon thermal curing were studied as a function of the content of the reactive comonomer, trimethoxysilylpropyl methacrylate (TSPMA), ranging between 8 and 25 wt-%. In particular, the sensitivity to both organic solvent (chloroform) and water and the thermomechanical properties were investigated by swelling experiments and dynamic-mechanical analysis (DMA). The results are interpreted in terms of a transition from uniform to microheterogeneous crosslinking regime, possibly as the result of formation of polyorganosilsesquioxane-like (POSS) crosslinking domains at higher TSPMA content.

Keywords: alkoxysilane; emulsion polymerization; POSS; reactive latex; self-crosslinking

Introduction

Water-borne polymer dispersions are rapidly becoming the coating materials of choice for an increasing number of industrial and consumer applications, thanks to their benign environmental, health and safety features. Indeed, over the last 20 years a rapid improvement of both performance and production costs has been prompted by a better understanding of the chemistry and mechanisms of film formation and development of the main macroscopic properties relevant to coating applications, such as adhesion, cohesion, curing mechanisms, surface properties, surface dynamics, and stability against aging.

However, while the technology gap between conventional (homogeneous) solvent-based and water-borne (heterogeneous) coating formulations has progressively narrowed, some issues related to the mechanisms and the physics of film formation and to the role of the

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various components in providing a given coating performance are still challenging and require further research.

Among the key features of water-borne coating materials, a critical one concerns their film forming behavior in the absence of coalescent agents or plasticizers; indeed these latter additives can allow to broaden the range of useful water-borne coating polymers, to include those with a glass transition temperature (T_g) higher than that typical for a given application. However, such low molecular weight additives represent a source of environmental pollution and health-related risks, in addition to making the coating polymer and its performance less stable towards aging processes. As amply reported in the scientific and patent literature[1-5], a typical approach to this problem is based on the introduction of crosslinks in the latex polymer, in order to improve cohesion and adhesion properties of the final coating, increase its surface hardness and lower its solvent sensitivity.

Among the features to be considered in the selection of functional groups or additives inducing the crosslinking in a latex polymer, the nature of the chemical reaction involved and its kinetics are crucial. In fact, untimely crosslinking during polymerization or in the latex dispersion can negatively affect both colloidal stability, causing coagulation, and film formation, hampering the last stage of interparticle polymer diffusion.

Several strategies are based on the introduction of a functional comonomer carrying reactive groups capable of reacting among themselves and build bridging bonds, thus acting as self-crosslinking sites for the polymer chain[6-8]. This can allow to obtain, in principle, one-pack water-borne formulations with extended stability and minimum variations of performance upon storage. However, as already mentioned, the crosslinking reaction must take place only upon film formation, as the result of polymer interdiffusion or of other external parameters such as variations in pH[8], temperature[9], or UV irradiation[10].

In this work we focus the attention on an acrylic copolymer latex (figure 1) with trimethoxysilane groups introduced as the self-crosslinking sites by copolymerization with trimethoxysilylpropyl methacrylate (TSPMA) under controlled process conditions and at nearly neutral pH. The influence of the curing temperature on the film formation process and on some of the material properties more relevant to coating applications have been investigated.

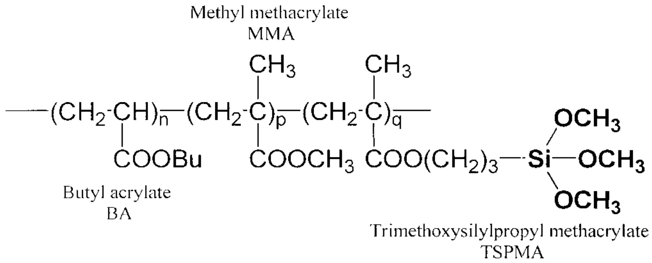

Figure 1. Structure of the reactive acrylic copolymer.

Experimental Part

Materials. Butyl acrylate (BA, Aldrich) and trimethoxysilylpropyl methacrylate (TSPMA, Aldrich) were distilled in a vacuum before use and stored under nitrogen at -20 °C. Methyl methacrylate (MMA, Aldrich) was distilled under nitrogen and stored at -20 °C. Potassium persulfate (KPS, Fluka), sodium dodecylsulfate (SDS, Fluka) and Brij^{TM} 58P (a polyethoxylated long chain aliphatic monoalkyl ether surfactant with 20 oxyethylene units, Fluka), and the buffering salts sodium hydrogencarbonate (Fluka) and sodium dihydrogenphosphate (Aldrich) were used as supplied. HPLC-grade water was used for the polymerizations.

Latex syntheses. Seeded semi-continuous emulsion polymerizations were carried out under nitrogen atmosphere in a conventional 250 ml jacketed glass reactor equipped with thermostated bath circulator, reflux condenser, mechanical stirrer and thermocouple. The reactive trimethoxysilane group of TSPMA could undergo hydrolysis and condensation, resulting in poor control of the final copolymer composition and causing colloidal destabilization of the latex as well as poor film-forming behavior due to incipient cross-linking. Therefore the polymerizations were run at nearly neutral pH ($7.3 < pH < 7.5$).

The seed latex was prepared by batch emulsion polymerization. The reactor containing a solution of SDS (0.31 g), $NaHCO_3$ (0.06 g) and NaH_2PO_4 (0.06 g) in 140 ml de-ionized water was loaded with the monomers (BA, 3.7 g; MMA, 3.2 g; TSPMA, 0.6 g), purged with nitrogen for 30 min, then heated at 70 °C under stirring (250 rpm) prior to addition of the initiator (0.11 g KPS in 2.5 ml of H_2O). After 90 min polymerization at 70 °C the resulting seed latex, nominally with 5 wt-% solids and 8 wt-% TSPMA vs. total monomers, contained monodispersed polymer particles of average diameter $d_p = 50$ nm according to Photon Correlation Spectroscopy (PCS, Brookhaven 90 Plus) analysis. The same seed latex was used for the synthesis of the final BA/MMA/TSPMA (hereafter

BMT) latexes by starved-feed semi-continuous polymerization. The procedure was adopted to produce polymer particles with controlled and monodispersed size, and to prevent the formation of heterogeneous particles and/or particles with shell-enriched reactive silane groups such as those resulting from compositional drift in monomer-flooded processes where the co-monomers' reactivities are quite different[11]. Feed compositions (table 1) were chosen in order to obtain copolymer latex films with nearly the same glass transition temperature T_g(Fox) ≈ 0 °C, irrespective of the TSPMA content.

Table 1. Composition and latex particle diameter (d_p) of BMT copolymers.

	TSPMA	BA	MMA	d_p	PDI[a]
	wt%	wt%	wt%	nm	-
BMT-8	8	49	43	109.9	0.033
BMT-14	14	45.5	40.5	108	0.022
BMT-25	25	39.7	35.3	112.2	0.017

[a] Polydispersity index.

In a typical polymerization 38 ml of the preformed seed latex (1.9 g of polymer) were purged with nitrogen and heated under stirring (250 rpm) at 70 °C; then two distinct and individually deoxygenated feeds with the monomers mixture (18.1 g) and the aqueous solution of surfactant (Brij 58P 0.355 g), buffer ($NaHCO_3$ 0.06 g, NaH_2PO_4 0.06 g) and initiator (KPS 0.055 g) were added by means of metering syringe pumps. During the monomer feed and throughout the polymerization the mixture in the reactor was stirred at 250 rpm and the circulating thermostated fluid maintained at 70 °C. The feeds were added simultaneously during 3 h, and the polymerization was then allowed to proceed for a further 60 min. The recipes were designed to provide a final latex with 20 wt.-% solids based on quantitative conversion. The actual conversions were typically in the 90-95 wt-% range, as determined gravimetrically. The narrow distribution of d_p (~110 nm for al samples) suggests that particle aggregation and secondary nucleation were always effectively suppressed.

A latex composed of TSPMA homopolymer particles was prepared by batch process according to the procedure adopted for the synthesis of the seed latex described above. The pre-emulsion of TSPMA (4 g), surfactants (SDS, 0.016 g, and Brij58P, 0.072 g) and water (36 g) was heated at 70 °C before adding the aqueous solution of initiator (KPS, 0.012 g) and buffer (NaH_2PO_4/$NaHCO_3$ 1/1 by weight). The reaction was allowed to proceed for 1.5 h, yielding a stable 10 wt.-% solids dispersion of particles with average diameter d=

169 nm by PCS. The resulting latex film has a $T_g \approx 267$ K according to DSC analysis.

Latex films characterization.

Latex films about 0.4 mm thick were prepared by simple casting at room temperature in a Teflon dish. Thermal annealing was performed in a ventilated thermostatic oven.

For the water absorption experiments a weighed amount of each film sample, which had been conditioned at least one week over silica gel in a desiccator, was soaked in distilled water at room temperature, and after each given time it was taken off the soaking water, padded with absorbing paper to remove excess surface water, weighed and soaked in water again. Water absorption (A_w) before and after thermal curing was calculated according to equation 1:

$$A_w(\%) = \frac{W_t - W_0}{W_0} \times 100 \qquad \text{Eq. 1}$$

where W_0 is the initial weight of the film and W_t the weight at a given soaking time t.

The swelling ratio S(%) was calculated according to equation 2. In this case a weighed amount of the films was allowed to swell in $CHCl_3$ for 24 h, then the solvent on the surface of the films was wiped off and the film was weighed again.

$$S(\%) = \frac{W_t - W_0}{W_0} \times 100 \qquad \text{Eq. 2}$$

Dynamic-mechanical investigations were carried out with a Perkin-Elmer mod. 7e DMA analyzer equipped with an extension probe. Rectangular strips (0.25 × 2.5 cm) were cut from cast films 0.2-0.4 mm thick conditioned at room temperature over activated silica gel. Dynamic scans were generally performed from -20 to 80 °C at 1 Hz and repeated three to six times on specimens cut from the same film.

Results and discussion

This investigation was aimed at understanding how the reactivity of the side chain trimethoxysilane groups in the BMT polymer, and in particular their condensation leading to the formation of bridging siloxane crosslinks, affects the film swelling behavior and its thermo-mechanical properties.

The BMT latex films obtained by casting at room temperature were transparent and characterized by a moderate (BMT-8) to low (BMT-25) flexibility. This trend is exacerbated by thermal treatments, as the result of extensive condensation and crosslinking occurring within the polymer film.

An important feature in a reactive polymer with trialkoxysilane reactive groups is the fractional distribution among the alkoxysilane, silanol and intra- or inter-molecular (bridging) siloxane groups, affecting both the thermo-mechanical properties (due to variations in dipolar, H-bonding and covalent type of interpolymer interaction) and the water absorption of the polymer film. In particular, the latter could even go through a maximum if extensive hydrolysis precedes condensation of the silane groups within a moderately hydrophobic acrylic matrix.

In order to evaluate semi-quantitatively the chemical evolution of the BMT latex films upon thermal treatment, a series of experiments were carried out, where the extent of swelling in chloroform (S) and the time-dependent absorption of water (A_w) were measured before and after thermal curing at 80 °C for 7 hours.

The swelling behavior in an organic solvent can provide useful indications on the crosslinks density. In fact, the latter can be quantitatively estimated when crosslinking is a secondary reaction occurring to a soluble polymer whose molecular weight is known, or if a reliable estimate of the Flory-Huggins key (e.g. solubility) parameters is available[12,13]. While this is not our case, a comparative evaluation of the amount of siloxane crosslinks among different samples is still possible if we assume that the initial polymer network structure, that is without any sol-gel type reaction having occurred, be the same for all the as-cast latex films.

No chloroform-soluble fraction could be extracted from any of the BMT as-cast films. Since preliminary results from solid state ^{29}Si-NMR measurements[14] had shown that under the reaction conditions (neutral pH) adopted here for the latex synthesis the buildup of siloxane bonds is almost negligible, the absence of soluble fraction can be ascribed at least partially to the fact that copolymerization of BA is well known to be conducive to chain extension and crosslinking due to chain transfer reactions.

The results of the swelling experiments, carried out on the three BMT polymer films before and after thermal curing, are reported in table 1. The given figures, calculated by gravimetry according to equation 2, are not corrected for the different densities of polymer and chloroform, and are thus overestimations of the volume swelling ratio. The as-cast BMT-8 film showed a much higher swelling ratio than the latex films with larger TSPMA content, as one would expect in case of a higher crosslinking density in the latter. However, this was in contrast with the above mentioned NMR observations, indicating an almost negligible presence of siloxane bridges irrespective of the TSPMA content. As a possible explanation one should consider that the limited resolution of the CP-MAS NMR technique does not allow to distinguish between alkoxysilane and silanol groups. Therefore, in case of extensive hydrolysis of the former, strong H-bonding interactions among silanols in the polymer network could result in a higher "effective crosslinks density" and thus account for the lower swelling at higher TSPMA content in a not H-bonding solvent. However, it can not be excluded that even a relatively low fraction of bridging siloxane groups be quite effective by itself in increasing the crosslinks density of BMT copolymers with higher functionality (BMT-14 and BMT-25).

Table 2. Chloroform swelling of the BMT films before (S) and after (S_c) thermal curing.

	S (%)	S_c (%)	%SR [a)]
BMT-8	623	305	51
BMT-14	316	196	38
BMT-25	324	172	47

[a)] Reduction % of the swelling upon curing.

The latter interpretation agrees with the general results of the water absorption experiments (see figure 2). In fact, the difference among the measured A_w for the three latex films is negligible at first, when water absorption is presumably hindered by hydrophobic unreacted alkoxysilane groups and siloxane bridges, but would be favored by silanol groups.

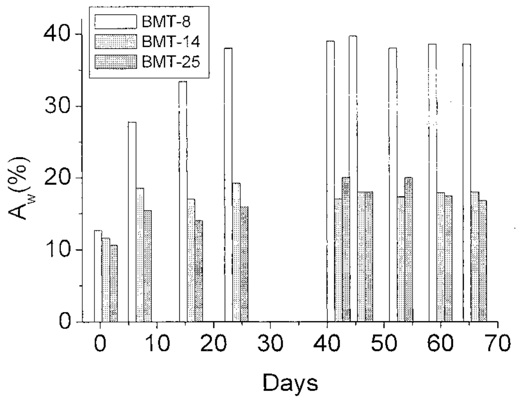

Figure 2. Time evolution of the water absorption (Aw) of BMT films.

The larger increase of A_w observed for BMT-8 at longer soaking times could indeed be related to the build-up of silanol groups, due to progressive hydrolytic decomposition of alkoxysilane bonds, not as effectively compensated by silanol condensation as in BMT-14 and BMT-25. In fact Si-O-Si bond formation is statistically less efficient in the case of BMT-8 because of the comparatively lower TSPMA molar fraction (about 3.9, 7.1, and 13.6 mol-% for BMT-8, BMT-14 and BMT-25, respectively).

Even a relatively mild thermal treatment at 80 °C caused a generalized reduction of the swelling ratio (%SR, see table 1). This was mainly ascribed to extensive silanol and/or alkoxysilane condensation, increasing the density of covalent crosslinks and thus making the film less accessible to the solvent.

The fact that thermal curing promotes the condensation of silane groups with formation of hydrophobic siloxane bonds is clearly shown by the water absorption behavior of the thermally cured latex films (figure 3). In fact, after the first 24 h A_w is only slightly lower than that of the uncured samples, where the alkoxysilane groups provide the initial hydrophobicity. However, differently from the latter, A_w increases only moderately or remains substantially stable for the cured films even after 60 days in water, indicating that in this case the hydrophobic protection is provided by more hydrolytically stable siloxane bonds rather than by the labile alkoxysilane groups.

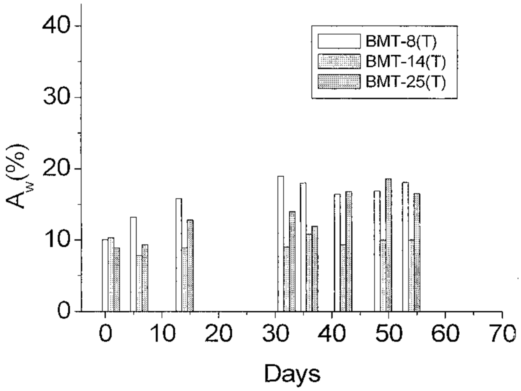

Figure 3. Time evolution of the water absorption (A_w) of annealed BMT films.

The lower water absorption of these latex films annealed well above their T_g can not be explained simply by a better film quality due to improved particle coalescence. In fact, this should have occurred nearly to the same extent for the three polymers, whereas a comparatively larger reduction of A_w is observed at longer soaking times for BMT-8.

The different hydrophobicity of the various samples is confirmed by the appearance of the soaked films, which become quickly opaque white due to not uniform water absorption when uncured, whereas the cured films remain almost translucent. In both cases the optical transparency of the films is recovered on drying.

As suggested by the water absorption and the swelling experiments, even a moderate thermal treatment can strongly affect the final properties of the films obtained from these reactive latexes. This is mainly due to the chemical evolution of the silane groups, eventually leading to condensation and build-up of both intra- and inter-macromolecular siloxane crosslinks. In particular, at higher TSPMA content the increased possibility of clustering of variously hydrolyzed side chain trimethoxysilyl groups could lead to the formation of grafted silica-like nanosized aggregates[15], down to structures resembling polyorganosilsesquioxane (POSS) cages. The latter, usually prepared from low molecular weight functional trialkoxysilanes precursors[16], have been studied as constituents of the dispersed phase in polymer nanocomposites showing improved thermal and mechanical properties with respect to the parent polymers[17].

The formation and main characteristics of a polymer network can be studied by measuring its dynamic mechanical properties, which are strongly affected by the crosslinks density immediately after the glass transition and, quantitatively, in the rubbery plateau.

The crosslinks density, ρ, can be calculated from the equilibrium storage modulus, E', in the rubbery region over the glass relaxation temperature according to equation 3 [18]

$$\rho(mol \cdot cm^{-3}) = \frac{E'(MPa)}{\varphi \cdot R \cdot T} \qquad \text{Eq. 3}$$

where φ, R, and T are the front factor, the gas constant, and the absolute temperature, respectively. Generally speaking, the front factor is an adimensional function of the crosslinking functionality[19]; here we have assumed $\varphi = 1$, which is the usually adopted value for permanent as opposed to temporary crosslinks. Calculations of crosslinks density were performed by considering the storage moduli from the DMA curves at 60 °C, that is well above the dynamic glass transition temperature.

As reported in table 3, ρ increases progressively with the TSPMA content. This applies for both the uncured and cured samples, even if in the former intermolecular condensation of the alkoxysilane groups was expected to have occurred to a very low extent. This is fairly consistent with the swelling data, where the apparently anomalous behavior of the uncured samples had been interpreted in terms of sensitivity of the characterization technique to both covalent and H-bonding type of crosslinks, the aforementioned "effective crosslinks density".

The lack of "crosslinks density increase" ($CD_{I\%}$) upon curing for BMT-14 confirms, again, what was observed from the swelling measurements. In fact, this sample shows after curing both the lowest reduction of swelling (see table 3) and the lowest $CD_{I\%}$, as if crosslinking had already partially occurred before film formation, possibly due to lack of control during polymerization, thus reducing the effect of the thermal curing.

Table 3. Storage modulus (E'), calculated crosslinking density (ρ), and % increase of crosslinks density upon curing ($CD_{I\%}$) for the BMT films.

	E' (MPa)		**ρ (10^{-2} mol·cm^{-3})**		**$CD_{I\%}$**
	as cast	**after curing**	**as cast**	**after curing**	
BMT-8	12.7	15.7	0.46	0.57	24
BMT-14	33.2	33.7	1. 20	1.22	2
BMT-25	54	99	1.95	3.58	84

By inspection of the E' and tanδ curves (figures 4 and 5), one can see that both the drop of E' and the maximum of tanδ are shifted towards higher temperatures with increasing TSPMA content and, for the same sample, upon curing. In addition, the absolute value of the storage modulus in the rubbery region increases with increasing content of TSPMA in the polymer and upon curing.

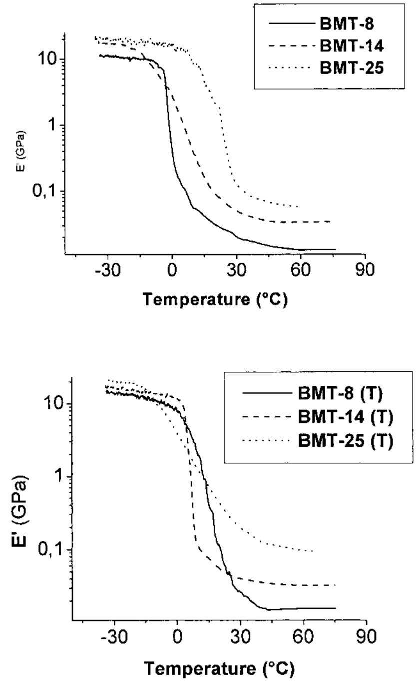

Figure 4. Tensile storage moduli (E') from DMA analysis of BMT films: a) as-cast, b) annealed 7 h at 80 °C.

Single DMA scans from -20 to either 140 (uncured) or 180 °C (cured samples) run on each latex film confirmed the absence of any activation of viscous flow, which would have caused an increase of tanδ due to the onset of dominant dissipative effects. A representative example is reported in figure 6.

These evidences are in agreement with the expected behavior of a homogeneous network with increasing density of crosslinks. However, in the case of BMT-25 both the drop of E' (figure 4a) and the perturbation of the baseline in tanδ resulting in a maximum at T_g (figure 5) are quite wide and delayed, indicating a broad glass transition. In particular, the plot of tanδ in the glassy region resembles the peculiar mechanical behavior of a heterogeneous soft-hard material with continuous softening of the glassy domains as the temperature increases.

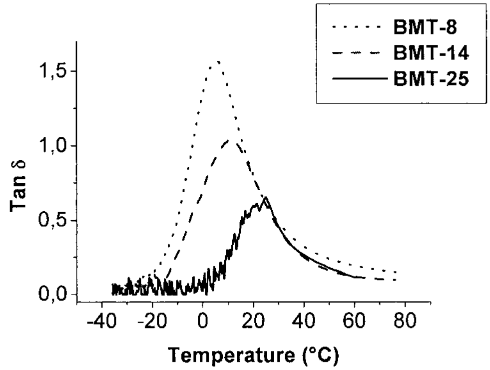

Figure 5. Plot of tanδ from DMA measurements on as-cast BMT films.

The curing behavior of BMT-25, showing by far the highest $CD_{I\%}$, could thus be explained in terms of the formation of heterogeneous crosslinks. Again, these are more likely to occur when molecularly rigid crosslinking clusters such as those resembling POSS-like structures build up within the polymeric matrix, as in the in-situ formation of a hybrid organic-inorganic nanocomposite. This process would result in a heterogeneous material with a broader glass transition and a higher storage modulus in the rubbery plateau following T_g, due to the rigid POSS-like inclusions acting as a nanofillers.

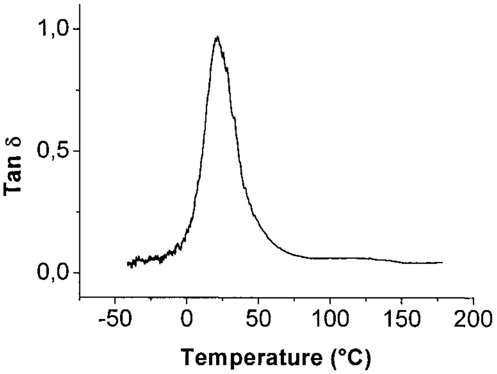

Figure 6. DMA analysis of BMT-14 after annealing at 80 °C.

Conclusions

The self-curing behavior of a class of reactive latexes based on an acrylic terpolymer with alkoxysilane groups in the side chain has been investigated in order to understand the influence of composition and film-formation conditions on the ultimate properties of these coating materials.

The complex swelling and water absorption behavior of the BMT films is clearly related to the chemical evolution of the reactive alkoxysilane groups, promoted by thermal annealing even at relatively mild temperatures. Their condensation is generally preceded by a hydrolytic step, where one or more of the three alkoxy group of each trialkoxysilane functionality can coexist with both hydrogen-bonding, hydrophilic silanols, and covalent, hydrophobic siloxane groups. Furthermore, the latter can constitute either inter- or intra-molecular bridges.

The results of the DMA measurements support the hypothesis of a parallel contribution from both covalent and H-bonding type of crosslinking to the "effective crosslinks density". At higher content of reactive groups the thermo-mechanical behavior can be interpreted in terms of heterogeneous crosslinking, as one would expect in case of build-up of silicon-rich highly crosslinked domains, similarly to the case of POSS cages embedded in an acrylic polymer matrix. Further investigations are in progress, involving the synthesis of latex polymers containing multifunctional POSS-acrylate co-units; these may provide additional evidences for the actual presence of heterogeneous crosslinks in highly functional BMT films.

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