UV PROCESSING AND CHARACTERISATION OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS®) NANOCOMPOSITES

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ABSTRACT

Nanocomposites based on a dimethacrylate matrix and different concentrations of two grades of polysilsesquioxanes (POSS®), MonoPOSS and OctaPOSS, have been prepared. A reactive solvent has been used to improve dispersion of the POSS in the matrix. The final conversion of the materials has been measured with infrared spectroscopy. Mechanical properties have been determined using tensile tests. Structure of fractured surfaces has been analysed with scanning electron microscopy. The solvent had a beneficial effect in improving both the Young modulus and the strength. The influence of the POSS on the properties is mostly related to their chemical reactivity, and it results in increasing properties only when OctaPOSSs is used. Large clusters of one grade of POSS have been identified, and the solvent has proved to be effective in destroying these clusters.

1. Introduction

Dimethacrylate-based network are frequently used in many applications, such as dental restorative materials, information storage systems and ophtalmic lenses. The main research on these materials has been devoted to chemical reaction analysis, properties of the copolymers, thermomechanical analysis and study of the fracture surfaces [1]. At the best of our knowledge, only little information on dimethacrylate-nanocomposites is available [2]. Nanocomposites represent nowadays a wide field of research in materials science because of their potential to be suitable for different applications, and their recent outstanding results in improving dramatically the properties of commercially available polymers [3]. Among these materials, one of the most attractive families is the one of hybrid nanocomposites based on an organic (polymeric) matrices and inorganic fillers. These nanocomposites should ideally exhibit both the high mechanical properties, typical of the inorganic compounds (i.e. hardness, high Young modulus and solvent resistance), and the properties of ductility and low cost of the organic matrices. Unfortunately, many problems of incompatibility between organic and inorganic compounds have limited and slowed down the development of the first generation of the nanocomposites, among which it is worth to quote silica and clay as fillers.

The new generation of fillers is well represented by the polysilsesquioxanes (hereafter POSS®). POSS are compounds with the generic formula $(RSiO_{1.5})_n$, where R denotes various hydrocarbons, and n=6,8,10 or higher number [4,5]. This class of materials, despite known since the 1950s [6], has only recently attracted a considerable attention because of the increased commercial availability and its feature to be simultaneously highly compatible with a wide range of polymers and directly reacting in the polymerisation reactions through the tailoring of the different organic groups R. Improvement of the mechanical properties and glass transition temperature has been reported for POSS-polymer nanocomposites and hybrid copolymers [5,4].

We have studied the effect on the tensile properties of the addition of two grades of POSS on two different methacrylate based matrices, polymerised under UV radiation. [1,2]. Infrared spectroscopy has been used to determine the conversion of the methacryl functionalities, and scanning electron microscopy (SEM) has been used to obtain information on fracture structure characteristics of these materials.

2. Materials

In this research we have used two POSS, the methacryilisobutylPOSS and the methacrylhoxypropylPOSS, respectively named MonoPOSS and OctaPOSS (Hybrid Plastics, USA). The OctaPOSS is a cage mixture of three cubic cages with 8, 10 and 12 silicon atoms. The two POSS used, differ in the number of functionality ligands: one methacryl functionality in the MonoPOSS and many methacryl groups (wirth most POSS havingt eight methacryl groups) for the OctaPOSS. Hence, the monoPOSS acts as a chain extender, while the OctaPOSS is essentially a crosslinking agent. The matrix used was the tetraethoxilated bisphenol A dimethacrylate (hereafter BisEMA), supplied by AkzoNobel. In order to better disperse the POSS, a reactive solvent, the cyclohexyl-methacrylate (CHMA), has been used with a ratio 1:1 (by weight) with the matrix. This solvent was effective up to 15% weight fraction (Wf) of the POSS, as shown by preliminary wide angle x-ray scattering (WAXS) analysis. The photocuring agents (2% Wf) used are 2-hydroxy-2-methyl-1-phenyl-propane-1-one (namely Darocur 1173, supplied by Ciba AG), and benzophenone (namely Darocur BP, supplied by Ciba AG). The amine reducing agent was N,N-Bis(2-hydroxyethyl)methylamine (namely nMDEA, supplied by Sigma-Aldrich). The weight fractions Wf of POSS (i.e. intended as weight fraction of the total system) have been: 0, 2.5, 5, 10, 20 and 30%.

3. Experimental section

- All the samples have been prepared according to the following protocol. Reactive mixtures have been prepared in a 10 ml glass vial and then stirred at room temperature under air for a range of time between 1 and 2 hours. After the mixing, the liquid systems were poured into "dog-bone" shaped silicon-rubber moulds. The samples were thus irradiated for 120s with an UV light lamp (Fusion F300 Fusion UV Systems Inc.). During the irradiation, the samples were subsequently carried back and forth under the lamp beam by an automatic belt to have the samples homogeneously irradiated. Post-curing has been perforemd to maximise the conversion of the methacryl double bond along with the crosslinking of the materials. The post-curing was carried out in an oven for 2 hrs at 130 °C (for the MonoPOSS-based materials) and 150 °C (for the OctaPOSS-based materials). The sample has got the typical dog-bone shape, with a thickness of ca. 1 mm, width ca. 2mm and gauge length of 10 mm.

- Measurements of the conversion of the C=C double bond in the methacryl chains have been performed using Near InfraRed (NIR) spectroscopy. For this purpose, we have monitored the evolution of two peaks: 6163 cm^{-1} and 4629 cm^{-1} [7,8]. The peak at 6163 cm^{-1} is due to the C=C double bonds and it decreases during the polymerisation, while the other one is not affected and it serves as a reference for the calculation of the double bond conversion. Conversion has been computed according to the literature [7,8]. The spectra were recorded in transmission mode using an InfraRed spectrometer EQUINOX 55 from Brucker. Each spectrum is obtained by 16 scans with a resolution of 4 cm^{-1} using the spectrum window 4000-8000 cm^{-1}.

- Mechanical properties (strength) have been measured with a Zwick Z010 Materialprüfung machine, and the deformation was monitored each 10s with the aid of a CCD camera and the software Aramis 4.7.5 (GOM mbH, Ulm, Germany) was used to analyse the data.

- SEM analysis has been done on specimens fractured during tensile testing using a LEO 435VP SEM equipped with secondary electrons detector. The samples were covered with 30 nm thick gold layer to prevent sample charging.

4. Results and discussion

The conversion has been measured as a function of the different matrices (BisEMA and BisEMA - CHMA) as well as concentration and grade of the POSS. The results are shown in Fig. 1.
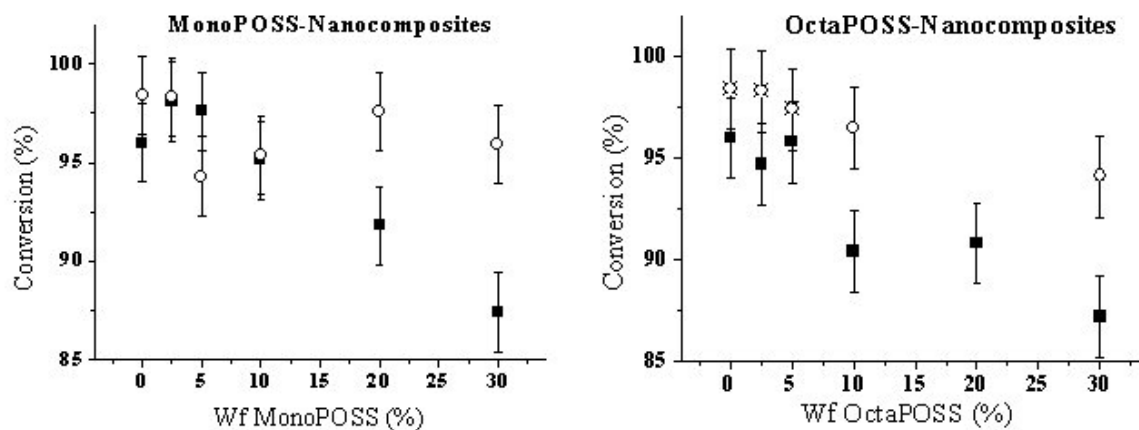
Figure 1. Conversion (%) of nanocomposites with POSS and BisEMA (full squares) and BisEMA-CHMA (empty circles) matrices.

The conversion tends to decrease with the increasing of both POSS content, especially for a Wf above 10% (see Fig. 1). Such effect is possibly due to the lower reactivity of both POSS molecules with respect to the methacrylate-based organic monomers [9]. For the BisEMA-MonoPOSS systems, we have detected POSS crystals using WAXS, and aggregates with SEM for all the MonoPOSS concentrations. It should be noted here, that the POSS-monomer systems are also immiscible, hence aggregates are present even before the polymerisation starts. Consequently, the presence of the POSS aggregates 'traps' the double bonds not allowing them to react. In the systems BisEMA-CHMA such effect does not occur, because of the solvent presence. For the OctaPOSS systems, our experimental results do not reveal any aggregation, thus the decrease of the conversion is likely to be related only to the low reactivity of the methacryl groups of the OctaPOSS molecules. Furthermore, WAXS analysis indicates that the solvent is effectively polymerised, albeit it is not clear at this point if it has copolymerised with the matrix or not.

It should be mentioned that the average functionality number "f" decreases from 4 to 2.47 when we add the solvent to the matrix. The influence of the variation of the average functionality number on the fractured surfaces has been investigated with SEM on poly(methyl-methacrylate) (PMMA) and poly(glycolethylene-dimethacrylate) (PEGDM) [10]. In figure 2 (left), the BisEMA shows an extended mirror-like surface, indicating slow crack growth. On the contrary, the BisEMA-CHMA (right) shows a mirror-mist-hackle surface, with the crack starting from the upper right corner [11]. The presence of a rougher surface indicates the existence of gross plastic flow on small regions, as seen by Simon et al. (see fig 12-13 in ref. [10]). This comparison indicates that the solvent induces localised plastic flow. We noticed that the solvent decreases the characteristic brittleness of dimethacrylate matrices. This reduction of brittleness, however, is not connected to a plasticisation of the materials. With the addition of CHMA, the experimental stress-strain curves do not generally change from brittle-elastic to elasto-plastic behavior.
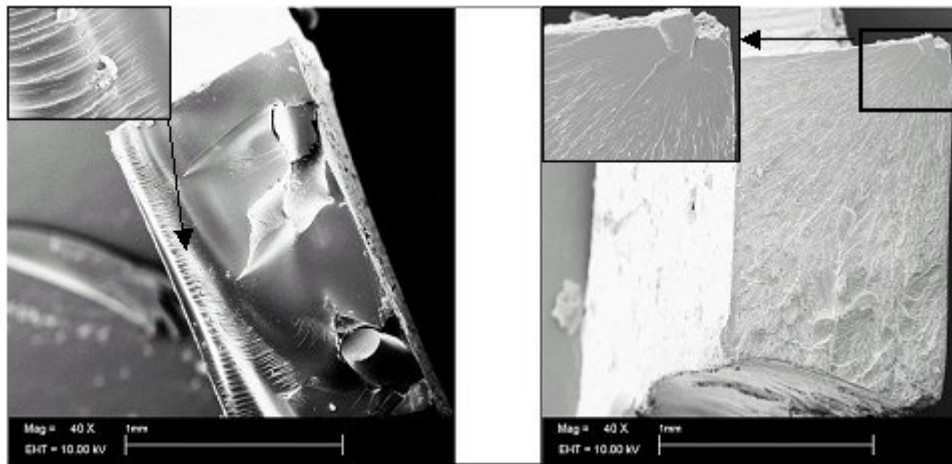
**Figure 2.** SEM picures of BisEMA (left), and BisEMA-CHMA (right)

In figure 3 (left) the SEM picture of the systems BisEMA-5% MonoPOSS (left) shows large clusters of POSS on the top of the mirror like surface, due to phase segregation. Moreover, around each cluster it is possible to see linear features on the side remote from the advancing of the crack. Haque and Turner have found similar phenomenon in highly crosslinked dimethacrylates filled with large hydroxyapatite particles (up to 60 µm) [12]. Haque and Turner suggested that the lines are due to localised plastic deformation because of the presence of stress concentration in the vicinity of filler particles, and the same may be said for our case.

On the other hand, the BisEMA-CHMA-5% MonoPOSS in figure 3 (right) does not show any cluster, and the features are similar to the ones observed for the neat matrix (Fig. 2 right). From this we can conclude that the CHMA is effective in dispersing the MonoPOSS at this concentration, at least above the resolution limit of the SEM. No voids have been detected at the interfaces in both systems, a fact that reflects a good compatibility between matrix and fillers for low concentrations (Wf < ~ 15%).
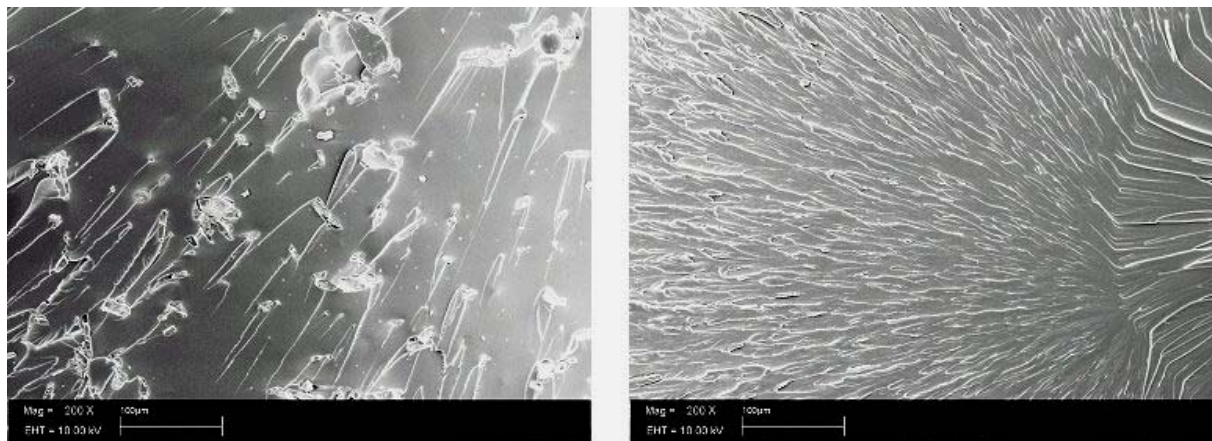

Figure 3. SEM picures of BisEMA-5% MonoPOSS (left), and BisEMA-CHMA-5% MonoPOSS (right)

The effect of large concentration of MonoPOSS in BisEMA-CHMA is shown in the figure 4. The SEM has detected a situation of phase segregation: (1) opacity of the surface at 40x (left picture), (2) presence of discrete particles at higher magnification (right picture). In our system, the origin of the phase segregation can be due to the lack of miscibility of the POSS above the critical value of 15% Wf POSS in the BisEMA-CHMA matrix.
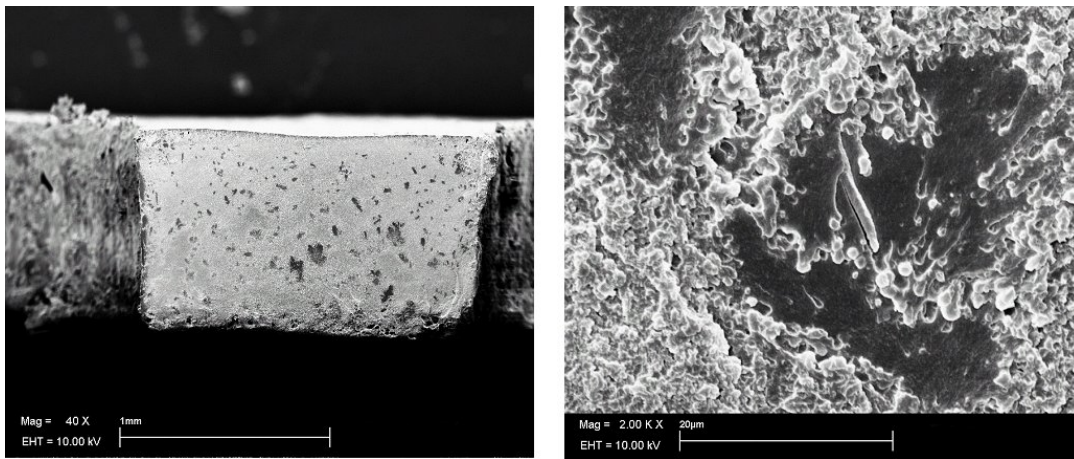
Figure 4. SEM picures of BisEMA-CHMA-30% MonoPOSS (40x left, 2000x right) showing phase-separation

The fracture behaviour is very sensitive to the presence of the solvent CHMA: (1) at low MonoPOSS content, the POSS aggregates were efficiently dissolved, (2) at high POSS content, POSS seggreagtion occurs, but the exact mechanism for this phenomenon is currently unknown. The influence of the different morphologies on the mechanical properties, Young modulus E and strength σ, under tension have also been investigated. All the materials exhibit brittle-elastic behavior under tensile-testing. The values of E for the nanocomposites with MonoPOSS are shown in Fig. 5.
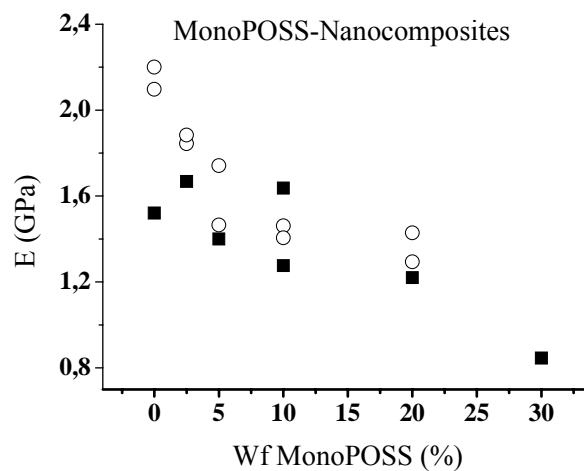
Figure 5. Young Modulus E of nanocomposites with MonoPOSS and BisEMA (full squares) and BisEMA-CHMA (empty circles) matrices.

- First of all, it should be outlined that the presence of the CHMA increases the Young's modulus. In fact, E passes from 1.521 GPa for BisEMA to 2.133 GPa for BisEMA-CHMA (see Fig. 5). This increase was already reported for similar systems [1], that is styrene (ST)-BisEMA matrices. This similarity could be due to the presence of bulky side groups in both styrene (S) and in CHMA. The Young's modulus of the BisEMA could be arisen by the simple presence of a stiffer material (E_{ST} = 2.5-3.3 GPa [13]) inside the BisEMA and the influence of the bulky side groups [14]. We assume that a similar effect can be produced by the CHMA, because of the above mentioned common feature with the styrene molecule. At the best of our knowledge, the value of Young's modulus for UV polymerised PolyCHMA

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has not been yet determined, since it is very difficult to prepare this polymer via UV radiation polymerisation. On the other hand, it is not likely to be less than the E for polymethyl-methacrylate (E = 1.8-3 GPa). Therefore, the Young modulus for BisEMA might be increased by the presence of a stiffer material along with the influence of the cyclohexyl side groups, and/or a reduction of the molecular motion of short segments. One aspect that is still unclear is whether the solvent has copolymerised with the matrix or not. The analysis in the styrene-BisEMA systems is based upon the fact that both constituents are copolymerised, which may very well be the case in the present system, albeit at the moment, we have no solid evidence for this.

- The MonoPOSS decreases the Young's moduli of both the matrices, even though with apparently different trend. Different phenomena are occuring in polymer-POSS systems: the hindrance of the movement of the polymer chains, and the reduction of crosslinking density. These two different mechanisms may increase or decrease E, in a manner which is not easy to be predicted. The decrease of the crosslinking density is due to two different reasons: (1) the decrease of the conversion (see fig. 1) and (2) the possible effect of "chain-end" caused by the POSS. The latter, recently proposed for similar systems [15], consists in the termination of the free radical reaction by the POSS molecules, thus giving shorter chains and therefore a reduction in the value of E. It may be that the depressing effects overcome the hindrance of the movement of the polymer chains.

- Increasing the MonoPOSS content, the BisEMA-CHMA systems show a steeper decrease of the E values compared to BisEMA systems. This can be due to the different particles sizes in the two matrices, as observed with the SEM (Fig. 3). It should be noted here that according to the stress transfer analysis of composites, there is always a critical scale below which the load cannot be transferred from the matrix to trhe filler. On the other hand, below also another critical length scale (at the nanometer scale) the properties of materials change altogether as described by Förster and Antonietti [16]. Hence, if the nanoparticles remain in this range where they are larger than the lower critical limit, and still smaller than the upper critical limit, no mechanism of load-transfer can operate at the interface [3], and hence, the POSS particles would be mechanically inert. We are currently investigating this hypothesis.

Similar study has been done using the OctaPOSS. The values of E for the OctaPOSS-based materials are shown in Fig. 6:
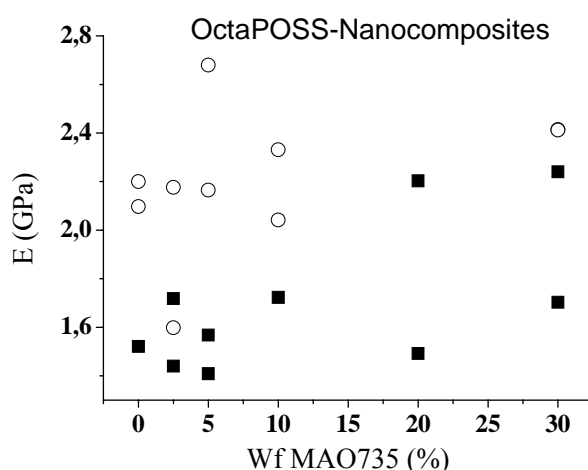
Figure 6. Young Modulus E of nanocomposites with OctaPOSS and BisEMA (full squares) and BisEMA-CHMA (empty circles) matrices.

The OctaPOSS increases the Young modulus, in similar proportion to what already present in the literature for other polymeric systems [17,18,19]. The effect is more relevant for the

BisEMA matrix. We stress here that the OctaPOSS play a role of crosslinking agent for the methacrylate matrices.

By comparison with the MonoPOSS, the OctaPOSS contains at least 8 methacryl chains able to react, thus not having the "chain-end" effect. The solubility in both the components of the matrices of the OctaPOSS, higher than the MonoPOSS, maintains a favourable aspect ratio via avoiding aggregation phenomena. Also the steric hindrance becomes more significant. The positive effects for the increasing of E (crosslinking effect, steric hindrances) overcome the decreasing of conversion. The tensile strength has been analysed assuming a Normal distribution of the values. Therefore the one-way analysis of the variance (ANOVA) has been applied along with complementary t-Test. In the present study all the ANOVA calculation has been performed at 0.05 significance level. In the table 1 the mean strengths with the standard deviations may be seen.

Table 1. Mean strength (±standard deviation) of different nanocomposites as function of the weight fraction (%) of POSS. All the values are expressed in MPa.

	0% POSS	2.5% POSS	5% POSS	10% POSS	20% POSS	30% POSS
BisEMA-MonoPOSS	40.2±2.81	35.24±4.45	34.65±4.18	24.78±6.41	18.64±2.51	12.0±2.61
BisEMA-CHMA-MonoPOSS	47.25±2.58	45.45±4.03	42.75±2.11	34.37±8.44	23.31±8.42	-
BisEMA-OctaPOSS	40.2±2.81	42.94±4.65	44.43±3.86	36.87±3.57	29.74±4.2	29.35±1.83
BisEMA-CHMA-OctaPOSS	47.25±2.58	51.4±2.56	55.34±0.34	45.72±3.69	-	40.57±3.85

The null-hypothesis, that is that the means are equal, is rejected for all the four different nanocomposites, i.e. the addition of POSS changes the strength. To determine which are the materials likely to have same strength, we have performed ANOVA only for the systems with W_f of POSS up to 5%. The results are shown in the table 2.

Table 2. One way ANOVA for nanocomposites with 0, 2.5 and 5% Wf of POSS at 0.05 level of significancy.

Material	F	F_{crit}
BisEMA-MonoPOSS	2,365207	3,982308
BisEMA-CHMA-MonoPOSS	3,749246	3,554561
BisEMA-OctaPOSS	1,393994	3,88529
BisEMA-CHMA-OctaPOSS	10,40198	3,88529

The null-hypotesis can not be rejected for the BisEMA-MonoPOSS and the BisEMA-OctaPOSS, that is, the strengths of these materials do not vary significantly adding up to 5% Wf of POSS. For the BisEMA-MonoPOSS, this result means that, adding the MonoPOSS, there is no diminution of the strength value. This effect was outlined as a problem in the literature counterbalancing the improvement of other properties (i.e. reduction of the shrinkage) [2]. For the BisEMA-OctaPOSS, the result of the ANOVA test states that there is not the increasing of the strength up to 5% Wf POSS, which could be hypothesized looking only to the values in table 1. On the other hand, a t-Test performed between the BisEMA matrix and the BisEMA-5% OctaPOSS revealed that these two values are different (t=1.999, t_{crit}=1.859), i.e. there is an improvement of the strength of ca. 10% adding 5% Wf OctaPOSS. The strength increases for the systems BisEMA-CHMA-OctaPOSS up to 5% POSS, then it stabilises on a plateau value of ca. 43 MPa up to 30% Wf POSS (see Table 1). In particular, the strength appears to increase by 18% through the adding of 5% OctaPOSS to the BisEMA-CHMA matrix. This increasing has been confirmed by a t-Test (t=8.583, t_{crit}=1.859). Another

t-Test has been used to determine that the difference of the strength between BisEMA and BisEMA-CHMA (respectively, 40.2±2.81 MPa and 47.25±2.58 MPa) is real (t=4.201, t_{crit}=1.943).

We summarise here the mechanisms operating in a dimethacrylate matrix during the break. It has been shown [1,10] that the strength in dimethacrylate systems is very much affected by the microgels formation. The dimethacrylate network is constituted by microgels with a highly crosslinked inner core surrounded by a less crosslinked shell [1,10]. In between these microgels it is possible to find pools with unreacted monomers and sol-species. Fracture of dimethacrylate network has been shown [1,10] to take place preferentially along the edge of the microgels, caused and also enhanced by the presence of the pools with unreacted monomers, which in turn represent points of weakness (see fig 10 in ref.1). This allows us to conclude that, the lower the presence of zones with unreacted (or partially reacted) monomer is, the higher the strength is.

- The positive effect of the CHMA on the strength may be due to the presence of less poorly crosslinked species trapped inside the network [1]. This can be explained by the solvent reduction of the viscosity of the not fully polymerised systems, which in turn increase the mobility of the polymer chains during the polymerisation, therefore produces less loosely crosslinked regions. The polymerisation of the CHMA will not create other weakness points.

- In BisEMA, at low MonoPOSS concentration, the strength is not affected by the POSS, because the conversion does not change, thus the presence of less crosslinked zone is not more probable than in the neat matrix. At higher concentration, the strength is decreased. This decrease is probably connected to the decrease of the conversion (see fig. 1).

- In BisEMA-CHMA, the depression effect of the MonoPOSS on the strength cannot be explained by the presence of these pools, because the conversion remains always high. We think that another mechanism could be operating , that is related to the phase seggregation (as evidenced on the SEM analysis, fig. 4). The connection between this phenomenon and the trend of the strength is still unclear.

- In the BisEMA and in the BisEMA-CHMA systems containing OctaPOSS, the initial increase of the strength can be attributed to the presence of more highly crosslinked points inside the systems, as well as the higher stiffness of the Si-O-Si cube, which now participates directly inside the network chains. This in turn produces a beneficial effect on the strength hindering the presence of loosely crosslinked regions (the above-mentioned pools). The further decrease is explicable again in terms of decreasing of the conversion.

We compare now the information from SEM and the mechanical testing, monitoring the size of the mirror zone as function of the strength for the OctaPOSS systems. According to Hull [11], when a brittle material is tested in tensile mode, the mirror region tends to decrease in size with the increasing of the fracture strength. Two examples are reported in figure 8 and figure 9:
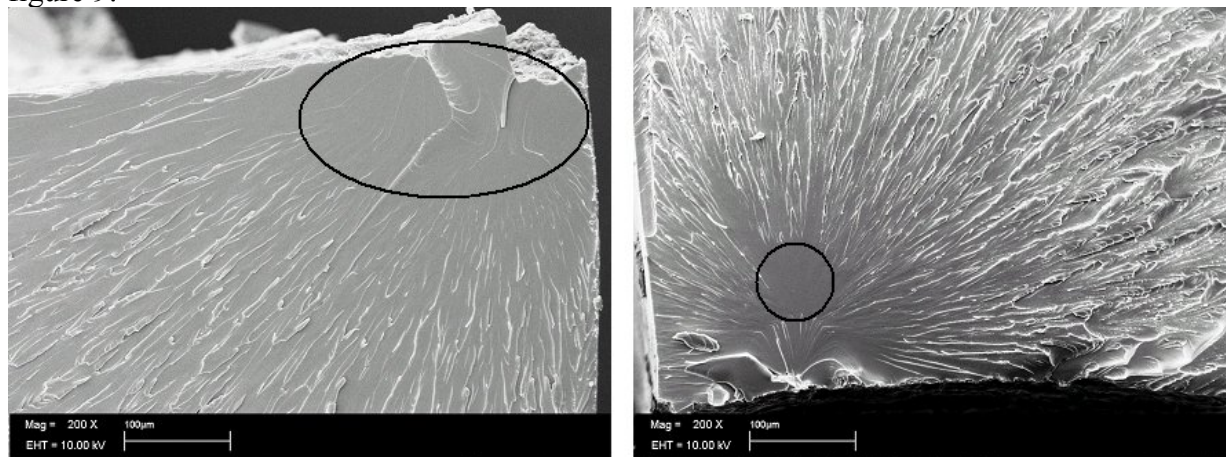
Figure 8. SEM picures of BisEMA-CHMA (left) and BisEMA-CHMA-5%OctaPOSS.
The circles evidence the mirror zone

The mirror zone decreases strongly simply adding 5% OctaPOSS. The difference of the strengths for the two samples is in agreement with the empirical rule of Hull, being 45 MPa (BisEMA-CHMA) and 55 MPa (BisEMA-CHMA-5%OctaPOSS).

Figure 9. SEM picures of BisEMA-5% OctaPOSS (left) and BisEMA-CHMA-5%OctaPOSS.
The circles evidence the mirror zone

The extension of the mirror zone is much larger for the BisEMA-5%OctaPOSS than BisEMA-CHMA-5%OctaPOSS. This happens even if the difference between the strengths is similar to the previous case (44 MPa for BisEMA-5% OctaPOSS and 55 MPa for BisEMA-CHMA-5%OctaPOSS), because intrinsically the matrix BisEMA shows a larger mirror zone than the BisEMA-CHMA one. This fact does not allow us to compare directly between samples with different matrices. However, the results presented here are in good agreement with the empirical rule of Hull.

5. Conclusions

- The fracture behaviour of the matrix is very sensitive to the presence of the solvent CHMA. It appears that without the presence of the solvent fracture proceeds in a slow crack mode, while with the solvent present fracture proceeds through a mirror-mist-hackle mechanism, indicating the exiostence of more locally plastically deformed regions.
- The presence of the CHMA increases the Young's modulus, as well as the strength of the matrix.
- The MonoPOSS decreases the Young's moduli of both the matrices, with and without the solvent present in the system, while in contrast the OctaPOSS increases effect on the Young's moduli.
- In BisEMA, at low MonoPOSS concentration, the strength is not affected by the presence of the POSS. For the case of the OctaPOSS a moderate increase of the strength in both systems was observed.

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