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Mechanical properties evaluation of new composites with protein biofibers reinforcing poly(methyl methacrylate)

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Abstract

Poly(methyl methacrylate) composites reinforced with natural protein biofibers from chicken feathers were prepared and evaluated through a series of tensile tests. Afterward, the samples were analyzed by optical and scanning electron microscopy studies, to obtain a clear picture of the tensile-induced damages.

The hydrophobic nature of keratin fiber produces an excellent compatibility between fibers and PMMA matrix. This fact is reflected in the good dispersion of protein fibers achieved without use of coupling agents. The normally rigid behavior of PMMA may be modified by using keratin fibers as were demonstrated by tensile test; while at the same time, Young's modulus of composite material is also increased. The microscopic studies realized at the corresponding fracture surface level show good adherence between fibers and matrix. These results demonstrate that feather fibers could be a new source of natural high structure fibers useful to create new materials provided with satisfactory properties.

Keywords: Keratin fiber; Poly(methyl methacrylate); Mechanical properties

1. Introduction

In recent years there has been a great interest in using polymeric composites reinforced with some material chosen from a huge diversity of systems. Natural fibers have attracted attention of scientists because of the advantages that these fibers provide as compared with synthetic reinforcement materials. Unfortunately, almost all research has been made around the so-called cellulosic fibers [1–5]. However, there are other resources in nature that must be studied in order to use them properly. Bovine leather [6,7], silk [8], wool and feathers are some examples of source materials from where high-quality fibers may be obtained.

Poultry feathers are a world-wide waste product and research should be undertaken to make good use of the interesting properties of keratin, their main component. Keratin is a special form of fibrous protein found in wool, nails, claws, horns and feathers, which protects animals against environmental conditions. This protein is durable, insoluble, chemically unreactive and pliable; moreover, it may recover its original mechanical properties, with little loss, after repeated deformations [9]. Keratin is distinguished from other fibrous proteins due to its structure has high stability, granted not only by the H bonds and van der Waals forces, but also by their high content of the amino acid cystine [10].

Among the few reports on keratin fibers from avian we may mention a Young's modulus evaluation of feathers from different species reported by Bonser et al. [11,12], the fiber separation from feathers by Schmidt et al. [13,14], followed first, by an exhaustive micro-structural characterization and second, by chemical modification of keratin fibers from chicken feathers [15,16]. In agreement to these

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references, fibers from chicken feathers are endowed with several important features: Surface toughness, flexibility, a high length to diameter ratio, hydrophobicity and a highly organized morphology characterized by a complex hierarchical structure [17]. To these advantages, we may add their low cost and density, good thermal insulation properties and non-abrasive behavior. Keratin fibers are not only a self-sustainable and continuously renewable but are ecologic, that is, biodegradable, due to their natural biopolymer origin.

PMMA is an important polymer because of its applications in very different fields, a fact which accounts for the large amount of research made to obtain more information on this material. PMMA has been modified with clay, graphite, rubber particles, carbon nanotubes, diamond and silicon carbide fibers [25–29], among other synthetic reinforcements. However, in spite of the importance of PMMA, research using natural fibers, as reinforcement with this polymer is scarce and the possible applications are promising. In addition, we chose PMMA because its rigidity, since if keratin fibers modify the elastic properties of PMMA, thus changing properties of other polymers is also possible with this new high structural fiber.

2. Experimental

2.1. Materials

Short keratin fibers, supplied by Dr Walter Schmidt from USDA, were employed as reinforcement. The process to obtain fibers is according to the patent US 5750030, 1998. In this procedure after leaving the poultry processing plant, the water-laden feathers are washed with ethanol and dried to have them clean white, sanitized and odor-free. These feathers are subsequently fed to a shredder, whose blades pulverize the quills, and to an air stream, to separate fibers from the rest.

Long keratin fibers were obtained by cutting the barbules from the barbs. The barbs are 10 mm in length and 50 mm in diameter. These fibers were characterized through a tensile test in order to know their mechanical behavior.

Methyl methacrylate (MMA) monomer was supplied by Sigma-Aldrich. The compound 2,2-azobis(isobutyronitrile) (AIBN) is used as reaction initiator for MMA polymerization.

2.2. Sample preparation

The composite preparation consists in a bulk polymerization of MMA initiated with AIBN at 70 °C in a reaction flask where a proper amount of fibers are added at the beginning of the reaction. After 90 min of reaction at constant temperature, the mix is transferred to a mold previously prepared as indicated by Sandler and Karo [18]. Then, it is placed in an air oven and heated to 70 °C for 24 h. Composites from 0 to 5% in weight of short keratin fiber were produced with this process according to the parameters listed in Table 1.

Three millimeter-diameter polyethylene tubing and 2 mm glass plates were used to build the mold while a silicon spray cover is used to facilitate the unmolding. After forming the composite, the casting is cooled gradually and the sheet is easily removed.

The resulting sheets, 0.3 mm in thickness, were cut into $38\times5\times3$ mm^3 specimens for the tensile tests.

2.3. Test methods

The tensile tests were performed using an Adamel Lhomargy DY.22 universal testing machine at a crosshead speed of 0.01 mm/min.

In order to study the fibers' distribution in the matrix a set of optical microscope pictures of transmitted light were made using a Nikon Optiphot 2-pol. The tested specimens were settled in silicon wafers, covered with gold, and observed through scanning electron microscopy using a LEO 1525 microscope.

3. Results and discussion

The methyl methacrylate (MMA) polymerization is carried out through an addition reaction which involves two kinetic steps: Radical initiator formation and propagation, in this case we use AIBN to form the free radical.

The reaction mechanism is depicted in Fig. 1. The free radical R* formed in the initial reaction joins, in the propagation step, to MMA monomer, producing a monomer radical, itself joined to another monomer molecule according with the reaction (ec. 1.2). The propagation step continues until a combination or disproportionation reaction occurs (reactions (ec. 1.4) and (ec. 1.5)) [19]. This process and the polymer used permit us to observe the interaction between the polypeptide and the growing polymeric chains, showing the good dispersion achieved by this system.

The average results concerning the stress–strain curve of five tensile tests, conducted on several long keratin fibers, are shown in Fig. 2. Here, we can observe that keratin fibers have a mechanical behavior between both α-helical structure (wool) [10,20] and β-sheet structure (fibroin)

Table 1
Reaction system for PMMA–keratin biofiber composites

Weight percent	Keratin fiber (g)	MMA monomer (ml)	2,2-Azobis (isobutyronitrile) (g)
0	0	45.00	0.0460
1.0	0.3370	44.55	0.0455
2.0	0.6741	44.10	0.0451
3.0	1.0111	43.65	0.0446
4.0	1.3482	43.20	0.0442
5.0	1.6852	42.75	0.0437

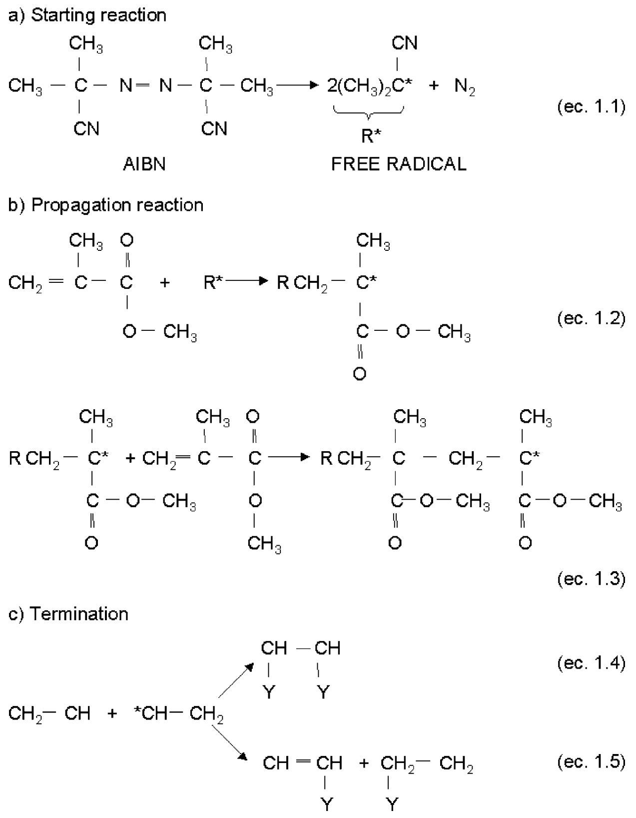

Fig. 1. Reaction mechanism in MMA polymerization initiated using AIBN to obtain the free radicals.

[21,22]. This behavior is due to itself, keratin from feathers is a composite material constituted by microfibrils or intermediate filaments soaked up by a matrix or keratin-associated protein. Thus, in the stress–strain curve there are two well defined zones: AB and BC.

AB, almost linear, known as Hooke's region and extending up to 280 MPa, is due to changes in bond angles and bond spacing but without affect the secondary configuration in the helical structure of the microfibrils. In this zone keratin fiber behaves as elastic solid, while the corresponding deformation ranges between 0.1 and 0.3%. Young's modulus associated to this zone is around 2.5 GPa, which agrees with other reported values [11,12].

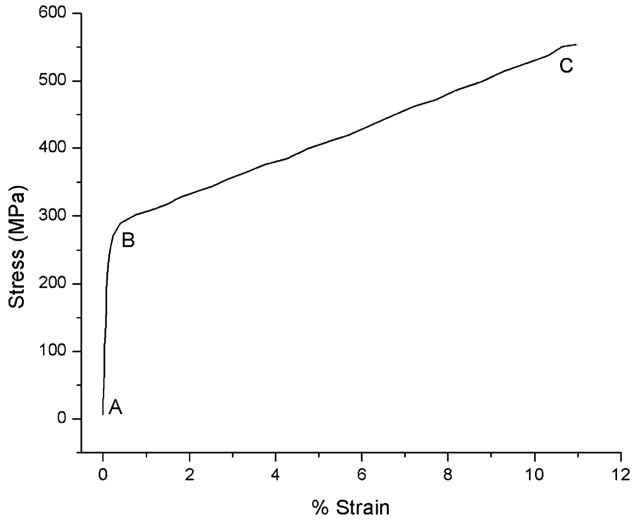

Fig. 2. Stress–strain curve for keratin fiber from chicken feather: AB, Hooke's region; BC, Yield region.

The zone BC, also called yield region, starts from a strain of 0.3% and extends up to 10%, corresponding to a 550 MPa stress. During the continuous development of strain, the helical structure is unfolded due to the realignment in the H bridges concerning to the keratin components, thus producing a change in the secondary structure called α–β transition [9,23]. At this range, the fiber's mechanical properties may be recovered if the fiber is released before its rupture. However, in the neighborhood of rupture, the fiber loses its mechanical properties and finally is broken because in this stage both hydrogen and disulphide bonding are destroyed, thus denaturing the protein [9,20–23]. A more detailed explanation about the α–β transition in keratin fibers from chicken feather is given elsewhere [9].

The tensile properties for the PMMA–keratin biofiber composites are given in Table 2. The theoretical Young's modulus is calculated using the Halpin–Tsai equation for short fiber reinforced composites [24]:

$$E = \frac{1 + 2(L/D)n_L v_f}{1 - n_L v_f} E_m$$

and

$$n_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(L/D)}$$

in this case E_f and E_m represent Young's modulus values, for keratin fiber (2.5 GPa) and PMMA (5.0 GPa), respectively. The aspect ratio (L/D) determinate by the length and diameter of fibers is estimated to be 350 according to the SEM evaluation reported elsewhere [15]. Finally v_f represents the fiber volume fraction calculated with the fiber's density (0.796 g/cm^3) and the corresponding mass used per each composite (Table 1).

The observed tendency of the values for predicted Young's modulus does not correspond with that for measured modulus as is observed. This variation indicates that the mechanical behavior of these composites cannot be explained by this kind of model, following just the relations between fiber volume used or aspect ratio; instead there is different behavior caused by good interactions between the protein fiber and the polymeric matrix at the interface level, due to the intrinsic properties of fiber.

All keratin biofiber composites have a Young's modulus larger than pure PMMA as observed in Table 2, reaching an increase of 29% in composite 5. This is result of the good compatibility between fibers and polymer reflected in the proper distribution between both phases. At the same time is possible to observe that composites 3 and 4 have great tensile strengths and smaller values in strain when they are

Table 2
Mechanical properties in PMMA–keratin biofiber composites

Sample[a]	Fiber volume fraction	Theoretical Young's modulus (GPa)	Young's modulus (GPa)	Maximum tensile strength (MPa)	Strain (mm/mm)
0	0	5.00	5.05 (0.112)[b]	29.68	0.0113
1	0.0095	4.98	5.50 (0.336)	29.33	0.0107
2	0.0190	4.95	5.66 (0.128)	28.85	0.0120
3	0.0285	4.93	5.97 (0.529)	34.82	0.0087
4	0.0380	4.91	6.17 (0.347)	31.72	0.0081
5	0.04758	4.89	6.50 (0.202)	27.89	0.0065

[a] Sample nomenclature corresponds with the included keratin biofiber weight percentage.
[b] These values corresponds with the standard deviation in Young's modulus.

compared with the other composites. This decrease in the elastic performance is attributed to those fiber contents are diminishing the material's flexibility, creating thus, a new material composite with different properties.

Thus, tensile strength is maintained in a homogeneous range between 28.85 and 34.82 MPa with the exception of composite 5, in which the tensile strength diminishes and is now 27.89 MPa. For higher concentrations the fiber's volume is too much and the polymer matrix formed by this method does not cover them completely, producing voids that weaken the interface and obstruct the load transfer between fiber and matrix. It may be remarked that the maximum tensile strength of 34.82 MPa achieved with the composite 3 shows an important contribution from the fiber to the new composite's mechanical properties.

A comparison between different results obtained from several papers may be made from the data shown in Table 3. It is apparent that Young's modulus varies according to the used reinforcement's nature: It diminishes with alumina and rubber particles, while it increases with other reinforcements, but not in a substantial quantity, due to the rigid characteristics in this polymer, which do not permit a bigger modification in its properties. The changes in these cited references are similar to the variations observed here; however all the reinforcements are synthetic inorganic materials.

Table 3
Mechanical properties of PMMA reinforced composites

Material	Young's modulus (GPa)	Reference
PMMA	5.00	[25]
PMMA–diamond fiber	8.19	[25]
PMMA–silicon carbide fiber	6.55	[25]
PMMA	1.77	[26]
PMMA–alumina	1.66	[26]
PMMA	3.66	[27]
PMMA–wallostonite	5.66	[27]
PMMA–wallostonite and stearic acid	6.09	[27]
PMMA	6.03	[28]
PMMA 20% rubber particles	4.97	[28]
PMMA 35% rubber particles	4.37	[28]
PMMA 50% rubber particles	3.97	[28]
PMMA	3.7	[29]
PMMA 1% Carbon MWNT's	7.8	[29]

Fiber distribution in composites may be appreciated in Fig. 3. The most striking fact is that there is no bundle formation, due to the hydrophobic behavior in keratin fiber previously reported [15]. The compatibility between the reinforcement and matrix is reflected also in the even distribution of fibers observed in Fig. 3. The hydrophobicity permits a complete fiber distribution in the MMA monomer during the reaction, and for this reason the composites do not have fiber bundles that could weaken the mechanical properties in the material.

Fracture surfaces of composites are shown in SEM pictures of Fig. 4(a) and (b). The images show a good fiber distribution in the PMMA matrix. In order to use completely the fiber's potential as reinforcement, a good impregnation and wetting of the fibers is necessary, to guarantee that the chemical or physical bonds are sufficiently strong and transfer the load between both phases. It is possible to observe these features in the keratin fiber–PMMA composites because of the good compatibility between these materials. The fibers contained in the matrix may be observed in Fig. 4, images (c)–(e). Although the fracture surface is irregular, it does not show any voids produced by

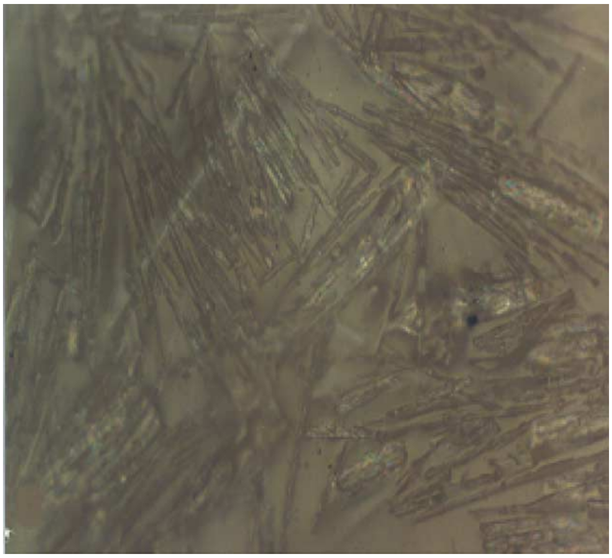

Fig. 3. Optical micrograph of 5% keratin biofiber–PMMA composite (20×).

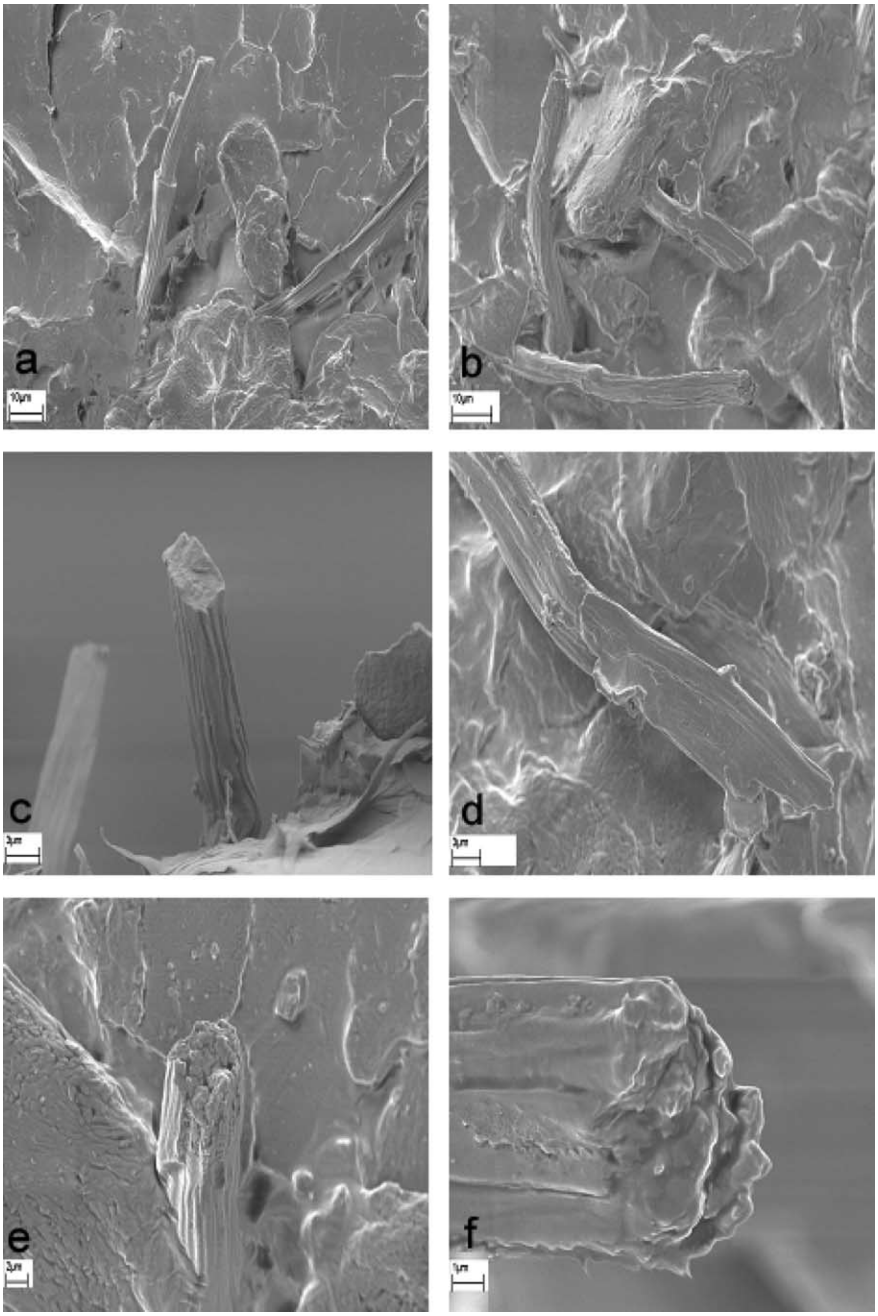

Fig. 4. Scanning electron microscopy of fractured surfaces of PMMA–keratin biofiber composites.

the pull out of fibers, a common feature of hydrophilic fibers [30,31]. As the composites were made without imposing any fibers' orientation, some are seen in the transversal sense to the tensile stress, pictures (a) and (b). In these images, the fibers are dispersed without the characteristic bundles presented by other natural fibers [32]. At the same time images (c)–(f), show that the keratin fibers are covered by a polymer coat adhered to the fiber surface, demonstrating thus the affinity between both. Pictures (d) and (e) show fiber's damage and its rupture as consequence of the applied stress.

4. Conclusions

Keratin biofibers have good compatibility with polymeric matrix due to their hydrophobic nature, a fact reflected in the increased Young's modulus obtained during composites' tensile tests.

This compatibility is also appreciated in the fibers' even distribution shown in the optical image and in the fracture surface interface observed by SEM. In these images, the completely wetted fibers are clearly seen, and, at the same time the matrix does not show any voids caused by fibers' pull out. Thus, it is possible to conclude that fibers truly take part as reinforcement in the load transfer process.

The tensile test results demonstrate that keratin fibers modify the PMMA's mechanical behavior in spite of being a rigid polymer, providing thus an important possibility to obtain great results when these new fibers are embedded in less rigid polymers. Currently research in this field is developed by the authors and includes the evaluation of mechanical and thermal properties of composites with other polymer matrices. The goal is to find the best application of this fiber [33].

The mechanical behavior in the synthesized composites shows that keratin fiber can modify the elastic properties of PMMA, a rigid polymer. This change is due to the inherent characteristics of protein fiber. At the interface level, polymeric chains are attached to fiber surface. They provide thus novel and unexpected mechanical properties to the composite when it is stretched, since the keratin fibers suffer rearrangements in their secondary structure. The α–β transition presented in the BC zone in Fig. 2 contributes also to the behavior observed in the composites through interface. Thus, when the tensile load reaches the fiber, it is possible that the microfibrils inside change from helical to pleated structure, reinforcing in this way not only its own keratin-associated protein matrix but the PMMA matrix also. This is noted, in the unpredicted properties, which are not in agreement with the theoretical model that applies to diverse composites. It is known that many kinds of proteins are intelligent materials that adapt their secondary structure according to their functional or environmental necessities. In this sense, with these composites we take advantage of this important characteristic of protein biopolymers, which in addition to the hydrophobic behavior put this new material in a superior level with respect to other natural fibers.

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