

## Preparation and Characterization of Polyacrylic/Keratin Composites: Physico-Mechanical and Biological Properties

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**Abstract:** Keratin powder (KP) was prepared from waste substrates; namely coarse wool and feather through two consecutive processes: dissolution and precipitation. The said “KP” was mixed with pre-solubilized polyacrylic fibre waste. The obtained polyacrylic/keratin composites was regenerated and casted into film (AKF). The thermal and hygroscopic properties of the obtained AKF were assessed using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and moisture sorption test. The mechanical properties of the obtained films; namely tensile strength, elongation at break, and bending stiffness, were altered to different extent depending on the polyacrylic/keratin ratio in an inverse relationship. Topographical investigation of keratin powder, used in formation of AKF, was conducted using transmission electron microscopy (TEM).

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### 1. Introduction

In textile sector, there is an upsurge demand for using polymer composite materials. Synthetic polymers, such as poly acrylonitrile, constitute a major environmental dilemma due to their non-biodegradability, besides the fact that their production requires large amount of oil as raw material, which is mostly not renewable [1]. Gradually, composite materials replace the conventional ones, presumably due to their lightweight, high strength, design flexibility and long life. Rudimentary, there are five types of composite materials; namely fibre, particle, flake, laminar or layered and filled composites [2].

The discarding of keratinous waste materials; viz. fibre byproducts from the combing of wool, low quality coarse wool, horns, nails, feather, results in intricate ecological and economical aspects. Yamauchi *et al* underwent extraction of protein material from low quality wools followed by successive purification and regeneration [3].

Mixture of solubilizing agents was used for dissolution of keratin. One component is responsible for breaking of hydrogen bonds, and the other one is devoted to reductive or oxidative action of the disulphide bonds. Solvent systems that have been utilized are: urea/reducing agent [4], alkali metal hydroxide/swelling agent/reducing agent [5], carbamide/H<sub>2</sub>O<sub>2</sub> and carbamide/2-mercaptoethanol [4], or Cuprammonium complex system [6]. Xie *et al* tested ionic liquids, particularly 1-butyl-3-methyl imidazolium chloride (BMIM<sup>+</sup>Cl<sup>-</sup>), as a solvent for keratin proteins [7]. Two new chemicals-free processes utilizing only water and heat had been

suggested for dissolution of keratinous materials [8, 9].

Polyacrylic fibre is lightweight, lenient, and warm, with a wool-like appearance attributes. However, polyacrylic fibers suffer from some major drawbacks; namely low moisture absorbency, and accumulation of electrostatic charge, which diminishes its utility [10].

Solvents that can dissolve polyacrylic macromolecules were divided into two classes: the first type is polar organic liquids containing carbonyl group such as; N,N-dimethylformamide, N,N-dimethylacetamide, and N,N-dimethyl sulfoxide [11]. The second one consists of aqueous ionic media such as aqueous zinc chloride and sodium thiocyanate [12]. Recently, room temperature ionic liquids (RTILs) were utilized as solvents for polyacrylic polymer, and could be precipitated from the RTILs solutions by the addition of water [13].

The present study aims to develop a new method for reutilization of selected domestic and/or industrial waste materials; namely feather, waste of combing process of coarse Egyptian wool, and waste of polyacrylic fibres. Keratin powder was prepared from the said keratinous substrates followed by its doping with soluble polyacrylic polymer and finally casting into film. Thermal, mechanical and physical properties of the obtained AKF will be investigated. The proposed process meets some ecological and economical demands through converting invaluable polluting materials into product of promising functional properties

### 2. Experimental

## 2.1. Materials

Polyacrylic waste fibre was kindly supplied by acrylic blanket factory. Egyptian coarse wool fleece (main fibre diameter 34 micron) was bought from the local market. Feather was collected from the local poultry market.

## 2.2. Chemicals

Dimethyl formamide (DMF) was purchased from El-Nasr for Pharmaceuticals and chemicals Company, Cairo, Egypt. Hydrazine hydrate was provided by Merck, Steinheim, Germany. All the other chemicals are of laboratory grads.

## 2.3. Methods

### 2.3.1. Scouring

Scouring of the keratinous materials has been carried out using 1 g/l sodium carbonate at 60 °C for 30 min. The scoured keratin was thoroughly rinsed with running water until the pH of the washing water is 7. The material was finally air-dried at room temperature (ca. 30 °C). Scouring of the keratinous substance was conducted to remove the superficial fatty matters, which act as barrier for any subsequent wet processing. The scoured substrates were cut into small pieces to increase the surface area of the substrate, which facilitates its dissolution in the selected reagents.

### 2.3.2. Preparation of keratin powder

Coarse wool fleece (5 g) was dissolved in an aqueous medium of 8% NaOH, 6.5% thiourea, and 8% urea at 50 °C for 30 min, after that the solution filtrated and the obtained soluble keratin was precipitated in a coagulating bath of (12% NH<sub>4</sub>Cl and 6% sulphuric acid). The regenerated keratin was then ground in a ball milling machine (Retsch Ball Mills, Retsch GmbH, Haan, Germany; Machine Type PM 100, 220 – 220 V, 50/60 Hz, 1250 Watt, 12 A) at 500 rpm for 3hrs.

### 2.3.3. Dissolution of polyacrylic fibre

Different masses (5, 7, and 10 g) of polyacrylic fiber were dissolved with occasional shaking in 100 ml of pure DMF at 70 °C for 30 min.

### 2.3.4. Preparation of polyacrylic/keratin composite film

Different amounts of keratin [10-50 % based on the weight of polyacrylic component] on the weight of polyacrylic fiber were added to the dissolved polyacrylic. The composite was well homogenized for 30 min at room temperature. Then the composite was casted into film (approximate thickness 3 mm) and kept to dry overnight at room temperature. The formed films were then thoroughly washed and air dried.

## 2.4. Analyses and Testing

### 2.4.1. Transmission electron microscopy (TEM)

The morphology of selected samples of keratin powder was investigated using TEM (JEOL, JEM-

1230, Japan, with an acceleration voltage of 120 kV). The sample for TEM analysis was obtained by placing a drop of the colloid dispersion onto a carbon coated copper grid. The samples were dried at room temperature and examined using a TEM without further modification or coating.

### 2.4.2. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimeter (DSC) of the selected polyacrylic/keratin films was performed on NETZSCH DSC 204 under nitrogen flow. The samples were cut into snippets to obtain uniform heat transfer from one position to another. The film sample (5–10 mg weighed to 0.1 mg precision) is heated from 30 to 300°C at a heating rate of 10°C min<sup>-1</sup> and a nitrogen gas flow of 20 ml/min.

### 2.4.3. Thermogravimetric analysis (TGA)

From each sample of 4-5 mg were cut and used for thermo-gravimetric analysis experiments. A NETZSCH TGA 209 thermo-balance, air flow of 10.00 cm<sup>3</sup> min<sup>-1</sup> and aluminum oxide crucibles were used for thermo-gravimetric measurements. The temperature range was 20 to 700 °C, and the heating rates were 10 °C min<sup>-1</sup>.

### 2.4.4. Moisture sorption analysis

The sorption and desorption properties of keratin, acrylic, and polyacrylic/keratin composite were assessed by using IGA-sorp (manufactured by HIDEN ISO-CHEMA, UK). Before starting test, each sample was dried for 120 min until complete dryness. The working conditions were: relative humidity (RH) 1–95 % at 25 °C by (the rate of RH increment was 10 %) under nitrogen gas flow 250 ml min<sup>-1</sup>.

### 2.4.5. Tensile properties

In all mechanical properties of the obtained polyacrylic/keratin film; namely tensile strength and elongation at break, "Instron 5500R Universal Testing Machine" was used. This type of Instron has a self-calibration, zero adjusting and automatic balance, which are done daily before or during testing. This testing instrument is accompanied by a highly reliable system for evaluating the mechanical properties.

The bending modulus of the formed films was measured using Shirley stiffness test, according to ASTM method D – 1388.

### 2.4.6. Insect resistance

The resistance of native coarse wool as well as selected samples from the polyacrylic/keratin films to moth larvae attack was carried out according to AATCC Test Method 24-1977. At least four test specimens and four control specimens (1g each) were prepared, each test specimen and control specimen weighed. Ten larvae, in the weight range of 6 to 7 mg, are placed on the top of each specimen in a covered cage. The cages containing the test specimens and larvae were kept in an incubator for

14 days at  $27 \pm 1^\circ\text{C}$  and  $55 \pm 5\%$  relative humidity. The loss in weight was determined according to the following equation:

$$\text{Loss of weight} = \frac{W_1 - W_2}{W_1} \times 100$$

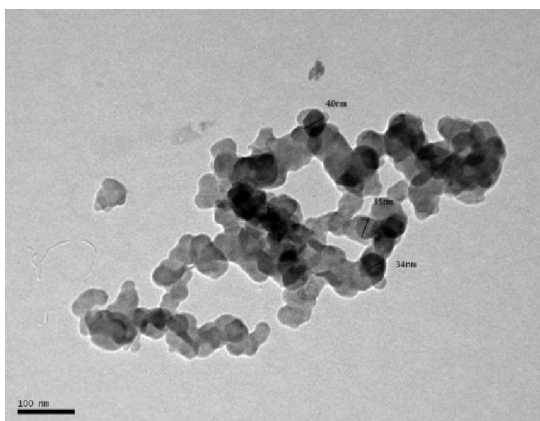
**Where:**  $W_1$  is the initial weight of the wool fabric, and  $W_2$  is the weight of wool fabric after insect exposure.

### 3. Results and Discussion

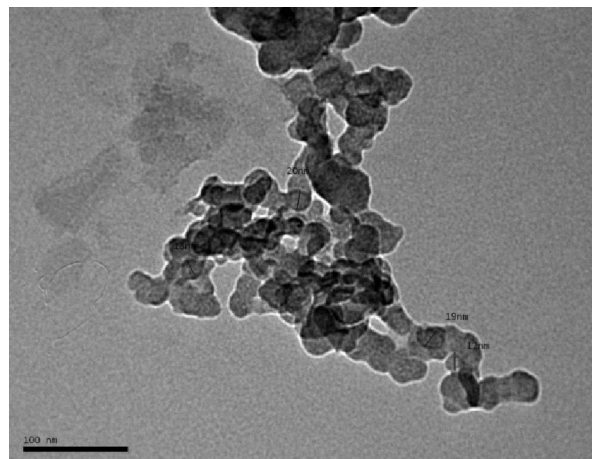
Polyacrylic fibre as well as keratin was dissolved, each separately, in its appropriate solvent. The soluble keratin was regenerated in a form of keratin powder, which was then dispersed inside the polyacrylic matrix. It is noteworthy to mention here that mixing of the soluble keratin and Polyacrylic fibre was impossible due to the difference in the dissolution medium. Wool and feather were dissolved in an aqueous medium, while Polyacrylic fibre was solubilized in aprotic solvent; namely DMF. Mixing of the two soluble polymers resulted in precipitation of Polyacrylic fibre. Consequently, it is more convenient to disperse keratin powder within the soluble Polyacrylic fibre medium rather than mixing the two soluble polymers before casting into film.

#### 3.1. Topographical study

Figures 1 and 2 show the Transmission Electron Micrographs (TEM) of keratin powder prepared from coarse wool and feather, respectively. These figures imply that the size of the obtained keratin powder is within the nano range (40-10 nm). The surface area of the used keratin, therefore, will be extremely high and assures its better dispersion within any composite prepared thereof.



**Fig. 1:** TEM of keratin powder prepared from Egyptian coarse wool



**Fig. 2:** TEM of keratin powder prepared from feather

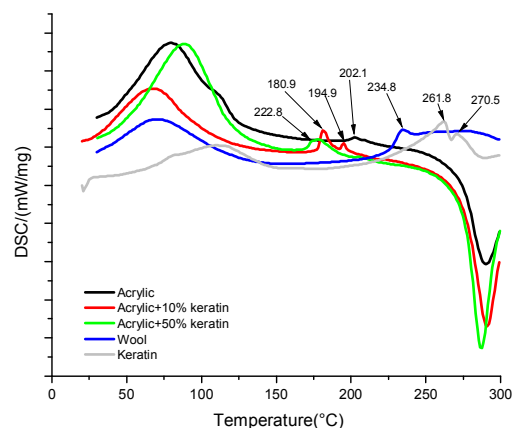
Thorough investigation of these figures reveals also that, adopting the same method of preparation, the average particle size of keratin powder derived from feather is smaller than that derived from Egyptian coarse wool

#### 3.2. Thermal properties

##### 3.2.1. Differential Scanning Calorimetry (DSC)

The DSC thermo grams of polyacrylic/keratin composite is not only give an indication of its thermal behavior, but also allot any probable chemical changes of constituents of the obtained films altering their relative thermal resistance.

Figure 3 shows the DSC analysis of polyacrylic film, native coarse wool as well as regenerated keratin thereof, polyacrylic/keratin (10 %), and polyacrylic/keratin (50 %).



**Fig. 3:** DSC of wool fibre, pure polyacrylic film, and AKF

Exhaustive investigation of figure 3 clarifies that the formation of polyacrylic/keratin composite resulted in significant decrease in the decomposition temperature (DT) of each macromolecules. The DT of coarse wool is  $234.8^\circ\text{C}$  and polyacrylic fibre is

202.1 °C. However polyacrylic/keratin (10 %) film has two DT values at 194.9 °C and 180.9 °C, and polyacrylic/keratin (50 %) film has DT value at 175 °C. The decrease in the DT value of the said films relative to its starting materials may be due to changing part of the crystalline structure of the starting polymers into amorphous regions; a hypothesis, which was supported by the enhanced dyeability.

### 3.2.2. Thermogravimetric analysis (TGA)

Figure 4 shows the TGA thermogram of native wool fibre, polyacrylic film, and polyacrylic/keratin composite films with 10 % and 50 % keratin content. The mathematical analysis of the thermogram of the said substrates (decomposition temperature, mass loss % and residual mass %) by TGA software were tabulated in Table 1.

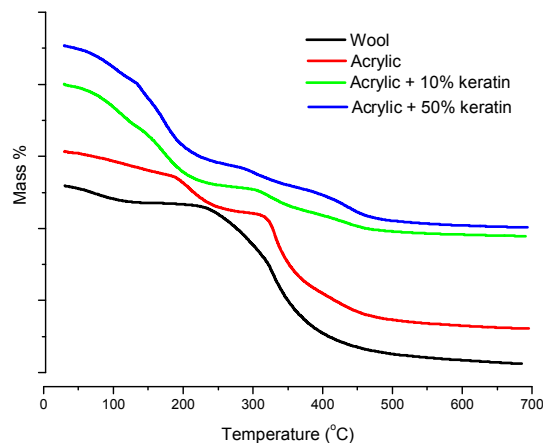
Results declared in figure 4 and Table 1 clarify the following:

- The TGA thermograms of all substrates exhibit a peak around 100 °C indicating loss in water. In case of raw wool fibres, the loss in weight amounts to 7.38 % due to the hygroscopic nature of wool. Surprisingly, polyacrylic film has similar result at 99 °C. This might be attributed to changing the crystalline region along the polymer matrix into amorphous one, which is more capable of retaining water therein. The loss in weight % is relatively high in case of AKF with keratin content 10 % and 50 % at 104.5 °C and 115 °C, respectively.
- Other peaks appear at 208 °C, 172.8 °C, and 173 °C in case of pure polyacrylic film, AKF with keratin content 10 % and 50 %, respectively. These peaks correspond to pyrolysis of short chain polymer in polyacrylonitrile and/or keratin macromolecules. It has been reported that a second stage (142 – 335 °C) is characterized by an endotherm of 0.42 kJ/g and a mass loss of 27.4% from the release of H<sub>2</sub>O, CH<sub>4</sub> and polyacrylic acid monomer [14].
- In all cases, a third stage at more than 320 °C, which is characterized by a mass loss of 70%, in case of wool fibres, 42 %, in case of pure polyacrylic film, and 24 % in case of AKF. The decrease in weight is owe to the decomposition of higher molecular weight species [15].

### 3.3. Moisture sorption analysis

The behavior of AKF with water vapour is of prime importance to a broad spectrum of applications. The moisture measurements are plotted in Figure 5. This figure illustrates that the moisture regain increased in the order: polyacrylic film < wool fibres < AKF with 10 % keratin content < AKF with 50 % keratin content. This result is in harmony of the findings of thermal

analyses. AKF has a higher ratio of amorphous regions relative to its starting materials.



**Fig. 4:** TGA thermogram of raw wool fibre, polyacrylic film, and polyacrylic/keratin films with different ratio

### 3.4. Mechanical and biological properties

The tensile strength, the elongation at break and bending modulus, as well as the resistance to moth larvae attack of AKF were assessed compared to the starting material. Results of this investigation, summarized in table II, reveal the following:

- The tensile strength of pure polyacrylic film is significantly lower than that of the native polyacrylic film. This can be attributed to transformation of most of the crystalline part of the polyacrylic polymer into amorphous regions as a result of its dissolution in DMF. Polyacrylic/keratin films, with any ratio, have lower strength than native polyacrylic or wool fibres as well as the polyacrylic film. As the ratio of keratin in the composite increases, the tensile strength decreases. Most of the inter- and intra-molecular bonds along the keratin macromolecules are supposed to be broken during dissolution step; consequently, the tensile strength of the film formed thereof will be reduced.
- The elongation at break of wool fibre is relatively high by virtue of its natural crimps [16]. Results of table II illustrate also that as the percent of keratin in the said composite increases, the elongation at break of the obtained film increases.
- No momentous change in the bending modulus was observed upon mixing polyacrylic polymer with keratin biopolymer. This finding emphasizes the hypothesis that no new crosslinks were formed upon blending the said two macromolecules. There is a direct



relationship between the film stiffness and the

degree of crosslinking therein [17].

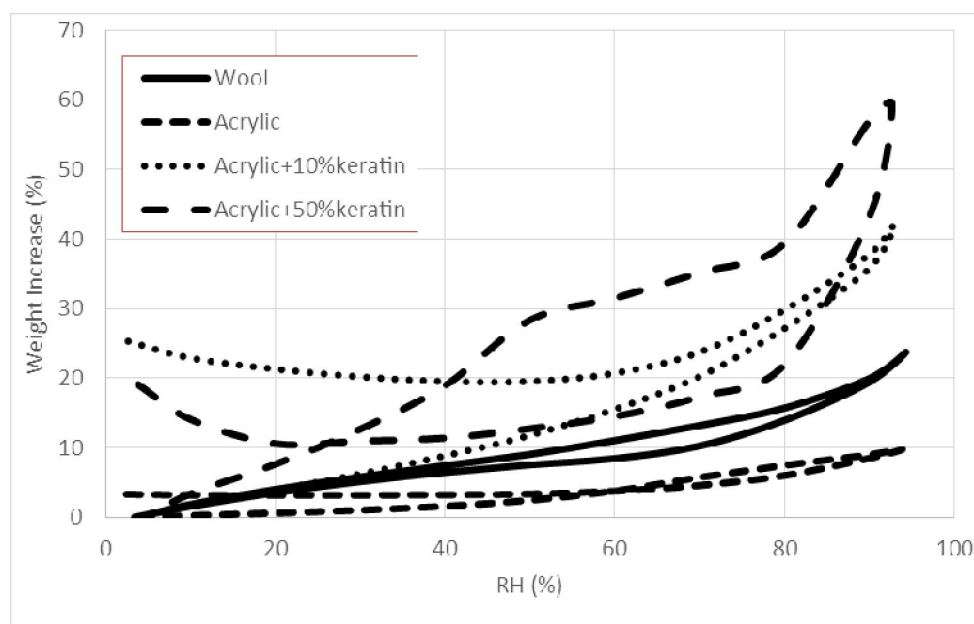
**Table I:** TGA data of raw wool fibre, polyacrylic film, and polyacrylic/keratin film with different ratio.

Sample	First stage		Second stage		Third stage		Residual mass %
	T <sub>d</sub> (°C)	Mass loss %	T <sub>d</sub> (°C)	Mass loss %	T <sub>d</sub> (°C)	Mass loss %	
Wool fibre	92	7.38	--	--	327.4	70.11	22.5
Polyacrylic film	99	7.5	208	14.87	329.4	42.5	35.13
AKF (10 % keratin)	104.5	13.5	171.8	29.7	373	23.8	26.5
AKF (50 % keratin)	115	16	173	33.3	357	24	29.2

- The resistance of any polymeric material to the attack of pests is of prime importance to assign its shelf-time and mode of care and storage. Keratinous substrates are the main targeted foodstuff to moth larvae [18, 19]. Results declared in table II demonstrate that mixing keratin with poly-acrylonitrile resulted in sharp enhancement in its resistance to moth larvae

attack. These findings is in harmony with the outcomes of the tensile strength measurements which leads to the hypothesis that there are no disulphide bonds in the keratinous part of the AKF, which are the palatable niches for the insect.

### Conclusion



**Figure 5:** Humidity measurement of raw wool fibre, pure polyacrylic film, and AKF

**Table II:** Tensile strength, elongation at break, bending modulus, and resistance to moth larvae attack, of selected polyacrylic/keratin films

Sample	Tensile strength (Kg/cm <sup>2</sup> ) <sup>a</sup>	Elongation at break (%) <sup>a</sup>	Bending modulus (N/m <sup>2</sup> ) <sup>a</sup>	Loss in weight (%) <sup>b</sup>
Native polyacrylic fibre	260.2	40.5	--	Nil
Native wool fibre	252.9	63.5	--	28.8
Pure polyacrylic film	213.1	44.5	3.4X10 <sup>8</sup>	Nil
Polyacrylic/keratin (10%)	193.2	54.5	4.13X10 <sup>8</sup>	Nil
Polyacrylic/keratin (20%)	166.8	55.5	5.9X10 <sup>8</sup>	Nil
Polyacrylic/keratin (30%)	152.7	59.6	6.6X10 <sup>8</sup>	4.1
Polyacrylic/keratin (40%)	138.9	61.0	8.5X10 <sup>8</sup>	4.5
Polyacrylic/keratin (50%)	132.0	66.2	9.5X10 <sup>8</sup>	5.6

a: the thickness of the tested film is 3 mm;

b: after 14 days of exposure to insect

Wastes or invaluable polyacrylic fibre and keratin were successfully solubilized and regenerated

into AKF using an economically and ecologically acceptable method. The nano-sized keratin powder

used in this study was used to impart new properties to PAN; viz. improved moisture regain, enhanced elongation at break, and boosted bending modulus. The new functional properties of the formed films, together with their thermal stability, make such films suitable candidates for various applications. Currently, further investigations in our laboratory are conducted to utilize AKF in removal of dyes and heavy metal ions from some industrial effluents including textile mills.

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