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## MECHANICAL PROPERTIES OF BIODEGRADABLE BONE CEMENT COMPOSITES

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### 1. Introduction

Biodegradable synthetic polymers offer a number of advantages over other materials for developing scaffolds in tissue engineering. The key advantages include the ability to tailor mechanical properties and degradation kinetics to suit various applications. Synthetic polymers are also attractive because they can be fabricated into various shapes with desired pore morphologic features conducive to tissue in-growth.

Biodegradable synthetic polymers such as poly (glycolic acid), poly (lactic acid) and their copolymers, poly (p-dioxanone) and copolymers of trimethylene carbonate and glycolide have been used in a number of clinical applications. The major applications include resorbable sutures, drug delivery systems and orthopedic fixation devices such as pins, rods and screws [1, 2, 4, 6, 14]

The advantages of bioabsorbable implants in bone surgery are significant: there is no need for removal operation, and osteoporosis associated with rigid metallic implants can be avoided or at least reduced and the bone itself heals better. The avoidance of removal procedures leads to financial benefits, psychological advantages, and it increases operative capacity [19, 24]

Biodegradable bone cement, showed a great potential in orthopedic applications for younger patients as it would provide immediate structural support and subsequently allow normal bone healing and remodeling processes to occur [3, 15].

Polymethyl methacrylate (PMMA) bone cement modification with  $\gamma$ -methacryloxy providing stable fixation for a long period after implantation [23].

A porous biodegradable scaffold coating for perforated and demineralized cortical bone allografts could maintain immediate structural recovery and subsequently allow normal healing

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and remodeling by promoting bony growth and avoiding accelerated graft resorption [16]. Mikos and co-workers developed degradable biomaterials for orthopedic applications based on polypropylene fumarate that could be polymerized in situ using benzoyl peroxide as an initiator similar to PMMA bone cement but the mechanical strengths of these materials were rather low ranging from 7 to 30 MPa in compressive strength [5, 20].

Acrylic bone cements modified with different additives such as oligomer filler, based on an amino acid or HA to improve mechanical strength and achieve biological compatibility [9–11, 20]. Polypropylene fumarate (PPF) is unsaturated linear polyester that can crosslink with itself or with a crosslinking agent such as N-vinylpyrrolidone (NVP) and methyl methacrylate (MMA) or their mixture in situ to form a degradable polymeric network [1–2, 4, 14, 19, 24]. Such crosslinking in situ of PPF was valuable for developing injectable materials that could fill skeletal defects of varying size and shape.

The in vitro tests in simulated body fluids also studied for the biodegradable composite materials to measure the mechanical properties of bone cement composites [12, 13, 17, 18, 21].

The aim of the present work is to develop some composites based on fumarate polyester with different crosslinking agents loaded with different concentrations of gypsum to be used as bone cements. The compressive properties of the different concentration of gypsum were studied before and after immersing in Simulated Body Fluid (SBF). The biodegradability of the composites under investigation were measured by the percentage of weight loss after 8 weeks. Also the microstructure for the samples under investigation was examined.

## **2. Experimental work**

### **2.1. Materials**

Diethyl fumarate, 1,2-propanediol and tetrabutyl titanate as the trans-esterification catalyst were reagent grade from Merck, Darmstadt, Germany and used as received. N-vinyl pyrrolidone, (NVP) or methyl methacrylate (MMA) (freshly distilled, were obtained from Merck, Darmstadt, Germany). Benzoyl peroxide, N, N-dimethyl-4-toluidine and gypsum [calcium sulfate dehydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )], were obtained from Aldrich.

#### **2.1.1. Synthesis of fumarate polyester resin**

Polypropylene fumarate (PPF) was prepared by Polymers and Pigments Department, National Research Centre, Dokki, Cairo, Egypt by the two-stage melt polycondensation method (esterification and polycondensation). A three necked flask equipped with a condenser, nitrogen inlet tube and magnetic stirrer was charged with (one mol) of diethyl fumarate and (2,2 mol) of 1,2-propanediol and catalyst. The reaction mixture was heated to 150°C for 3 hours. This first step (esterification) is considered to be completed after the collection of theoretical amount of ethanol, which was removed from the reaction mixture by distillation and collected in a graduate cylinder. In the second step of the transesterification of bis(hydroxypropyl)

fumarate was carried out by heating the vessel at 200°C for 4 hours, producing PPF and 1,2 propanediol as a by-product. The mixture was dissolved in methylene chloride and precipitated in diethyl ether. The ether phase was decanted and the product was vacuum dried at room temperature to remove any remaining solvents.

### 2.1.2. Crosslinking of the prepared fumarate polyester

Fumarate polyester resin (PPF) was crosslinked with 30% by weight of N-vinyl pyrrolidone (NVP) or methylmethacrylate (MMA) monomer or a mixture of NVP/ MMA in the ratio of 1:1 by weight using benzoyl peroxide as initiator (2% w/w). 0.2% of N, N-dimethyl-4-toluidine was added with rapid stirring, then, the mixture was molded using appropriate molds for different tests. Curing occurred after leaving the mixtures at room temperature (25°C) for 24 h.

### 2.1.3. Polymeric composites

The bone cement composites were prepared by mixing different ratios of gypsum (60, 65 and 70 wt %) with a mixture of fumarate polyester resin and crosslinking agents namely NVP, MMA and NVP/ MMA. Curing occurred at the same condition mentioned above.

## 2.2. Hydrolytic degradation

Crosslinked polyester and its composites were immersed in SBF solution pH 7.3 in an incubator at 37°C. Reagents used for SBF formulation are listed in Table 1.

TABLE 1  
Reagents for preparation of the Simulated Body Fluid (SBF) (g/L)

Order	Reagent	Amount in grams
1	NaCl	7.996
2	NaHCO <sub>3</sub>	0.350
3	KCl	0.224
4	K <sub>2</sub> HPO <sub>4</sub> .3H <sub>2</sub> O	0.228
5	MgCl <sub>2</sub> .6H <sub>2</sub> O	0.305
6	1M HCl	40 ml
7	CaCl <sub>2</sub>	0.278
8	Na <sub>2</sub> SO <sub>4</sub>	0.071
9	(CH <sub>2</sub> OH) <sub>3</sub> CNH <sub>2</sub>	6.057

To determine the weight loss during degradations, preweighted disks (5 cm diameter and 4 mm thickness) were each placed into a tared scintillation vial. Periodically, the samples were removed from the incubator, rinsed with distilled water and dried in vacuum until a constant weight is reached. The mass loss was recorded as the average of the three individual degraded samples after immersion. The percentage of weight loss was determined for each sample by comparing the dry weight ( $w_d$ ) remaining at specific time with the initial weight ( $w_0$ ).

$$\% \text{ weight loss} = \frac{w_0 - w_d}{w_0} \cdot 100 \quad (1)$$

### 2.3. Mechanical Tests

The compressive tests were conducted according to ASTM D 695 — ISO 604. The cylindrical specimens were prepared for compression test with aspect ratio 2:1 (length to diameter ratio). Hounsfield (100 KN) universal testing machine were used. Axial compressive load was applied to the specimen with head speed 3 mm/min.

### 2.4. Micro examination

- The microstructure of the samples under investigation was examined using Lieca optical microscope (Japan) with magnification 100 x.
- Scanning electron microscope.

A scanning electron microscope model Joel JAX 840 A — Electron probe. Micro analyzer was used to identify the crystal structure and the elements formed after immersing in SBF solutions.

## 3. Results and Discussion

### 3.1. The compressive Properties

#### 3.1.1. MMA group

The compressive stress — strain diagrams for MMA group are shown on Figure 1. From this figure it can be noticed that the compressive strength for specimen MMA contain 60% gypsum, was 6.59 MPa and the strain at fracture was 17%. It can also be noticed that increasing of the gypsum to 65% in MMA group led to increase of the compressive strength to 10.7 MPa and the strain at fracture was 20%, while subsequent increase in gypsum to 70% in MMA led to decrease of the compressive strength to 8.7 MPa and strain at fracture was strain was 21%.

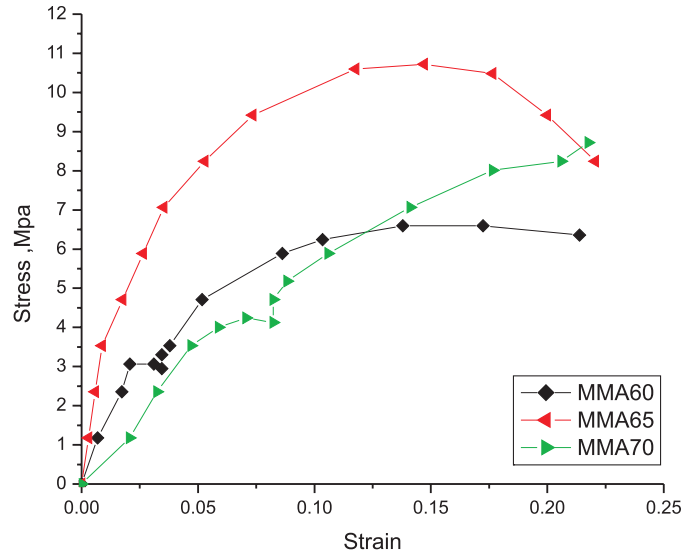


Fig. 1. The compression stress — strain diagrams for specimens of MMA group

The modulus of elasticity for MMA 65% showed the maximum 121 MPa as shown in Table 2.

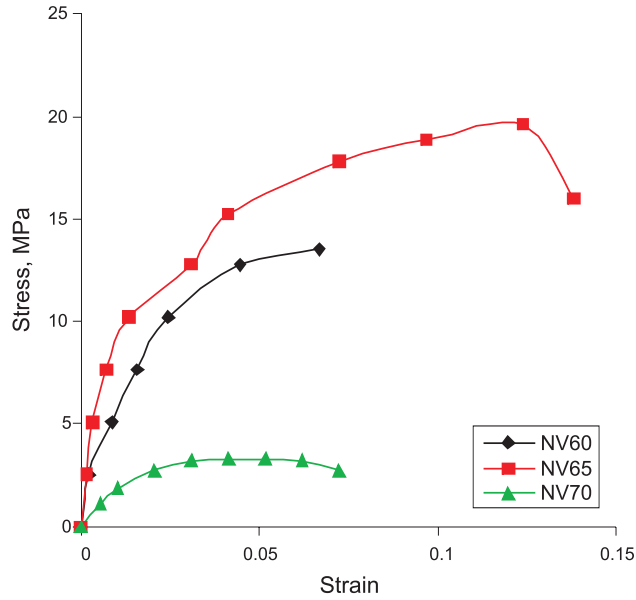
TABLE 2  
The mechanical properties of MMA group

Composition	$E$ , MPa	Max. Strength, MPa	% strain
MMA-60	83	6.59	17.4
MMA-65	121	10.7	20
MMA-70	74	8.7	21.7

### 3.1.2. NV group

The compressive stress — strain diagrams for the NV group are shown on Figure 2. From this figure it can be noticed that increasing of the concentration of gypsum from 60% to 65% led to increase of the compressive strength from 13.5 to 19.6 MPa, while successive increase of gypsum to 70% NV led to sharp decrease of the compressive strength to 3.29 MPa.

From the results of mechanical properties in Table 3, it is clear that the modulus of elasticity for NV contain 60 and 65% gypsum double the modulus of elasticity of MMA with the same gypsum concentration. This can enhance the fixation in the initial stage of treatment of broken bone. On the other hand increasing the gypsum cement concentration to 70% led to decrease the compressive strength.



**Fig. 2.** The compressive stress — strain diagrams for NV group

TABLE 3

**The mechanical properties of NV group**

Composition	$E$ , MPa	Max. Strength, MPa	% strain
NV-60	395	13.5	15
NV-65	223.5	19.6	12.4
NV-70	58.6	3.29	5.1

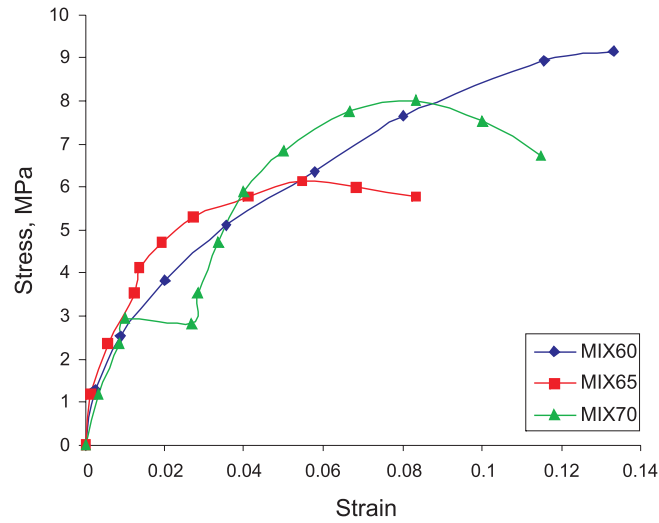
### 3.1.3. Mix group

The compressive strength — strain diagrams for samples contain a mixture of MMA and NV group with 1:1 ratio are illustrated in Figure 3. It can be noticed that the highest compressive strength was recorded for specimen contains 60% gypsum cement. From Table 3 it is clear that mixing NV with MMA led to improve the modulus of elasticity compared to MMA group.

TABLE 4

**The mechanical properties of Mix group**

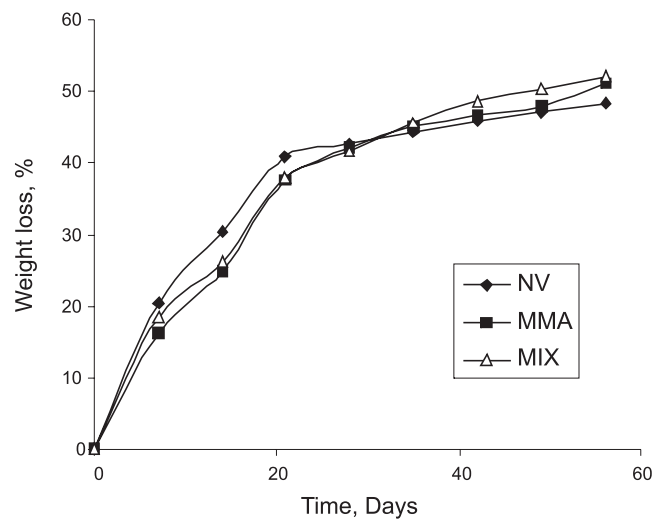
Composition	$E$ , MPa	Max. Strength, MPa	% strain
Mix-60	94.86111	9	13
Mix-65	133.3714	6.12	8
Mix-70	114.0169	8.3	11



**Fig. 3.** The compressive stress — strain diagram for MMA/NV (Mix) group

### 3.2. Biodegradability

The biodegradability of PPF crosslinked with NVP, MMA and NVP/MMA loaded with 60 wt % gypsum is attributed to their ability to undergo hydrolysis to their respective monomeric carboxylic acids and diols.



**Fig. 4.** The percentage of the weight loss over time of exposure to the SBF solutions

In vitro demonstration of biodegradation requires experimental conditions mimicking the physiological characteristics of the living media. Thus SBF (pH 7.3) was used as in vitro

medium in order to provide iso-osmolality and to neutralize the generated carboxyl groups. The degradation rate of crosslinked fumarate based polyesters as well as bone cement composites were measured in terms of the weight loss over time of exposure to the SBF solutions as shown on Figure 4. Degradation of PPF crosslinked with NVP is slower than that of MMA and NVP/MMA.

From this figure it is clear that the weight loss reach to 40% after four weeks. Increasing the time to eight weeks of exposure in SBF solutions caused the fact that the percentage of weight loss increased to 50%.

### **3.3. Effect of SBF solutions on the mechanical properties**

In order to study the effect of SBF solution on the mechanical properties, the specimens containing 60% gypsum were immersed in SBF solutions for four weeks. This is because the formation of carbonate apatite occur when immersed in SBF solution for four weeks. Figure 5 shows that the compressive strength for the MMA after immersing in the SBF solution increased dramatically to four times of its compressive strength before immersing, while the compressive strength of MIX increased from 9 to 25 MPa. On the other hand, immersing NV in the SBF solution, led to slight increase in the compressive strength (from 13.5 to 15.5 MPa).

From these graphs it can be noticed that the modulus of elasticity of MMA and MIX increased from 83 and 94 MPa to 510 and 640 MPa respectively, while the modulus of elasticity of NV decreased from 395 to 175 MPa. Basing on these results it is clear that the MMA and MIX are useful for treatment of bones which need the fixation to be more resistant to the stresses exerted from bones during growth. On the other side, the NV can be used in cases where the fixation needs higher initial strength and lower strength during the healing progress to allow the growth of bones.

### **3.4. The Micro examination**

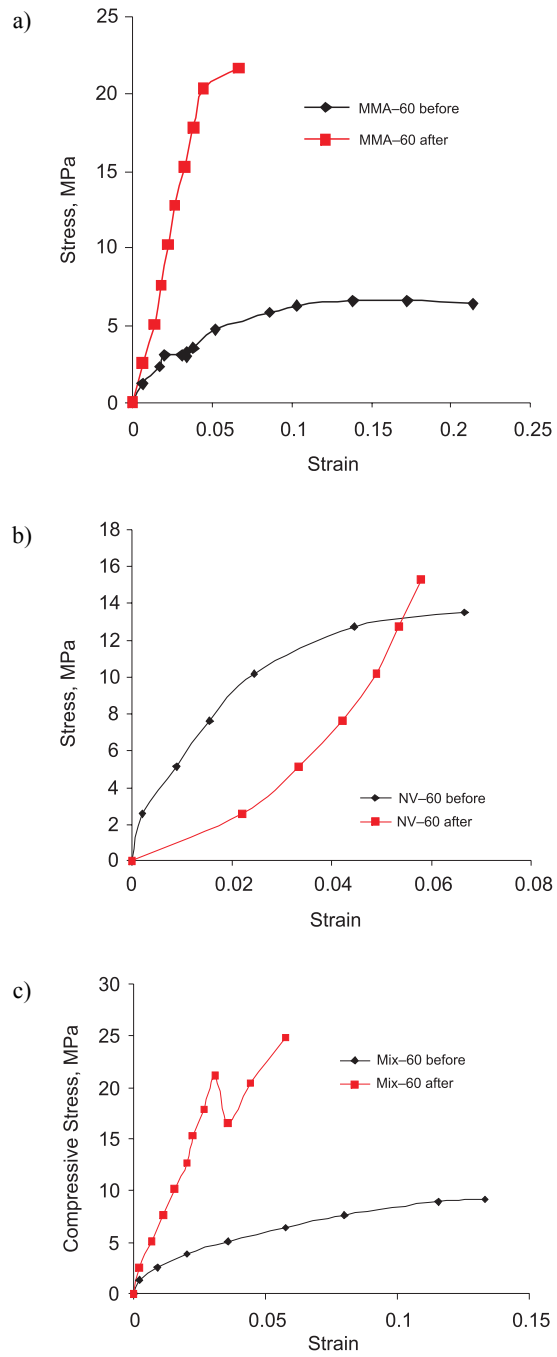
The microstructure of the biodegraded PPF crosslinked with NVP, MMA and NVP/MMA loaded with 60% gypsum after immersing in the SBF solution is illustrated on Figure 6.

From this figure it is clear that after immersing the specimens for four weeks in the SBF solution the structure indicated pores and cavities. This is attributed to their ability to undergo hydrolysis. It can also be noticed that NV showed lower porosity than MMA and MIX samples.

Scanning electron micro examination for fracture surface of the specimens containing 60% gypsum after immersing in SBF solutions for four weeks are illustrated on Figure 7.

Polymeric areas are observed on the fracture surface of MMA-60 as shown on Figure 7a, while the crystalline structure of calcium apatite with the hexagonal shape can be identified all over the fracture surface of NV-60 (Fig. 7b). On the other hand, the fractography of MIX-60 shows that the crystalline structure is imbedded in the polymeric matrix as illustrated on Figure 7c.

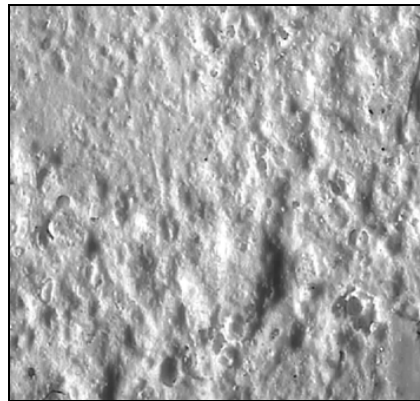




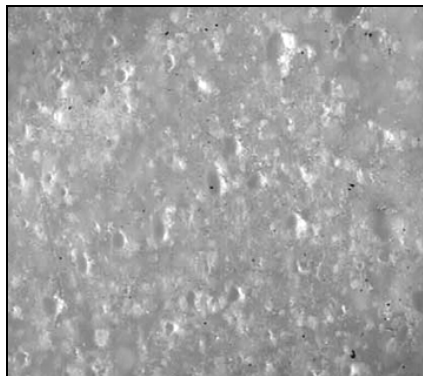
**Fig. 5.** Effect immersion in SBF solution on the compressive properties: a) MMA-60; b) NV-60; c) MIX-60



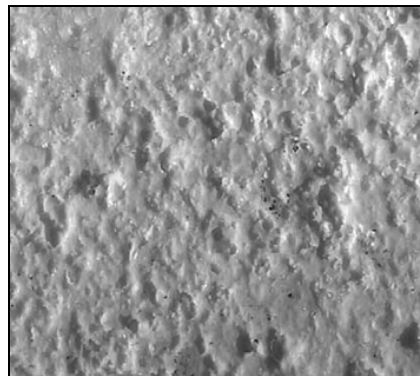
MMA before immersing



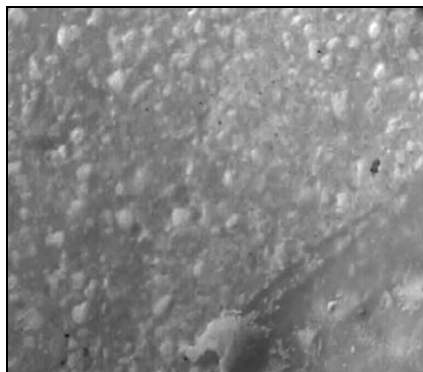
MMA-60% after immersing



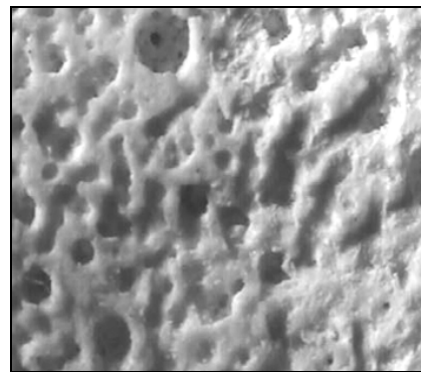
NV before immersing



NV after immersing

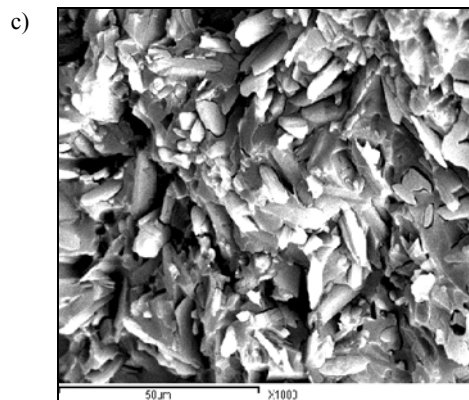
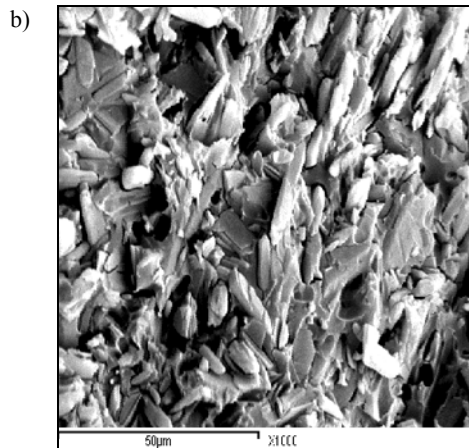
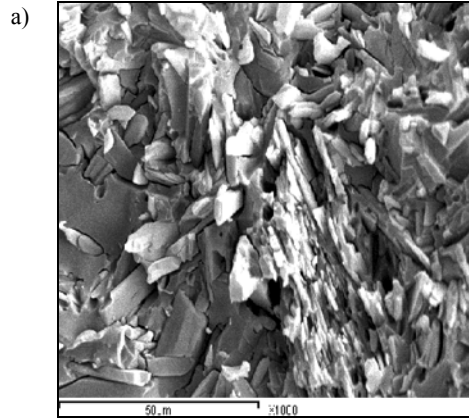


Mix-60% before immersing



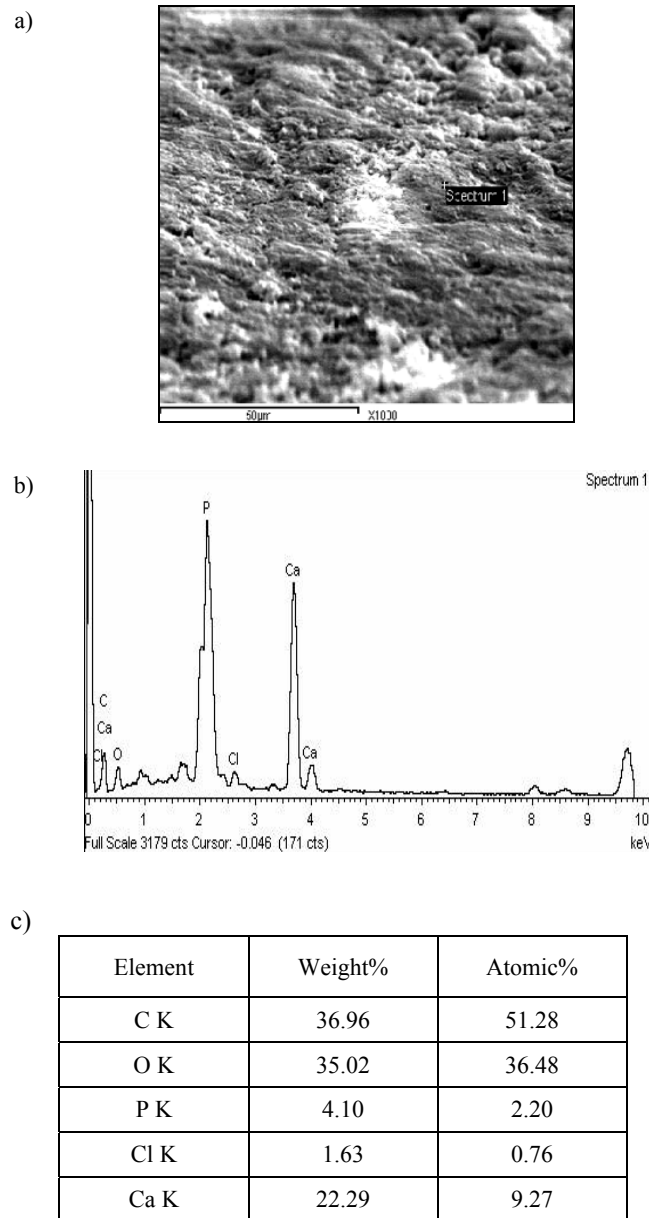
Mix-60% after immersing

**Fig. 6.** Micro examination of specimens containing 60% gypsum before and after immersing four weeks in SBF solutions (100X)



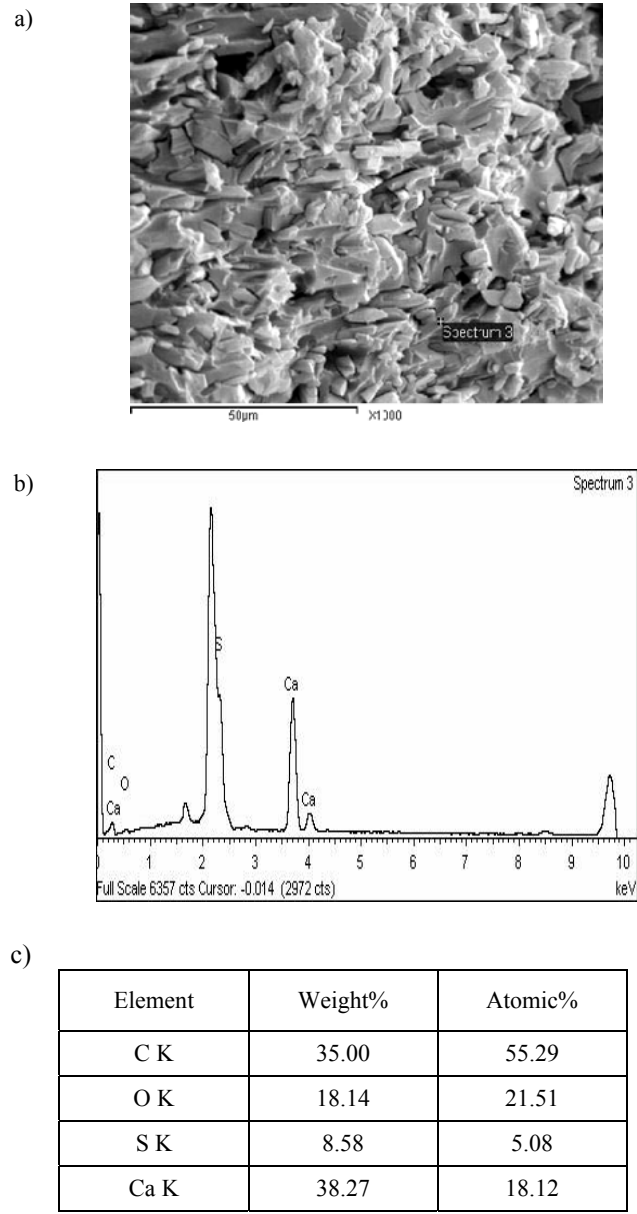
**Fig. 7.** Fractograph for samples contain 60% gypsum cement — polyester composites:  
a) MMA-60; b) NV-60; c) MIX-60

This emphasizes that the increase in compressive strength of MMA-60, and MIX-60 in comparison with NV-60 after immersing in the SBF solution. EDAX (energy-dispersive x-ray spectroscopy) microanalysis for MIX-60 is shown on Figure 8.



**Fig. 8.** The EDAX of the surface of MIX-60 after immersion in SBF solutions

The elemental analysis of spectrum — 1 shown on Figure 8 (parts b, c) indicates presence of phosphate. On the other hand the EDAX of the fracture surface of MIX-60 after immersion in SBF illustrated on Figure 9 the hexagonal structure.



**Fig. 9.** The EDAX for spectrum — 4 on the fracture surface for Mix-60

From this figure it is clear that sulfur element existing in spectrum 3 in the fractured surface is replaced by phosphorus element on the surface due to the reaction with SBF solution. It can also be noticed that the crystal structure is hexagonal which is typical to hydroxyl apatite [7–8].

#### 4. Conclusions

- 1) Increasing concentration of gypsum cement bone more than 65% led to decrease the compressive strength for polyester resin NV, MMA, and NV/ MMA mixture.
- 2) Fumarate polyester resin (PEF) crosslinked with N-vinyl pyrrolidone (NV) recorded the highest modulus of elasticity and compressive strength.
- 3) The rate of biodegradability of PPF crosslinked with NVP, MMA and NVP/MMA loaded with 60 wt % gypsum over four weeks increased to 40%.
- 4) The compressive strength for MMA increased to four times its strength after immersing in SBF for 4 weeks.
- 5) MMA and Mix are useful for treatment of bones which need the fixation to be more resistant to the stresses exerted from bones during growth.
- 6) The modulus of elasticity of NV loaded with 60 wt % gypsum decreases after immersing in SBF.
- 7) The polyester resin MMA, NV/ MMA mixture loaded with 60 wt % gypsum shows high degradation rate and more porous after immersing in SBF.
- 8) The scanning electron microanalyses for fractured surface indicate the hexagonal structure of hydroxylapatite.

References and further reading may be available for this article. To view references and further reading you must purchase this article.

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