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Study on the preparation of some biocomposites based on silicone elastomers and collagen

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This work presents investigations carried out with the aim of obtaining biocomposites based on silicone elastomers and collagen with an improved biocompatibility as compared to the single silicone elastomer. To prepare the above biocomposites the following procedures were used: - preparing a blend of silicone elastomer and a natural polymer – collagen; SI-COL biocoposites based on silicone elastomer containing 5 %, 10 %, 15 % and 20 % (by weight) collagen hydrolysate were obtained; three types of collagen hydrolyzates – HOC2, HOC8 and HOG8 were used; - the accelerated electron irradiation crosslinking was used instead of thermal crosslinking by peroxides. The highest crosslinking in the silicone elastomer was obtained with an irradiation dose of 20 Mrad. At this dose the crosslinking in the SI-COL biocomposite blends was achieved. When comparing physico-mechanical characteristics of these biocomposites crosslinked with accelerated electrons with those of biocomposites crosslinked with peroxides, the irradiation assisted crosslinking has resulted to be more efficient because of a homogeneous crosslinking within the biocomposite blend mass. The biocomposite blends containing HOC8 collagen hydrolysate crosslinked by irradiation have shown higher values of such characteristics as elasticity, tensile strength and tear strength; this can be explained by the homogenous morphology of such biocomposites. Further investigations with biological tests on cell cultures are to be performed. As the starting, biomaterials are known to be biocompatible, when preparing blends of silicone elastomer with 5, 10 %, 15 % and 20 % (by weight) natural polymer (collagen), the biocomposite biocompatibility is expected to be improved.

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Keywords: Biocomposite Silicone elastomer, Collagen hydrolysate, Biocompatibility

1. Introduction

Silicone elastomers have been used for over 40 years in obtaining human body implants, and further studies are being performed to improve their biocompatibility [1-3].

Three ways of *increasing material biocompatibility* are known as follows:

1) maximizing the inertness state by lack of any interaction between the material and tissue;

2) supervision of specific interaction techniques by avoiding the occurrence of undesirable constituents;

3) enhancing specifically the desired constituents that can occur with biomaterial-tissue interactions [1-9].

The collagen meets to a great extent the referred to requirements, being used in the bio-medicinal field with many applications in urology, dermatology, orthopaedy, vascular and general surgery [10-12]. Taking these into account, blends of silicone elastomers containing 5, 10, 15 and 20% (by weight) collagen were prepared. Furthermore, the accelerated electron irradiation was used instead of the thermal crosslinking, to avoid the thermal decomposition of collagen macromolecules. According to some *in vivo* tests [9], irradiation assisted crosslinking of silicone elastomer has led to its improved biocompatibility. Crosslinking by accelerated electrons also shows a series of advantages, like as: (1) the resulted products are pure as no peroxide is added; (2) lack of wastes; (3) reduced crosslinking time and power expenditure; (4) the resulted products are sterile, and (5) improved characteristics of the crosslinked products.

The objective of this work is to conduct some investigations on the preparation of some biocomposite materials based on a silicone elastomer and collagen hydrolyzates estimated to show an improved biocompatibility to the starting silicone elastomer.

2. Materials and methods

The following materials were employed: (1) silicone elastomer Elastosil R 701/70 OH (Wacker-Chemie), (2) three types of collagen hydrolysates of various molecular weights: HOC2 (M_{HOC2} = 25000 Da), HOC8 (M_{HOC8} = 7 000 Da) and HOG8 (M_{HOG8} = 13 000 Da); the HOC2 and HOC8 collagen hydrolysates were prepared from bovine hide, and HOG8 collagen hydrolysate was prepared from bone gelatin; collagen hydrolysates were obtained within the Department of Collagen Biomaterials in ICPI; (3) benzoyl peroxide Perkadox 14-40B-GB (Akzo Nobel).

SI-COL biocomposites based on silicone elastomer with 5, 10, 15 and 20 % (by weight) collagen hydrolysate were prepared by blending on a Brabender Plasticorder.

The biocomposite blends were homogenized on a laboratory roller mill at the room temperature for 2-3minutes. Crosslinking was achieved by two methods:

(1) thermally, by means of benzoyl peroxide for the control samples: an electrical hydraulic presser was used at 160^{o}C and 150 MPa, and the best curing time was established by means of the Monsanto rheometer;

(2) irradiation by accelerated electrons: the samples were subjected to irradiation in an electron accelerator, at a irradiation dose of 20 Mrad for about 60 sec.

Curing characteristics were determined by an oscillating disk rheometer (Monsanto), according to the SR ISO 341/1997. The biocomposite morphological structure was assessed by a stereomicroscope WILD Heerbrbrugg. Physico-mechanical characteristics were measured according to the international standards in force (SR ISO 7619/2001, SR ISO 37/1997, SR ISO 34-1/2000, 1817/2000, STAS 5787/1992, STAS 5570/1987).

3. Results and discussion

Biocomposite processability

The plots of torque force against time (Figs. 1-3) obtained on the Brabender Plasticorder have revealed changes in the composite blend processability by adding collagen hydrolysates and dispersing these, it being dependent on the amount of collagen hydrolysate being added, that is of the reacting groups in the collagen hydrolysates and their molecular weights. The torque values reveal a good blend processability, and that they can be processed on a mixer, roller mill, etc., which a commonly used in the rubber industry.

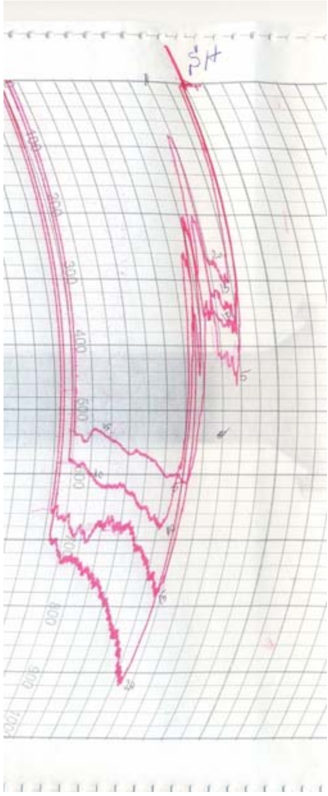

Fig. 1. The plot of torque against time for the SI-HOC2 blends.

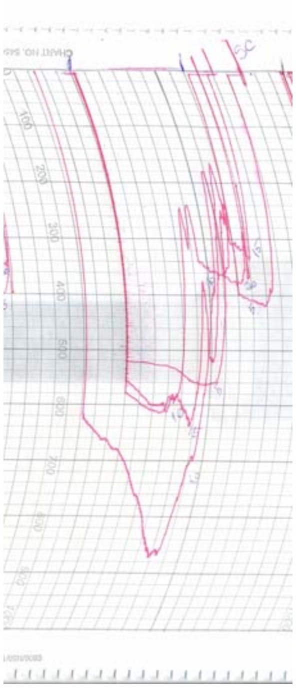

Fig. 2. The plot of torque against time for the SI-HOC8 blends.

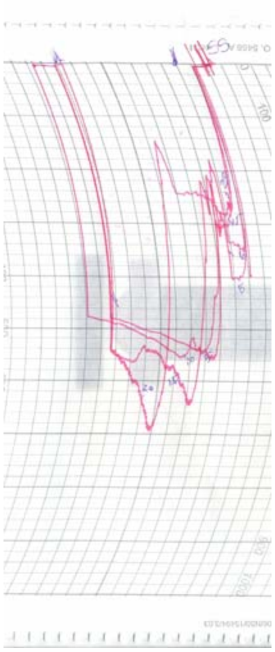

Fig. 3. The plot of torque against time for the SI-HOG8 blends.

Rheologic characteristics

Tables 1-3 show the results from reading the variables on the curing curves obtained with the Monsanto rheometer. These reveal that the minimum moment and maximum moment values decrease with the increase in the added collagen hydrolysate amount as this acts as a plasticizer in the biocomposite blends.

Table 1. Minimum, maximum and optimum curing moments for the biocomposite blends based on silicone elastomer and HOC2-collagen hydrolysate.

Characterisitc/ Percentage and type of collagen hydrolysate in the biocomposite blend	0 % HOC2	5 % HOC2	10 % HOC2	15 % HOC2	20 % HOC2
Moment min (M_L), Nm	2	2	1.8	2	0.8
Moment maxim (M_H), Nm	40.8	38.3	37.7	35.8	33.1
The best curing time (T_{90}), min.	5’15”	6’	7’30”	6’75”	7’24”

Table 2. Minimum, maximum and optimum curing moments for the biocomposite blends based on silicone elastomer and HOC8-collagen hydrolysate.

Characterisitc/ Percentage and type of collagen hydrolysate in the biocomposite blend	0 % HOC8	5 % HOC8	10 % HOC8	15 % HOC8	20 % HOC8
Moment min (M_L), Nm	2	1.4	1.3	1.2	1.8
Moment maxim (M_H), Nm	40.8	37.2	35	34.8	30.6
The best curing time (T_{90}), min.	5’15”	4’40”	4’24”	4’12”	5’54”

Table 3. Minimum, maximum and optimum curing moments for the biocomposite blends based on silicone elastomer and HOG8-collagen hydrolysate.

Characterisitc/ Percentage and type of collagen hydrolysate in the biocomposite blend	0 % HOG8	5 % HOG8	10 % HOG8	15 % HOG8	20 % HOG8
Moment min (M_L), Nm	2	0.1	1	0.1	1
Moment maxim (M_H), Nm	40.8	33.8	32.2	30	25.7
The best curing time (T_{90}), min.	5’15”	6’	5’45”	5’40”	5’36”

The values of the best curing time (T_{90}) for the resulted blends show changes according to the type and amount of the collagen hydrolysate being added (Tables 1-3). Thus, in case of HOC2 hydrolysate of a high molecular weight (25000 Da), the curing time show generally an increase with the increase in the amount of collagen hydrolysate being added into the blend. A close behaviour has shown the blend with added HOG8 of 13 000 Da molecular weight. The best values for the curing time were obtained with the blends containing HOC8 collagen hydrolysate (molecular weight of 7 000 Da); in this case, the best curing time have shown a light decrease with a minimum at 15 %. This reveals the influence of the technique used in preparation of collagen hydrolysates and their molecular weight on the biocomposite blend curing.

Biocomposite morphological structure

The morphological structure in biocomposites was assessed by means of a stereomicroscope WILD Heerbrbrugg that has enabled magnifications of 6x, 12x, 25x, and 50x. The microscopic examination has revealed a homogeneous structure in the biocomposite blends based on silicone elastomer and HOC8 collagen hydrolysate, specific to the biocomposites (Fig. 4). This can be explained by the low molecular weight (7 000 Da) of this type of collagen hydrolysate, enabling a better blending of the silicone elastomer.

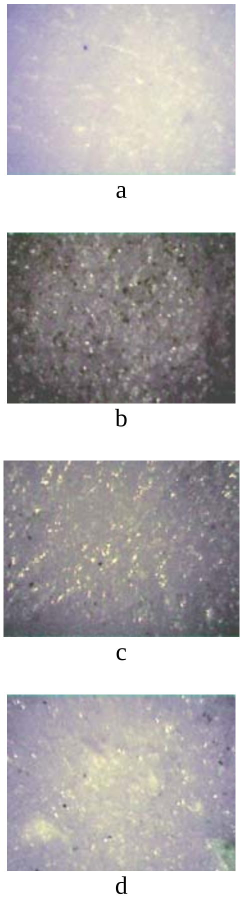

Fig. 4. Morphological structure of polymer biocomposites: (a) free of collagen hydrolysate, (b) with 20% HOC2, (c) with 20% HOC8, (d) with 20% HOG8 (magnification: 50 x).

Physico-mechanical characterisitcs

Figs. 5-8 show the changes in physico-mechanical characteristics of the polymer composites, obtained by the both crosslinking techniques (irradiation and with peroxid), with changes in type and amount of the added collagen hydrolysate.

From the review of the obtained results the following conclusion could be drawn:

- The biocomposites crosslinked by irradiation have shown higher hardness (84-91°ShA) than those crosslinked by means of peroxides (61-69 °ShA);

- The biocomposites crosslinked by irradiation have shown a decrease in elasticity with the increase in the amount of collagen hydrolysate being added, and the biocomposites crosslinked by peroxides have shown irregular changes; the elasticity values for the biocomposites crosslinked by irradiation were higher than for those crosslinked by peroxides;

- Tensile strength has shown low and varying changes with the increase in the amount of collagen hydrolysate, both for the biocomposites crosslinked with peroxides and by irradiation;

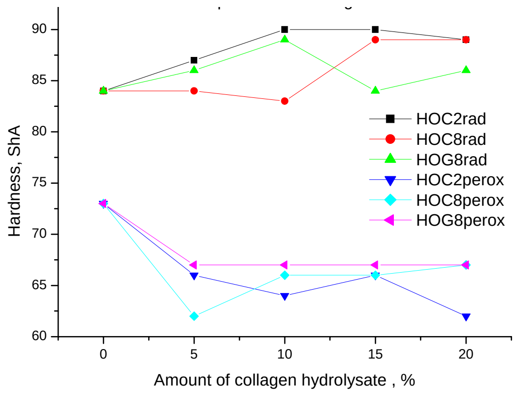

Fig. 5. Changes in the hardness with the amount of collagen hydrolysate in the SI-COL composites and curing time.

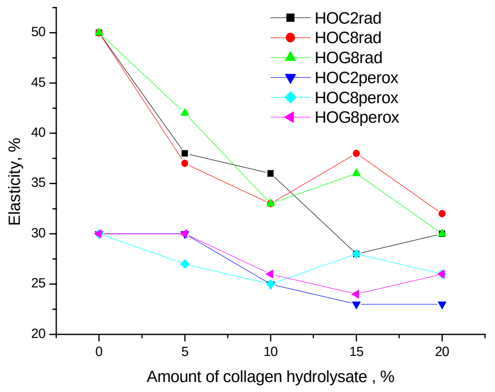

Fig. 6. Changes in the elasticity with the amount of collagen hydrolysate in the SI-COL composites and curing time.

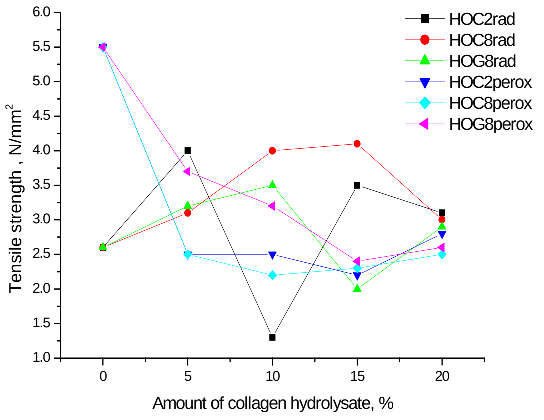

Fig. 7. Changes in the tensile strength with the amount of collagen hydrolysate in the SI-COL composites and curing time.

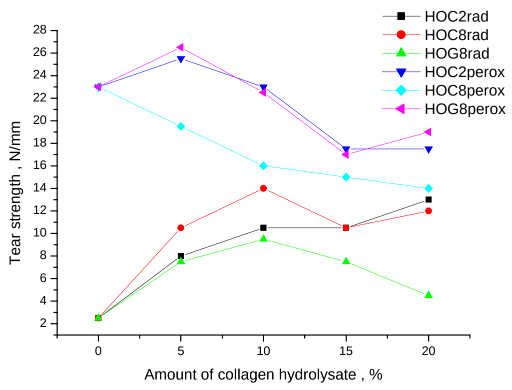

Fig. 8. Changes in the tear strength with the amount of collagen hydrolysate in the SI-COL composites and curing time.

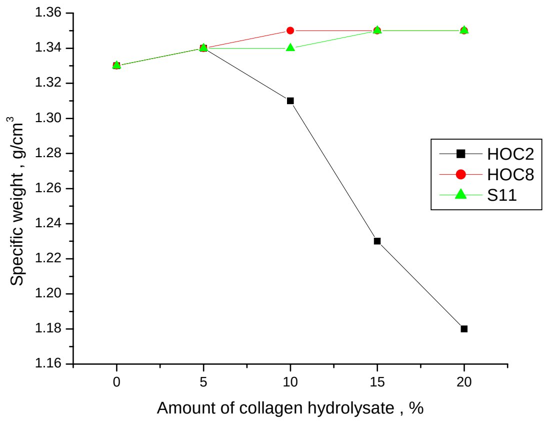

Fig. 9. Changes in the specific weight with the amount of collagen hydrolysate in the SI-COL composites.

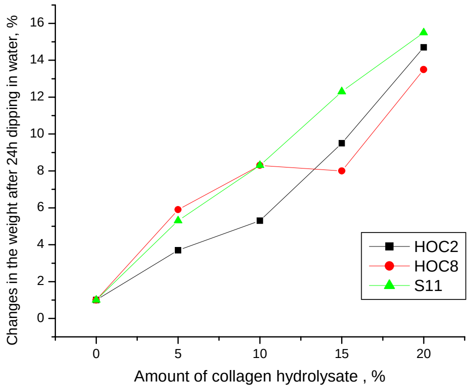

Fig. 10. Changes in the weight after 24h dipping in water with the amount of collagen hydrolysate in the SI-COL composites.

- The tear strength values are higher for the biocomposites crosslinked by peroxides than for those crosslinked by irradiation;

- Biocomposites with HOC8 or HOG8 collagen hydrolysates have shown a light increase in specific weight with the increase in the amount of collagen hydrolysate being added, and those with HOC2 collagen hydrolysate have shown a decrease in specific weight with the increase in the amount of collagen hydrolysate. This reveals compact structures in the biocomposites containing collagen hydrolysates of low molecular weight (HOC8 and HOG8) and porous, less homogenous structures in those containing collagen hydrolysates of high molecular weight (HOC2) because of the packing type of the macromolecular chains (Fig. 9);

- Fig. 10 reveals increased changes in the weight after 24 h dipping in water with the increase in the amount of collagen hydrolysate added to the biocomposite as the collagen is soluble in water at any level;

- Biocomposite blends with HOC8 collagen hydrolysate, crosslinked by irradiation have shown higher elasticity and tear strength values; this could be explained by the less molecular weight of this type of collagen hydrolysate enabling a better blending with the silicone elastomer, resulting in a homogeneous structure (Figures 6, 8).

When comparing the physico-mechanical characteristics of biocomposites crosslinked by accelerated electrons with those of the biocomposites crosslinked by peroxides (controls), the irradiation crosslinking can be said to be more efficient from the crosslinking homogeneity point of view, also leading to higher elasticity and hardness.

4. Conclusions

The results of this study have revealed the following features: (1) the biocomposite blends show a good processability; (2) the irradiation assisted crosslinking is more efficient than that with peroxides; (3) biocomposites with HOC8 collagen hydrolysate content crosslinked by irradiation were selected. Further investigations are to be performed by conducting biological tests on cell cultures. As the starting, biomaterials are known to be biocompatible, when preparing blends of silicone elastomer with 5, 10 %, 15 % and 20 % (by weight) natural polymer (collagen), the biocomposite biocompatibility is expected to be improved.

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