

POLYMER REINFORCEMENT

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Our technology uses a biopolymer called keratin as a filler to reinforce polymers thereby improving the thermal and structural properties. Our approach produces superior results compared to methods that use simple mixing. We have demonstrated our technology in the lab, primarily on poly(methyl methacrylate) (PMMA) but also with other polymers. See Attachment 1 for selected experimental results.

Our technology has the following benefits:

- Keratin is a natural hydrophobic biopolymer (as opposed to cellulose which is hydrophilic) and is thus better suited as a reinforcing agent for those applications where water entering the composite can lead to its degradation. Our experiments indicated that the measured contact angle of water with the keratin biofiber surface is around 90°.
- Keratin's well ordered structure gives it high tensile strength even before being added to a composite. Keratin essentially "heals" itself when subjected to a mechanical load due to structural rearrangements in the molecular chain.
- Keratin biofibers have a high aspect ratio (length / diameter) of approximately 350, supporting effective load transfer from the matrix to the fiber.
- The Young's modulus of the composite showed significant improvement of around 66% compared to pure cast-prepared PMMA.
- There were significant improvements in several mechanical characteristics of the keratin composites for various percentages of fiber (Table 1 in Attachment 1).
- A stress-strain curve obtained for keratin fibers demonstrates that they have a large yield zone, far beyond the linear zone (Figure 1 in Attachment 1).
- Even though the fracture surface is irregular, it does not have any voids produced by the pull out of fibers, which is a common problem with hydrophilic fibers (Figure 2 in Attachment 1).
- The keratin disperses homogeneously in the matrix (Figure 3 in Attachment 1).
- A differential scanning calorimetry (DSC) study showed that the glass transition temperature (T_g) increased with the biofiber content due to an increase in the rigidity at a molecular level caused by the polypeptide chains joining with the PMMA. For standard PMMA the T_g is 72 °C compared to 109 °C for the 5% biofiber composite (Table 2 in Attachment 1).
- A thermo-gravimetric analysis (TGA) of the reinforced PMMA showed a decomposition temperature above 300 °C, compared to approximately 175 °C for standard PMMA. This analysis also showed that the 30% weight loss temperature increased from 269 °C for standard PMMA to approximately 330 °C for the 5% biofiber composite (Figure 4 in Attachment 1).

- Keratin's dispersion properties are such that there is no need for chemical compatibilization between the fibers and the PMMA matrix. However, by grafting the polymer onto the keratin we were able to improve the mechanical and thermal behavior of the resulting composite.
- Keratin fibers are available from renewable sources. Currently, keratin from animal processing is largely viewed as waste. Productively using this waste is both environmentally friendly and a potential source of joint benefit with the animal processing industry.
- There should be minimal changes to current production techniques, involving some functionalization and preparation of both the filler and the matrix. We are in discussions with a company that is scaling up to produce keratin in bulk. The other materials that our process requires are available in bulk at relatively low prices.

Potential applications for keratin-reinforced composites include:

- Construction materials;
- Automotive applications;
- Insulation for electrical and acoustic uses; and
- Disposable plastic materials such as dishes, containers, etc.

The keratin biofiber itself can be used for:

- Membranes and filters to remove contaminants; and
- Ecologically friendly biopolymers for biomedical or other applications.

Essentially, this technology can be used in any application where improving polymer properties would be of value – either by improving existing materials or by reducing the amount of material required to match current physical capabilities.

Future developments include:

- Adapting the technology for different types of polymers;
- Biodegradable composites;
- Self-healing materials; and
- Potential use for electrical purposes. Many of the electrical and conductive properties of keratin have not been explored in detail but our work so far indicates some definite potential in this area.

Attachment 1 – Experiments Conducted to Validate Technology

The following are the key experiments conducted with keratin reinforced polymers:

- Composites were evaluated via stress-strain testing and dynamical-mechanical analysis (Table 1 and Figure 1 below).
- Tensile-induced damage was assessed using a series of tensile tests followed by optical and scanning electron microscopy studies (Figure 2 below).
- Grafted keratin samples were characterized by IR and Raman spectroscopy and by scanning electron microscopy (Figure 3 below).
- Thermal behavior was studied by using both differential scanning calorimetry and thermo-gravimetric analysis (Table 2 and Figure 4 below).
- Some earlier work was done with another polymer (Table 3 below).

Table 1: Mechanical properties of PMMA–keratin biofiber composites

Percentage of Biofiber by Weight (%)	Fiber Volume Fraction	Measured Young's Modulus (GPa)¹	Ultimate Tensile Strength (MPa)	Strain (mm/mm)
0	0.00000	5.05 (0.112)	29.68	0.0113
1	0.00950	5.50 (0.336)	29.33	0.0107
2	0.01900	5.66 (0.128)	28.85	0.0120
3	0.02850	5.97 (0.529)	34.82	0.0087
4	0.03800	6.17 (0.347)	31.72	0.0081
5	0.04758	6.50 (0.202)	27.89	0.0065

(1) The values in the brackets are the standard deviation of the corresponding measurement of Young's modulus

Figure 1: Stress-strain curve for keratin fiber - A to B is the linear region and B to C is the yield region

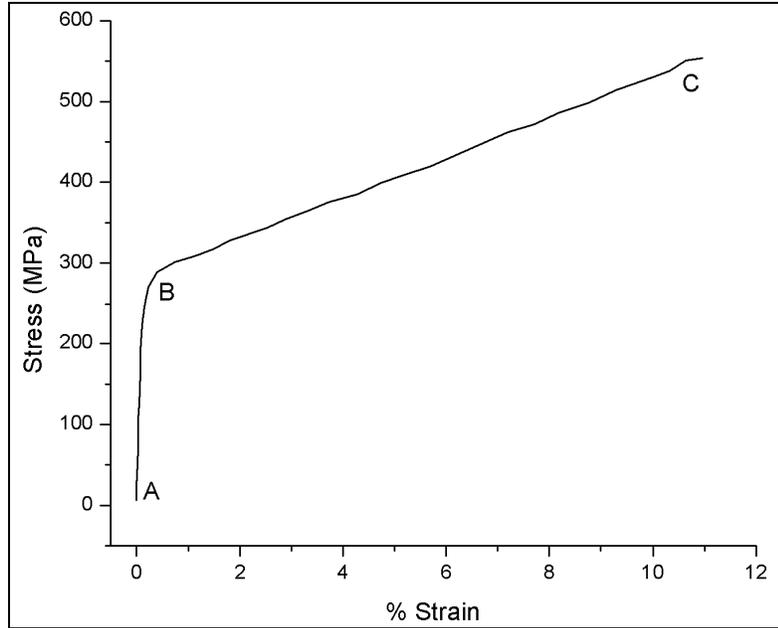


Figure 2: Scanning electron microscopy of fractured surfaces of PMMA-keratin biofiber composites

Good impregnation and wetting of the fibers is necessary to completely achieve the reinforcement potential of a fiber. This indicates that the chemical and/or physical bonds produced are sufficiently strong and will transfer the load between both fiber and the matrix. The images in “a” and “b” support this as they show a relatively even fiber distribution within the PMMA matrix, indicating good compatibility between these materials. Also, the fibers are well dispersed, without the characteristic bundles that result from using other types of fibers for reinforcement.

Images “c”, “d” and “e” show that although the fracture surface is irregular, it does not have any voids produced by the pull out of fibers, which is a common problem with hydrophilic fibers. Also, images “c” to “f” show that the keratin fibers are covered by the polymer which has adhered to the fiber surface.

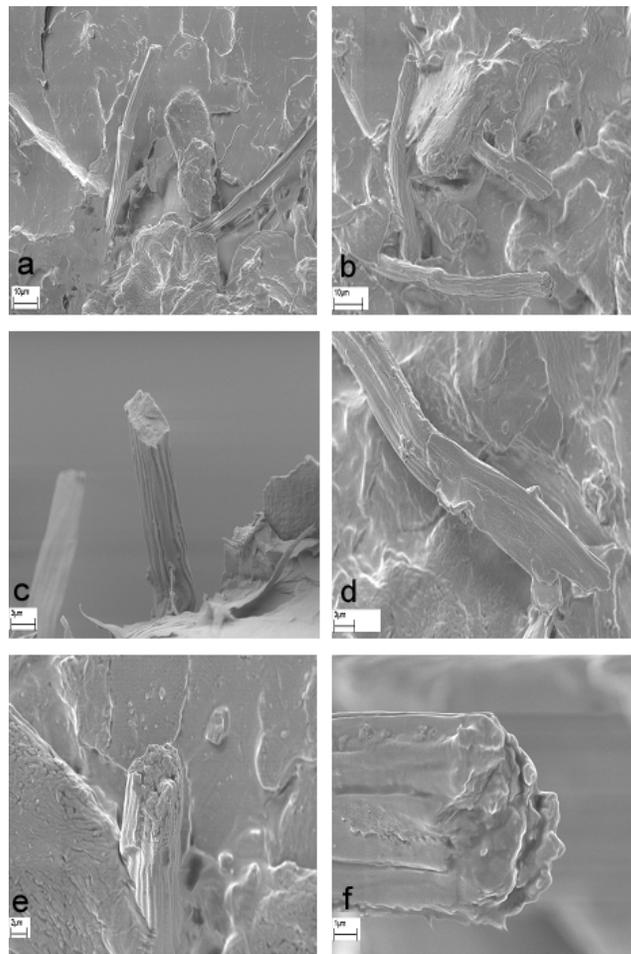


Figure 3: Scanning electron micrograph showing the keratin homogeneously dispersed within a nylon matrix

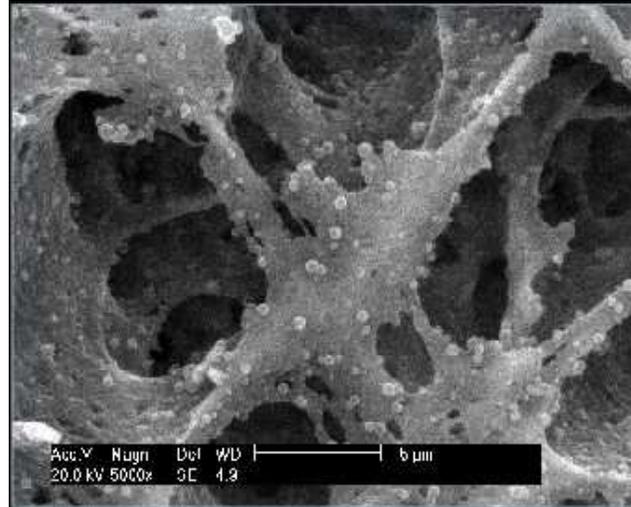
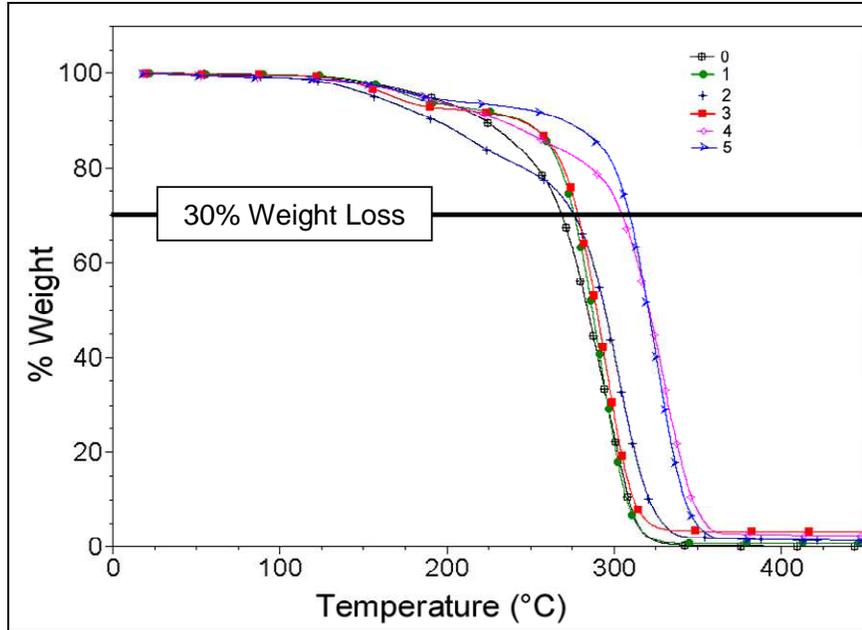


Table 2: Glass Transition Temperature for Keratin Biofiber - PMMA composites

Percentage of Biofiber (%)	Glass Transition Temperature (°C)
0	72
1	95
2	97
3	100
4	101
5	109

Figure 4: Thermo-Gravimetric Analysis Curves of Keratin Biofiber - PMMA composites from 0 % to 5 % weight of keratin biofiber



In the past, we did some experimentation adding keratin fibers to polypropylene (PP) using an earlier version of the technology. The following table shows the results achieved:

Table 3: Effect of keratin fiber in PP on Young's modulus

Percentage of Keratin Fiber (%)	Increase in Young's Modulus (%)
0	-
5	7.2
10	33.3
15	54.4
20	66.6

Note that this was achieved using recycled PP – we expect the results with new PP to be much better. PP is one of the cheapest polymers and the current approach is to use inexpensive fillers such as chopped wood. These can lead to technical problems such as degradation, sensitivity to microorganisms, etc.