Influence of Some Alumina and Titanium Nanoparticles on the Mechanical Properties of the Composites Based on Poly (methyl methacrylate)

ILEANA COJOCARU[1]*, MARIOARA MOLDOVAN[2], MARCELA TRIF[2], DOINA PRODAN[2], GEORGE LIVIU POPESCU[3], IONEL CONSTANTINESCU[4]

[1] University of Craiova, 13 A. I. Cuza, Craiova, 200585, Romania

[2] Babes Bolyai University -Raluca Ripan Chemistry Research Institute, 30 Fantanele, 400294, Cluj-Napoca, Romania

[3] Technical University of Cluj-Napoca, 15 Constantin Daicoviciu, 400020, Cluj-Napoca, Romania

[4] Politehnica University of Bucharest, 149 Calea Victoriei, 010072, Bucharest, Romania

The polymers with special properties represent the starting point in order to obtain a wide range of new materials used in various fields of activity. Poly (methyl methacrylate) (PMMA), a transparent thermoplastic material, is an attractive polymer because of it's unique properties, in comparison with other polymers, such as: high mechanical strength, special optic properties, and durability. The incorporation of silicate layers (for example, clay, minerals) in the polymer microstructure in order to improve the mechanical, thermal and interface properties has become one of the interesting of the researchers nowadays. Thus, depending on the working conditions and the interactions between the clay layers and the polymer system, a series of composites with different morphology, for instance, agglomerated, intercalated and exfoliated, has become accessible. In order to promote solutions for improving PMMA properties and to have a better general view on the action of oxide nanoparticles, we chose to analyze the structure and mechanical properties of some methacrylic composites with TiO_2, Al_2O_3, and PMMA fillers.

Keywords: nanocomposites, mechanical properties, poly(methyl methacrylate), SEM

The use of polymeric materials, either for mass production of commodities or in the form of individual components, which replace other materials in certain consumer goods such as cars, has increased considerably in the last decade. At the same time, with the increase and diversification of the use of polymeric materials, the attention of worldwide researchers has been focusing on the increasing of accumulation of solid waste that has an impact on the pollution of the environment. The main alternative of control from the viewpoint of environmental pollution is the recycling process. An important problem raised by the recycling process is to maintain the polymer up to the performance level, which can allow its re-use in the same applications or in other important technological applications. In this case, it is important to know the physical, thermal, mechanical, electrical and optic properties for the poly(methyl methacrylate), obtained by synthesis, comparing to the one obtained by recycling.

In the last 10 years the efficiency of some component additives from various micro or nanofillers as regards the improvement of the thermal stability in different polymeric composites has been proven [1,2]. A number of studies have shown good properties in the case of clay/polymer composite systems [4-6]. Also, there have been a number of reports on the elaboration of the PMMA porous polymer and PMMA/clay composites resulted from polymerization in suspension and emulsion [7-11]. As far as poly (methyl methacrylate) (PMMA) is concerned, numerous studies about the use of modified organic-clays [12-16], carbon nanotubes [16,17] and silica particles [18-20] have been published, while other studies have concentrated on the effect of metallic oxide particles [21, 22]. The studies prove that the use of metallic oxide particles leads to the improvement of thermal stability [21] and burning properties [22]. The phenomenon has been mainly attributed to the restriction of mobility of the polymer chains and to the thermal properties that raise the thermal transfer within the material, which limits the surface reactions, the reactions of migration of gas bubbles, and the reactions of volatile fuel release. A recent paper explains the existence of some synergic effects between alumina particles and ammonium polyphosphate (APP) based on additives [23], which after burning lead to an improvement of PMMA. The improvement of performance has been highlighted by: a reduction of the release rate of thermal energy, the reduction of released heat, higher burning and a significant increase in the total burning in time.

The purpose of the present study is to observe the effect of some nanofillers on the mechanical properties by determining the compression strength (CS), diametral tensile strength (DTS), flexural strength (FS) and by establishing the structure of eight experimental composite materials.

Experimental part

Because the methacrylic composite material is a biocomponent material made of a liquid part and a powdery one, the synthesis of monomer-oxide and/or polymer powder took place by obtaining each component separately. The polymerization occurs by mixing the two components, (MMA monomers and PMMA powders) which leads to the formation of hardened composite. The mechanism of hardening consists of radical polymerization of monomers in the organic phase, resulting a cross-linked polymeric structure that embedded the polymer pearls inside the network. The liquid component of the methacrylic composite is made of *methyl methacrylate* (obtained by recycling) and commercial methyl

* email: i_cojocaru2005@yahoo.com; Tel.: 0724227678

Table 1
THE COMPOSITION OF SELF-CURED METHACRYLIC COMPOSITES [wt%]

Composite	Bis-GMA	MMA (M1)	MMA commercial (M2)	PMMA (P1)	TiO_2 (P2)	Al_2O_3 (P3)
CM1	10	27	-	63	-	-
CM 2	10	-	35	65	5	-
CM 3	15	25	-	35	25	-
CM 4	15	25	-	30	-	30
CM 5	-	-	37	50	-	13
CM 6	-	-	38	47	15	-
CM 7	5	20	12	55	8	-
CM 8	5	18	15	53	-	10

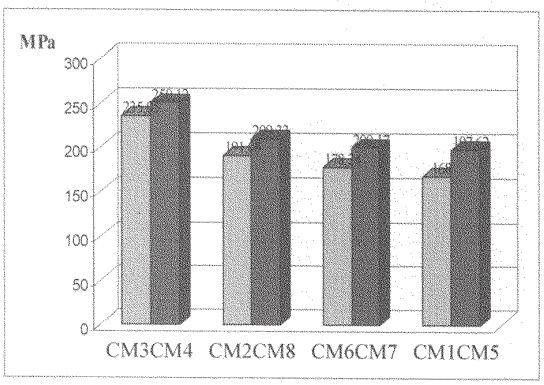

Fig. 1. The values for the compression strength of the investigated composites

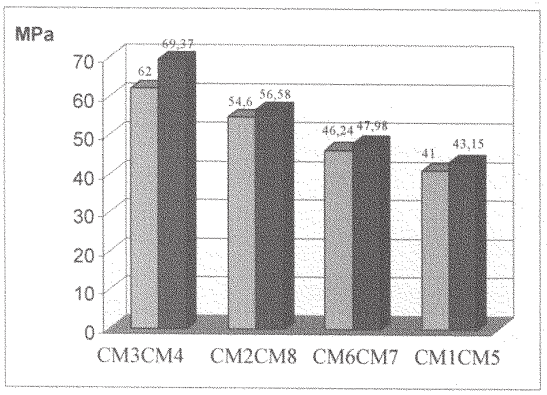

Fig. 3. The values for the flexural strength of the composites investigated

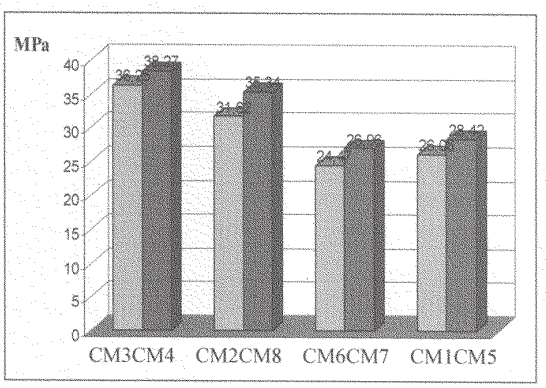

Fig. 2. The values for the diametral tensile strength of the investigated composites

methacrylate (Merck), a small quantity of crosslinking monomer *bis*-GMA - $C_{29}H_{36}O_{28}$ - 2,2-*bis* (2-hydroxy-3-methacryloxy-propoxy) phenyl)-propanol (synthesized at UBB-ICCRR-Cluj-Napoca)), and the polymerization activator (N,N- dimethyl-*p*-toluide (Merck)).

The solid component in the form of powder was obtained by mixing the methyl methacrylate powders with TiO_2 and Al_2O_3 powders and a peroxide initiation activator. The polymerization of the methyl methacrylate was made by polymerization in suspension, in our laboratory. TiO_2 and Al_2O_3 powders (Degussa), with the size of the particles ranging from 21 to 13 nm, and the BET specific surface, being 50 and 100 m^2/g, respectively. The filling mixture was made in a ball mill by mixing the two powders with the PMMA polymer. The composition of the experimental composites is shown in table 1.

By mixing the two components, the polymerization takes place, leading to the formation of hardened composite. As a result of chemical initiation for 1-3 min, the reticulate polymerization of the monomers occurs in the mixed paste (initiator/accelerator), forming a three-dimensional polymeric matrix to which the filling granules are bound. By measuring the jellifying and the hardening times, it was found that their values ranged from 1.5 to 2 minutes for the jellifying times and from 5 to 7 min for the hardening times. After separation, the self-cured composite pastes were hardened in the shape of some standard specimens, made in specially constructed Teflon moulds in order to measure the mechanical properties (CS, DTS, FS). The compression strength was calculated from the equation $CS = 9.81/0.785d^2$, where F is the force to fracture and d the specimen diameter. The diametral tensile strength was determined by the relation $DTS = 2xF/\pi xDxT$, F is the force to fracture, where D is the diameter; T is the thickness of the specimen. The flexural strength was determined by using the expression $FS = 3xFxl/2xbxh^2$, where l is the distance between props, b is the thickness of the test piece and h is the height of the test piece. The tests were carried out on a universal testing system LLOYD LR5K Plus. The scanning electron microscope (SEM) QUANTA 133 from FEI Company was used for the examination of the samples by electronic microscopy.

Results and discussions

The addition of TiO_2 and Al_2O_3 powders has led to a change in the PMMA structure (which is a porous material) and this is essential in order to improve the mechanical properties. The incorporation of some metallic oxides or silicate for example, mineral clays) into the polymer in order to improve its mechanical, thermal and surface properties have been presented in the literature [24, 25]. In figure 1-3 the values obtained for the compression strength (CS), diametral tensile strength (DTS), and flexural strength (FS) are presented. The results for the mechanical properties of the experimental materials elaborated in this study show a slight decrease in the values for the recycled monomer, as compared to the commercial monomer. The mechanical properties have been improved with the

increase of the filler concentration and vary according to the composition of the filler. This improvement of the mechanical properties is due to a good insertion of titanium and alumina nanoparticles in the polymeric matrix, as well as to the creation of chemical bonds between the organic phase and the inorganic one.

The best results for the compression strength of 250.12 MPa have been obtained in the case of the CM4 composite, formulated with the M1 monomer, in combination with *bis*-GMA and poly(methyl methacrylate), mixed with Al_2O_3 powder, followed by the CM3 composite, formulated with the M1 monomer, with the same percentage of Bis-GMA, and poly(methyl methacrylate) obtained in the laboratory and TiO_2. In decreasing order, but with almost the same values, we find the CM8 composite, CM2, and CM7, formulated with the M1, *bis*-GMA, P1 and P3, and M2, *bis*-GMA, P1 and P2 monomers, but the percentage of *bis*-GMA and TiO_2 and Al_2O_3 particles is lower. An increase of resistances has been observed for all of the analyzed composites, having the same type of methacrylic monomer, obtained by recycling or commercial, for the samples cured with BisGMA.

One of the factors that influence the composite diametral tensile strength is the homogeneity of distribution of polymer and oxide particles in the methacrylate monomer. If there are many pores in the hardened resin, the diametral tensile strength may decrease by 30% of the optimum value. The values of the diametral tensile strength follow the tendencies of increase or decrease as in case of compression strength. The best results have been recorded for CM4 composite, followed by

CM3>CM8>CM2>CM7>CM6>CM5> CM1

The results obtained for resistances to bending for the experimental composites, show values ranging from 41 to 69.37 MPa, the highest value being recorded in the CM4 composite. Just like in the case of the measurements of the compression strength and diametral tensile strength, the results show the role of the Bis-GMA and Al_2O_3 powders on achieving higher resistances to bending. The resistance to bending reflects the rigidity and the resistance capacity of the materials to bending or breaking after mechanical stress. We can say that weaker mechanical properties, sensitivity to fracture, impact strength, or low stress strength, make PMMA the most used material in medical applications. The improved mechanical properties can also be ascribed to the fact that the dispersion of titanium and alumina particles is very even, as well as to the formation of covalent bonds at the interface of the organic-inorganic phases.

In all cases, the incorporation of the titanium dioxide and aluminum oxide improves the storage mode of the composites with PMMA and the mechanical properties. These increased performances are achieved by a good dispersion of the inorganic particles in the polymer matrix. As a rule, the creation of a powerful interaction between the polymer matrix and the dispersed particles is of major importance. Therefore, this explains the linear behavior mode, depending on the fillers of the polymeric matrix. In comparison, the composites containing alumina have higher values for strength than those with TiO_2, and this can be ascribed mainly to the compacting degree, which is probably smaller for the composites with TiO_2. By comparing the results obtained from this study with those presented in the literature, involving other types of polymers and other type of particles, we can say that the differences in results may be due to their different chemical nature. Moreover, in most cases, the particle concentration in the polymer matrix is not the same. Nevertheless, in this study, the best results have been obtained with 33% Al_2O_3 - 30% PMMA, combination which, compared to the composite with PMMA 60%, increases and is comparable to the values obtained in other similar systems, in an approximate concentration.

The scanning electron microscopy (SEM) examinations of the formulated self-cured composites have shown a texture relatively homogenous, with the shape of the spherical particles in PMMA (fig.4) similar to beads. The shape and the size of the particles have a preponderant influence on the charging degree, which is experimentally determined so as to ensure an adequate consistency and obvious plastic properties for the composite mixture.

We may specify that the bond between the filler and the organic matrix is the most important for a composite with appropriate properties, and, from this point of view, it is easy to justify why the break of the bond between the fillers and the organic matrix could be the first destruction

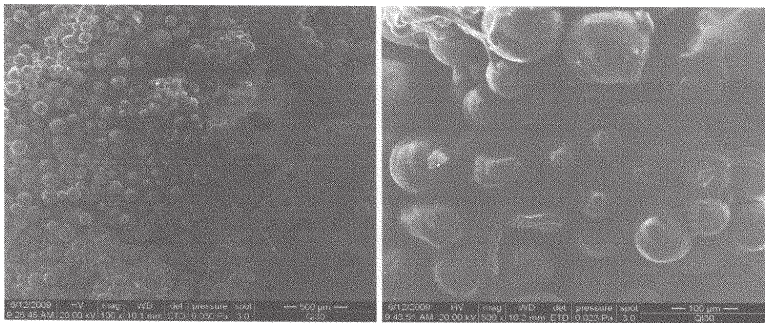

Fig. 4. SEM image for PMMA

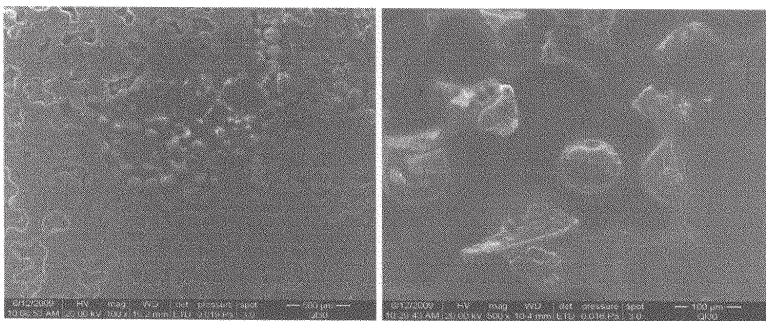

Fig. 5. SEM image for PMMA –TiO_2

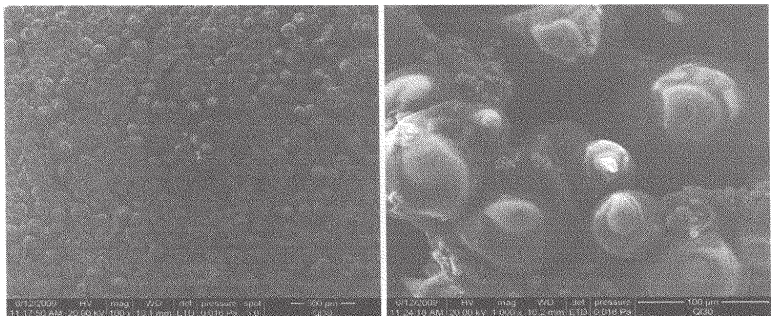

Fig.6. SEM image for PMMA-Al_2O_3

mechanism that appears in the process of composite degradation.

The advantages of using hybrid filler in formulating composites are that PMMA offers optimum physical properties, and the TiO_2 and Al_2O_3 particles offer better mechanical properties.

The use of smaller particles creates the possibility to minimize the space between the particles and to have a more even arrangement of the particles (fig.6).

The SEM images for the composites with PMMA-TiO_2 and PMMA-Al_2O_3 (fig.5 and fig. 6) show compact structures, the filler particles are well incorporated in the organic matrix and give hardness to the composites. These performances, besides good polizability, are due both to the spherical nature of some PMMA particles and to the large granulometric distribution, which allows for a good arrangement of the particles in the monomer structure and a high charging degree in the process of making the composite material. In general, the composite materials that contain a filler with an irregular shape have a bigger content of filler and the mechanical properties and the resistance to breaking are greater. The examinations by electronic microscopy of the self-cured composites, formulated and analysed physicochemically and mechanically (CM1-CM8 composite) have highlighted the shape of the particles, the relatively homogenous texture with traces of Al_2O_3 and TiO_2 crystals.

Conclusions

The best results have been obtained with 33% Al_2O_3 - 30% PMMA, combination which, compared to the composite with PMMA 60%, increases the values for mechanical strength and is comparable to the values obtained in other similar systems, for near the concentration. The scanning electron microscopy (SEM) examinations of the formulated self-cured composites have shown a texture relatively homogenous, with the shape of the spherical particles of PMMA similar to beads. The TiO_2 and Al_2O_3 particles offer better mechanical properties.

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