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Material Properties

Micromechanical assessment of PMMA microcapsules containing epoxy and mercaptan as self-healing agents

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ABSTRACT

Mechanical properties of microcapsule shell have great influence on microcapsule suitability as a mechanical trigger in a self-healing composite. The elastic modulus and hardness of polymethyl methacrylate (PMMA) microcapsules containing epoxy prepolymer (EC 157) and pentaerythritol tetrakis (3-mercaptopropionate) (PETMP) as healing agents were investigated using nanoindentation technique. The influence of the PMMA average molecular weight (M_w), the kind of core material, and the mechanical mixing rate on the mechanical properties of the microcapsule shell were studied using the Taguchi experimental design approach. The results indicated that the most important factors which affect the elastic modulus and the hardness of microcapsules shell are the M_w of PMMA and the kind of core material. The average elastic modulus of PMMA shell of epoxy and mercaptan-loaded microcapsules was found between 2.386 and 3.495 GPa. The hardness of PMMA shell of healing agent microcapsules was obtained in the range of 0.064–0.219 GPa. This constitutes essential knowledge in order to design capsules with tailored properties for self-healing materials.

1. Introduction

Polymer composites often experience mechanical damage during their application. A self-healing composite containing encapsulated healing agents offer tremendous potential for repairing the mechanical damage, such as micro-cracks, automatically [1,2]. Healing agent microcapsules are the mechanical triggers that initiate the repair response of a self-healing polymer composite [3–5]. Micro-cracks propagate through the material and encounter microcapsules, easily cause their rupture, thus release the healing agents along the crack surface. These healing agents react together and heal the damaged region [6].

For self-healing applications, an optimal combination of mechanical properties of microcapsule shell and polymeric matrix is essential to ensure mechanical triggering when the composite is damaged [5,7]. A very stiff microcapsule shell cannot rupture easily and prevents the release of the healing agent. On the other hand, when the capsule shell is too weak, the healing agent may be lost within the polymeric matrix even without any micro-cracking. The elastic response and stiffness, as well as the failure strength of the capsules, as compared with those of the polymer matrix, constitute pivotal parameters for efficient healing agent delivery [7]. The capsule mechanical behavior depends largely on the molecular weight of the polymer used. In addition, the kind of core

material (healing agent) may affect the mechanical strength of the shell as the organic chemicals may plasticize the polymeric shell differently and reduce its mechanical strength, particularly elastic modulus and hardness. For a given amount of shell material, the mean size of capsules may affect the mean thickness of the capsule, thus ultimately affecting the elastic modulus and hardness of the capsule.

Experimental investigation of mechanical properties of the capsule shell can be carried out by various methods. This include application of a local stress on a single capsule (single-capsule compression) through micropipette aspiration [8], compression between two parallel plates (micromanipulation technique) [9], compression with an atomic force microscope (AFM) [10,11], or nanoindentation [12]. Each technique is by essence designed for a limited range of capsule size and mechanical resistance. Nanoindentation has high resolution for the measurement of mechanical properties. It has become an important technique in measurements of elastic modulus and hardness for small scale materials such as microcapsules [13–16].

Several studies reported the mechanical properties of healing agent microcapsules [7,12,17,18]. Keller and Sottos studied mechanical properties of poly (urea-formaldehyde) (PUF) microcapsule filled with dicyclopentadiene (DCPD) as healing agent through single-capsule compression test [7]. Lee et al. reported the micromechanical

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properties of epoxy and mercaptan microcapsules with poly (melamine-formaldehyde) (PMF) as shell by nanoindentation [12]. Hu et al. studied the mechanical properties of DCPD/PMF microcapsules by micromanipulation technique [17]. Lv et al. investigated mechanical properties of DCPD/poly (phenol-formaldehyde) (PF) microcapsules using nanoindentation [18].

In spite of above-mentioned works, there are very few reports available on the encapsulation of healing agents in polymethyl methacrylate (PMMA) as shell material [19–21]. In our previous works, we investigated the effects of processing parameters on the encapsulation of low viscosity self-healing agents in PMMA shell [22]. Then, in the next work, we theoretically investigated the morphology of microcapsules filled with different self-healing agents (low viscosity epoxy, mercaptan, and cycloaliphatic amine), in separate PMMA shells [23]. To the best of our knowledge, the mechanical properties of PMMA microcapsules containing self-healing agents have not yet been reported in the literature. In addition, there is no report available on the statistical analysis of these systems by using an experimental design approach. This is despite the mechanical properties of PMMA microcapsules being crucial for the material designer in order to prepare capsules with tailored properties for self-healing purposes.

Therefore, in the current study, PMMA microcapsules containing epoxy prepolymer (EC 157) and pentaerythritol tetrakis (3-mercaptopropionate) (PETMP) as healing agents have been prepared separately by internal phase separation method within oil-in-water (O/W) emulsion droplets. The Taguchi experimental design approach was used to investigate the effects of the kind of core material, average molecular weight of PMMA and mechanical mixing rate on mechanical properties of the PMMA shell. The influence of the capsule size was studied with variation of the mechanical mixing rate used in generation of the O/W emulsions. The elastic modulus and hardness of epoxy and mercaptan-loaded PMMA microcapsules were investigated using nanoindentation technique.

2. Experimental

2.1. Materials

Epoxy prepolymer (EC 157, Elantas Co. Italy) as the polymerizable component, pentaerythritol tetrakis (3-mercaptopropionate) (PETMP, Sigma Aldrich, USA) as the hardener, and PMMA with two different molecular weights ($\overline{M}_1 = 36,000$ g/mol, LG Co. Korea and $\overline{M}_2 = 550,000$ g/mol, Alfa aesar Co. USA) as polymeric shell were used to produce healing agent microcapsules. Dichloromethane (DCM, Acros Organics Co. Belgium) was used as solvent. Sodium dodecyl sulfate (SDS, Sigma Aldrich Co. USA) and cetyltrimethylammonium bromide (CTAB, Sigma Aldrich Co. USA) were used as emulsifiers. Heat-softening glue was used to fix microcapsules on the aluminum stub. All materials were used as received without further purification.

2.2. Design of experiments

The first important step in the experimental design is the proper selection of factors and their levels. In this study, two quantitative factors (Mw of PMMA and mechanical mixing rate) and one qualitative factor (core material) all in two levels were considered (Table 1). For

Table 1
Selected factors and their levels.

Factors			Levels	
Description	Unit	Symbol	1	2
Core material	–	C	Epoxy	Mercaptan
M _w of PMMA	g/mol	M	36000	550000
Mechanical mixing rate	rpm	R	400	1200

Table 2

Taguchi orthogonal array for designed experiments based on coded levels.

Run no.	Operating variables		
	C	M	R
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	1

designing the experiments with the selected factors and levels, a standard L4 Taguchi array was employed (Table 2). Elastic modulus and hardness of the microcapsules polymeric shell were considered as the statistical responses. No factor interaction was considered in this analysis. In order to avoid systematic bias, the sequence by which these runs were carried out was randomized [24,25]. The results were statistically analyzed by using Qualitek-4 software (Nutek Inc. USA).

2.3. Preparation of the healing agent microcapsules

PMMA microcapsules containing the epoxy and mercaptan were prepared separately according to phase separation technique [22,23]. PMMA (0.5 g) with specified Mw, together with a specified core material (0.5 g) were dissolved separately in 20 ml DCM for the oil phase preparation. The above solution was added to the aqueous phase (50 ml of 1 wt% aqueous solution of emulsifier) under specified mechanical mixing rate by using propeller mixer for 30 min at room temperature to produce an O/W emulsion. The resulting mixture was then poured into 80 ml of 1 wt% aqueous solution of emulsifier under continuous agitation. DCM was allowed to evaporate completely to produce PMMA microcapsules containing the healing agent material. In this study, CTAB and SDS were used as emulsifier for microencapsulation of epoxy and mercaptan, respectively. The PMMA microcapsules were filtered, washed several times with distilled water and dried at room temperature.

2.4. Characterization

The size and morphology of the healing agent microcapsules were analyzed with scanning electron microscopy at different magnifications (Philips ESEM-XL30, The Netherlands). The mean size of microcapsules was measured using dynamic light scattering (DLS) (Brookhaven Instrument Co., USA). Nanoindentation measurements were carried out by employing an MTS Nanoindenter XP (MTS Nano Instruments, Oak Ridge, TN, USA) with a pyramidal Berkovich tip at room temperature. An aluminum stub was used to fix the microcapsules using heat-softening glue. During the measurement, a total of 10 microcapsules for every sample were selected for test and the indentation depth was set to 1000 nm. In this test, the allowable drift rate was 0.09 nm/s and the surface approach velocity was 10 nm/s.

3. Results and discussion

3.1. Morphology and size distribution of microcapsules

Four experiments were carried out separately for encapsulation of epoxy and mercaptan within the PMMA shell, according to Table 2. The micrographs of epoxy and mercaptan-loaded microcapsules are presented in Fig. 1 (a and b) and (c and d), respectively. As observed, all of the microcapsules have a spherical geometry, most probably as a consequence of the original micelle shapes. This is in accordance with results obtained by previous studies about encapsulation of different materials with PMMA shells [19,21,26]. Two different morphologies are observed for surface of epoxy and mercaptan capsules. The former is smooth (runs 1, 2 and 4), and the latter has holes (run 3). The epoxy

Fig. 1. FESEM images of the prepared epoxy (a and b) and mercaptan-loaded microcapsules (c and d) according to the designed experiments (Table 2): (a) run 1, (b) run 2, (c) run 3, (d) run 4.

and mercaptan were encapsulated using two different Mw of PMMA. The formation of holes was only observed on the surface of mercaptan-loaded microcapsules prepared using PMMA with low Mw. In our previous studies, it was found that the surface morphology of PMMA microcapsules critically depended on the chemical nature of the core materials and Mw of PMMA. The difference in the equilibrium morphology of PMMA microcapsules can be described according to total interfacial energy changes. In different encapsulation systems, when the processing parameters such as core material, Mw of PMMA, type and concentration of emulsifier change, the interfacial tensions and the interfacial energies of emulsion system change, too. It can be concluded that surface morphology and appearance of holes on the PMMA microcapsule surface is due to the interfacial tension gradients in emulsion system [22,23].

The results of mean size of microcapsule measurements are reported in Table 3. As it can be seen, the mean size of microcapsules for runs with high mixing rate (1200 rpm, in runs 2 and 3) are several times smaller than those with low mixing rate (400 rpm, in runs 1 and 4). Some authors have suggested a direct relationship between the emulsion structure and the capsule dimension. In particular, the smaller emulsion droplets result in a smaller capsule mean diameter as a consequence of an increased mechanical mixing rate. Indeed, under high mechanical mixing rate, the shear forces would overcome the interfacial tension forces and form fine droplets in the emulsion system [27,28]. The size distributions of microcapsules are indicated in Fig. 2. A narrow spread of size distribution is seen for healing agent microcapsules (runs 2 and 3) prepared under high mechanical mixing rate (1200 rpm).

Table 3
Mean size of epoxy and mercaptan-loaded microcapsules.

Run no.	Mean size (μm)	Mean size distribution (μm)
1	35	9–62
2	10	2–21
3	5	2–9
4	45	16–110

Fig. 2. Size distributions of epoxy (Run 1 and Run 2) and mercaptan-loaded microcapsules (Run 3 and Run 4).

3.2. Mechanical properties measurement

The elastic modulus and the hardness of PMMA shell of epoxy and mercaptan microcapsules were determined directly by nanoindentation instrument. For this purpose, the force and depth of penetration of indenter is calculated as load is applied from zero to maximum force and then from maximum back to zero. The loading and unloading processes and the parameters of nanoindentation test for polymeric material are shown schematically in Fig. 3. In the loading-unloading curve, h_b , h_e , and h_r are total depth of indentation at load P_b , the displacement associated with the elastic recovery during unloading, and the depth of residual impression, respectively. h_a is the displacement of the surface at the perimeter and h_p is the contact indentation depth.

The elastic modulus (E) of the specimen can be determined from the slope of unloading of the load-displacement response [12]:

$$E = \sqrt{\frac{\pi}{A_r}} \frac{dP}{dh} \quad (1)$$

Fig. 3. Load-displacement schematic curve of polymeric materials resulted from nanoindentation test [12].

where A_r and dp/dh are residual indentation area and slope of the elastic unloading, respectively.

Hardness (H) is calculated from the maximum indentation load (P_{max}) divided by the residual indentation area (A_r) [12]:

$$H = \frac{P_{max}}{A_r} \quad (2)$$

The typical load-displacement curves resulted from the nanoindentation tests on epoxy and mercaptan-loaded microcapsules are shown in Fig. 4. In these curves, the load increases gradually to P_{max} , then decreases sharply on unloading. The loading curve with linear and nonlinear parts represents both elastic (recovery) and plastic (inelastic) deformation [29,30]. The results of mechanical properties of all microcapsules are summarized in Table 4.

3.3. Statistical analysis of the results

In this section, the effects of the kind of core material, Mw of PMMA and mechanical mixing rate on the responses (elastic modulus and hardness of PMMA shell) are statistically determined and discussed. The influence of the capsule size was studied with variation of the mechanical mixing rate used in generation of O/W emulsions. The analysis

Fig. 4. Typical load-displacement curves for epoxy (run 1 and 2) and mercaptan-loaded microcapsules (run 3 and 4).

Table 4

Measured parameters of nanoindentation test for healing agent/PMMA capsules.

Run no.	Elastic modulus (GPa)	Hardness (GPa)
1	3.495 ± 0.525	0.064 ± 0.021
2	2.682 ± 1.318	0.189 ± 0.105
3	3.282 ± 1.593	0.153 ± 0.060
4	2.386 ± 0.715	0.219 ± 0.055

Table 5

ANOVA for elastic modulus of epoxy and mercaptan-loaded microcapsules.

Factor	Degree of freedom	Sum of square	Variance	F-ratio	Pure sum	Percent
Core	1	0.064	0.064	37.671	0.064	7.921
Mw of PMMA	1	0.73	0.73	424.657	0.728	91.513
mixing rate	(1)	(0.001)	Pooled	Pooled	Pooled	Pooled
Other/Error	1	0.001	0.001	–	–	0.566
Total	3	0.796				100.00%

The numerical values between the circular brackets indicate the values after pooling.

of variance (ANOVA) is a powerful technique that explores the significant factors affecting the response by using a criterion such as F-ratio. For a L_4 Taguchi design with 2-level factors and confidence level of 90%, if the F-ratio of a control factor is equal to or greater than 39.86, then the factor has an important influence on the response, otherwise it is insignificant [24]. The ANOVA statistical terms representing the effects of factors on elastic modulus and hardness of PMMA shell of microcapsules are shown in Tables 5 and 6, respectively. The results showed that, in the range of levels studied in this study, the most important factor affecting the elastic modulus of PMMA shell was the PMMA average Mw (F-ratio = 424). The core material and particularly the mixing rate were insignificant factors on elastic modulus of the shell. The effect of the latter is so small that is pooled with the error term. The last column in the ANOVA table contains the percent contribution of each factor affecting the response. As observed, over 91% of the effect is attributed to the PMMA average Mw.

According to the ANOVA table for the hardness (Table 6), the most important factors affecting the hardness of the polymeric shell were the M_w of PMMA and the kind of core material. The mechanical mixing rate and, consequently, the size of microcapsules had a minor effect on these two responses, and therefore it is pooled with the error term. The other/error term in the last row of the ANOVA tables contains information about three sources of variability of the results: uncontrollable factors, factors that are not considered in the experiments, and the experimental error [24]. It should be emphasized that the interpretation of ANOVA is valid only in the range of levels considered for every factor.

Table 6

ANOVA for hardness of epoxy and mercaptan-loaded microcapsules.

Factor	Degree of freedom	Sum of square	Variance	F-ratio	Pure sum	Percent
Core	1	0.003	0.003	4.068	0.002	20.538
Mw of PMMA	1	0.009	0.009	10.48	0.008	63.461
mixing rate	(1)	(0)	Pooled	Pooled	Pooled	Pooled
Other/Error	1	0		–	–	16.001
Total	3	0.013				100.00%

The numerical values between the circular brackets indicate the values after pooling.

Fig. 5. Main effect plots for elastic modulus of epoxy and mercaptan-loaded microcapsules.

3.4. Influence of different parameters on the mechanical properties

Main effect plots for elastic modulus of PMMA shell of healing agent microcapsules are presented in Fig. 5. These plots represent the trends in which the elastic modulus is influenced when the factors are varied within their specified levels.

According to Table 5, the elastic modulus of PMMA shell of microcapsules strongly depends on the PMMA average Mw. As the Mw of PMMA increases, the elastic modulus of microcapsule shell decreases (Fig. 5). The effect of the polymer average molecular weight on the mechanical properties of microcapsule shell was investigated in a few studies [31–35], often with conflicting suggestions. Gao et al. reported that the elastic modulus of multilayer shell of poly (styrene sulfonate, sodium salt)/(polyallylamine hydrochloride) (PSS/PAH) capsules increases with increasing the Mw of at least one of the polyelectrolyte layer components of the shell. The elastic modulus of the PSS/PAH multilayer shell was enhanced with higher molecular weight of PAH [31]. Lulevich et al. studied the effect of Mw of polyelectrolytes on mechanical properties of multilayer microcapsule shell by using a combination of atomic force and confocal microscopy. They found that molecular weight of polyelectrolytes has no effect on the mechanical properties of microcapsule shell [32]. It is suggested that the elastic modulus of microcapsules with multilayer shell depends strongly on the charge density of polyelectrolyte layers of shell because the shell of microcapsules are composed via a layer-by-layer electrostatic self-assembly [33,34]. Lisunova et al. investigated the mechanical properties of hydrogen-bonded layer-by-layer microcapsule shells constructed from tannic acid and poly (vinylpyrrolidone) (PVPON). They reported that the increase in the molecular weight of the PVPON component promotes chain entanglements and increases the elastic modulus value [35]. Kawaguchi et al. reported that by increasing the molecular weight of PMMA, the mechanical properties of PMMA decreases. It is suggested that a lower Mw polymer has more homogeneous macromolecular structure compared to higher Mw one [36]. This can be justified easily as the cumulative polydispersity index in the free-radical polymerization is increased highly at very higher molecular weights [37].

In the encapsulation process through internal phase separation method (O/W emulsion), the organic phase (oil droplet) contains a mixture of healing agent and dissolved PMMA in DCM. While the volatile solvent (DCM) gradually evaporates from the organic phase, PMMA chains migrate to the oil/water interface to form polymeric shell. It was observed that when the Mw of PMMA increases, the elastic modulus of microcapsule shell decreases. This result could be explained according to the entanglement network model that describes the

structure of amorphous polymers. Generally, it is accepted that the entangled macromolecules behave as mobile transient cross-links. The chain ends, impurities, and low molecular weight molecules are concentrated inside the mesh. Therefore, the mesh region is mechanically weaker or softer than the entanglement network [38]. For higher Mw and greater PDI, the mechanically weak regions are increased. As a consequence, this would explain the tendency of elastic modulus to decrease slightly with increasing Mw of PMMA. It should be noted that the concept of elastic modulus may differ for nanoindentation techniques as compared with the conventional definition for bulk systems. Indeed, if the capsule thickness is small enough, it is conceivable that the mechanical response cannot be purely classified as a bulk one, but strongly related to the shell thickness. The same might apply when making allowances for the kind of material encapsulated (Fig. 5). It is observed that the elastic modulus of PMMA shell in epoxy-loaded microcapsules with epoxy core is higher than those containing mercaptan. The increase in elastic modulus for epoxy-loaded microcapsules is probably due to the fact that the viscosity of epoxy prepolymer (0.5–0.6 Pa s) is greater than that of mercaptan (0.4 Pa s). As a result, the resistance of PMMA shell of microcapsules containing epoxy for elastic deformation under the load is higher than those containing mercaptan. This is in accordance with results obtained by a previous study about mechanical properties of epoxy and mercaptan encapsulated with PMF shell [12]. The reduction in mechanical strength of PMMA shell of mercaptan-loaded microcapsules can also be ascribed to the different plasticizing effects and/or chemical nature of the healing agent cores. It seems that the plasticizing effects decrease the mechanical strength by reduction of stiffness and increasing the flexibility of polymer chains [39].

It is implied also from Table 5 and Fig. 5 that the mixing rate and, therefore, the mean diameter of microcapsules in the range of 5–45 μm had no significant effect on elastic modulus of PMMA shell. Keller and Sottos reported that the size of PUF microcapsules filled with dicyclopentadiene (DCPD) has insignificant effect on the elastic modulus of shell. They studied PUF capsule groups with mean diameters about 65, 187, and 213 μm [7]. However, some other authors reported that the microcapsule size has significant effect on mechanical properties of polymeric shell [17,18]. Hu et al. studied the DCPD/PMF microcapsules in the range of 10–16 μm , depending on agitation speed which was used in generation of emulsion [17]. Lv et al. studied the DCPD/PF microcapsules with mean diameter in the range of 352 to 218 μm [18]. It seems that the nature of polymeric shell and the range of capsules size probably dictate the dependency of mechanical properties of capsule shell on the capsule size.

As observed in the ANOVA table (Table 6 for the pooled factors), the last column contains the contribution percent of each factor affecting the response. The results show that about 63% and 20% of the total effect contributions for hardness of PMMA microcapsules belong to the effects of Mw of PMMA and core material, respectively. The changes in the hardness of PMMA microcapsules when core materials, Mw of PMMA and mean size of microcapsules are varied within the low and high levels are shown in Fig. 6. The hardness of microcapsule shell is a measure of its resistance to deformation by surface indentation. This response is increased by increasing the Mw of PMMA, most probably due to chain entanglements that prevent the penetration of indenter [40]. It is observed that the microcapsules with different core material, have a significantly different shell hardness. This can be associated with the different chemical nature and plasticizing effect of core material on the microcapsule shell [12]. The mean size of microcapsule as a consequence of mechanical mixing rate was also found to have a minor effect on the hardness of capsule shell. It seems that the thickness of shell that is influenced by variation of microcapsule size is responsible for the resistance of polymeric shell against the permanent indentation.

Fig. 6. Main effect plots for hardness of epoxy and mercaptan-loaded microcapsules.

4. Conclusions

PMMA microcapsules containing epoxy and mercaptan with mean diameters in the range of 10–35 μm and 5–45 μm were prepared, respectively. Micromechanical properties of healing agent/PMMA microcapsules including elastic modulus and hardness were measured using nanoindentation. The elastic modulus of PMMA shell of microcapsules was found to have an average value between 2.4 ± 0.7 to 3.5 ± 0.5 GPa. The hardness of microcapsules shell was in the range of 0.064 ± 0.021 to 0.22 ± 0.055 GPa. The elastic modulus of PMMA microcapsules containing epoxy was higher than mercaptan-loaded microcapsules. The mercaptan may affect the mechanical strength of the PMMA shell through the plasticizing effect on the polymeric shell. The results indicated that the Mw of PMMA was the most significant factor on mechanical properties of healing agent/PMMA microcapsules. In this study, the mean size of microcapsules in the range of 5–45 μm had a minor effect on mechanical properties of microcapsule shell.

It is conceivable that the observed behaviors are related to complex interplay between the plasticizing effect of the encapsulated material, the bulk mechanical properties of the shell as well as its thickness. More fundamental studies are needed in order to further clarify such interplay. For the present purposes, the obtained statistical inferences constitute a valuable tool for the material designer in order to prepare microcapsules with tailored mechanical response.

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