

Enhancing the Long-term Durability of Historical Wool Textiles Using Water Dispersed Nano Polymers

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Abstract: Polymers are common used in conservation of museum textiles. This study aims to evaluate some selected nano polymers in conservation of museum wool textiles. Nano polymers used in this study are microemulsion polymers prepared from Methyl methacrylate (MMA) and Hydroxy ethyl methacrylate (HEMA) monomers using Eco-friendly initiation system represented as ultrasonic mechanism. Wool textile samples were treated with different types of prepared nano polymers, to evaluate the long-term effect of these polymers on the physical and chemical properties of these materials. Two different types of accelerated ageing methods, heat and light were used in this evaluation. The change of the physical and chemical properties of the untreated and treated wool textiles after ageing was assessed by different methods. The results showed that all selected polymers improve the long-term durability of treated wool samples. However the results show that both treated and untreated wool samples became progressively darker and showed progressive losses in tensile strength after ageing by different methods. The results of this study will assist a conservator who seeks information about nano polymers suggested to be used in conservation of wool textiles.

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1. Introduction:

The fragility of certain deteriorated textiles has caused particular conservation problems, and a wide variety of polymers have been used in an attempt enhance their long-term preservation. Polymers can be used as consolidating materials or adhesives in conservation of deteriorated textiles [1-8]. Depending upon conservation needs, polymeric material should be characterised by physicochemical properties suitable for binding damaged fibres and yarns, imparting physical strength to the artefact or improving the adhesion between the artefact and a support fabric. The ideal properties should be flexibility, transparency, adhesion, cohesion, lack of colour, long-term durability, reversibility, possibility of reactivation for adhesives, ease and rapid application with no risks for the operators [9].

The most polymers widely used for textile conservation purposes are water dispersed polymers composed of ethylacrylate-co-methylmethacrylate polymers [1, 2&9]. Miniemulsion polymer having smaller particle size than emulsion polymer could be prepared using ultrasonic irradiation in presence of little amount of chemical initiation materials [10-12]. The extended of this work, microemulsion polymerization can be used to prepare nanosized particle by the application of ultrasonic. Newly in a previous study new nano polymers were produced

from methylmethacrylate to be used in textile conservation. These nano polymers are Microemulsion copolymers prepared from MMA and MMA/HEMA (having different monomers composition ratios) using Eco-friendly initiation system represented as ultrasonic mechanism [13].

When considering the use of a new polymer for the conservation of textile objects, several important factors must be addressed: will the treatment improve the physical, chemical or appearance properties of the object; and, if so, will the enhanced properties remain stable long enough so that the "useful lifetime" of the object will be substantially prolonged [14]. Accelerated tests are designed to find materials which can be safe for long-term use and would not cause degradation of treated artefacts [15]. Accelerated light ageing is often used in evaluating the durability of materials used in conservation of artefacts [2, 14, 16 & 17]. The samples are exposed continuously to artificial light. In real museum conditions, lights are not on continuously and are at lower intensity. Based on a typical museum exposure of 3000 h per year (six days a week, 10 h a day), five years of continuous exposure to fluorescent lights at 700-800 lx is equivalent to about 200 years in a museum at 50 lx [17]. It was confirmed that 500 h of continuous exposure to artificial daylight is equivalent to about

100 years in a museum at 150 lx [18]. Feller presented a rough estimation of possible testing times for different classes of thermal stability based on the crude approximation that the rate of deterioration will double for a rise of 10 °C and on the statement that heating paper for 72 h (3 days) at 100 °C is equivalent to about 25 years of ageing under normal condition ageing. He also showed that heating paper for 36 h (3 days) at 140 °C is equivalent to about 100 years of ageing under normal conditions [19].

This paper aims to evaluate the use of new types of water dispersed nano polymers for enhancing the physical and chemical properties of museum wool textiles. Accelerated ageing techniques were used to predict the change in the properties of wool textiles with time under defined exposure conditions. The results of the ageing experiments can then be used by the conservator in defining a “useful lifetime” for treated wool textiles. Consideration must be given, in assessing the long-term durability of the treated wool textiles, to the environmental conditions that would be encountered in the display or storage of wool textile artefacts. Accelerated thermal and light ageing were carried out to determine the long term effect of selected polymers on the properties of wool textiles.

2. Experimental

Fabric

Scoured, plain wool textile fabric was used (from WOOLTEX manufactory, Egypt).

Chemicals

Methyl methacrylate (MMA) and Hydroxy ethyl methacrylate (HEMA) monomers were supplied by Merck-Schuchardt, Germany and redistilled before use. The purified monomer was sealed and stored below 4 °C until further use. Sodium lauryl sulphate (SLS) was product of the BDH, Australia. Distilled water was used as the polymerization medium.

Polymerization procedure

The polymerization reactions were carried out with a total sample volume of 100 ml, Specific amount of purified monomers (MMA & HEMA) (8gm), surfactant (SLS) (2 gm) and desired amount of distilled water (to complete the reaction volume 100ml), were introduced into the reaction vessel conducted with circulated water to maintain the desired temperature. Then the ultrasonic generator (Branson Sonifier S-450 A, USA) was switched on and the reaction was subjected to ultrasonic irradiation. After a certain time of the reaction, ultrasonic irradiation was stopped. The power input

was adjusted to be 0.1 W/ml. The produced polymers used in this work are listed in Table 1.

Table (1): Recipe of micro emulsion polymerization of different composition ratios MMA/HEMA at constant concentration of emulsifier 2 gm /l and ultrasonic irradiation

Sample code	Feed monomer composition ratio (%)	Average particle diameter D_v (nm)
Polymer I	MMA (100)	68
Copolymer II	MMA/HEMA (93.75/6.25)	88
Copolymer III	MMA/HEMA (87.5/12.5)	118
Copolymer IV	MMA/HEMA (81.75/18.25)	129
Copolymer V	MMA/HEMA (75/25)	140

Preparation of samples

Wool textile fabric samples were cut into 12x2 cm (length x width) warp test specimens. The warp strips were produced by raveling away yarns on each side forming 1.5 cm wide strips with a 2.5 mm fringe down each side. Five samples were used for each test.

Treatments

Wool textile samples were treated with the selected polymers in 6% concentration according to the standard method.

Accelerated aging types

Thermal aging

The treated and untreated (control) wool textile samples were artificially thermally aged at 140 °C in precision forced convection oven for 144 h according to Abdel-Kareem. [2].

Light aging

For ageing by exposure to light, tests were carried out according to international standard tests for colour fastness (ISO 105-B02:1994) [20]. The treated and untreated wool samples were mounted in standard specimen holders and were exposed to light irradiation for 200 h. Irradiation of the samples was carried out using Atlas Light Fastness Tester. Type of Atlas Fade-Ometer used in this study is XENOTEST®150S⁺. A light filter was used to simulate light in museums. Exposure conditions were 50°C and 55% of RH.

Testing and analysis

Colour differences were measured on Optimach 3100 colour spectrophotometer using the CIELab colour system. The CIELab colour

coordinates for L, a, and b values were recorded. Five colour readings were made and averaged for each sample. Colour changes are the differences between aged and untreated unaged wool sample are expressed as ΔL , Δa , and Δb . Calculation of total colour change (ΔE) was achieved by the use of the following equations: $\Delta E = [(\Delta L)^2 + \Delta a^2 + (\Delta b)^2]^{0.5}$. Tensile strength and elongation of the treated and untreated wool samples before and after ageing by different methods were measured using a Tensile Testing Machine Type Zwick 1445. These tests were done according to ASTM (2000) D 5035-95 [21]. The initial jaw spacing was 50 mm and the test speed was 25 mm/min, temperature was 23 °C, and R.H. 65%. FTIR spectroscopy was carried out using Nicolet 380, Thermo FTIR spectrophotometer. The surface morphology of treated and untreated samples before and after aging was investigated by scanning electron microscope. Very small pieces of wool samples were attached to a metal stub and coated with gold layer of about 200Å^o thick. Then the coated samples were examined A JSM-400 scanning electron microscope. The Thermogravimetric analysis (TGA) for the wool samples were carried out at a temperature range starting from 50°C to 700°C under nitrogen atmosphere with heating rate of 10°C/min using Shimadzu TGA-50 Japan. X-ray diffraction analysis (XRD) of the treated and untreated wool samples before and after ageing by different methods was

carried out on a Philips X-ray diffractometer, type PW 1840, giving 40 kV Cu Ka radiation at 25 mA.

3. Results and Discussion:

Colour differences

The results of colour changes in both untreated and treated wool samples before and after the ageing by different methods are shown in Tables (2-6). The results in Table 2 confirm that there are no noticeable changes in the colour of wool textile samples after the treatment by all tested polymers before the ageing. The results in Tables (3-6) show that there are noticeable changes in both treated and untreated samples after ageing by light and heat. However the results confirm that there are no noticeable differences between the colour changes in the wool samples treated with polymers numbers I, II, III and untreated wool samples after the ageing by light. In the same time by comparing all obtained data it is clear that there is more decrease in the colour changes in the wool samples treated with polymers numbers IV, V than those treated with polymers (I, II, III) and untreated samples after light ageing. These results indicate that all tested polymers do not cause any increase in the color change of the treated samples after ageing by different methods. But polymers IV, V decreased the colour changes in the treated samples by light. This means that the polymers IV, V improve the durability of wool textiles against the deterioration by light.

Table 2: The changes in the colour values for the control wool samples after treated with the selected polymers before any ageing

Polymer	Colour values			Changes in the colour			
	L	A	B	ΔL	Δa	Δb	ΔE
0	83.92	-1.37	11	0	0	0	0.00
I	83.12	-1.55	10.36	-0.8	-0.18	-0.64	1.04
II	83.19	-1.56	11.07	-0.73	-0.19	0.07	0.76
III	82.6	-1.59	10.99	-1.32	-0.22	-0.01	1.34
IV	82.26	-1.63	10.99	-1.66	-0.26	-0.01	1.68
V	83.02	-1.7	10.78	-0.9	-0.33	-0.22	0.98

Table 3: The colour values for the wool samples before and after light ageing

Polymer	Before			After		
	L	A	b	L	a	B
0	83.92	-1.37	11	81.61	-2.47	22.93
I	83.12	-1.55	10.36	80.75	-2.72	20.14
II	83.19	-1.56	11.07	80.26	-2.4	20.24
III	82.6	-1.59	10.99	81.37	-2.21	24.12
IV	82.26	-1.63	10.99	79.67	-2.56	16.37
V	83.02	-1.7	10.78	78.94	-2.45	14.74

Table 4: the changes in the colour values for the wool samples after light ageing

Polymer	ΔL	Δa	Δb	ΔE
0	-2.31	-1.1	11.93	12.20
I	-2.37	-1.17	9.78	10.13
II	-2.93	-0.84	9.17	9.66
III	-1.23	-0.62	13.13	13.20
IV	-2.59	-0.93	5.38	6.04
V	-4.08	-0.75	3.96	5.74

Table 5: The colour values for the wool samples before and after heat ageing

Polymer	Before			After		
	L	A	B	L	A	B
0	83.92	-1.37	11	79.61	-0.51	0.99
I	83.12	-1.55	10.36	77.85	-0.87	21.82
II	83.19	-1.56	11.07	79.28	-1.54	20.88
III	82.6	-1.59	10.99	78.26	-1.49	21.83
IV	82.26	-1.63	10.99	79.39	-1.46	23.34
V	83.02	-1.7	10.78	79.86	-2.14	21.52

Table 6: the changes in the colour values for the wool samples after heat ageing

Polymer	ΔL	Δa	Δb	ΔE
0	-4.31	0.86	-10.01	10.93
I	-5.27	0.68	11.46	12.63
II	-3.91	0.02	9.81	10.56
III	-4.34	0.1	10.84	11.68
IV	-2.87	0.17	12.35	12.68
V	-3.16	-0.44	10.74	11.20

Tensile strength and Elongation

The results of changes in the tensile strength and elongation of wool samples after the treatment by tested nanopolymers in Figure (1) show that all tested polymers increase the tensile strength of wool samples after treatment by most of all tested polymers. These results show that most of all tested polymers improve the strength of wool samples. The results show that the percent of the increase in the tensile strength depends on type of the polymer. It is clear that the relationship between the percent of the improvement in tensile strength and the percent of HEMA in the nanopolymeric copolymers is an inverse relationship. But in the same time the results show that relationship between the percent of the improvement in elongation and percent of HEMA in the nanopolymeric copolymers is a direct relationship. It is clear that the samples treated with polymer I became more rigid as the elongation of the sample is decreased. While the samples treated with polymer V became more elastic as the elongation of the sample is increased. By comparing the results of both the tensile strength and elongation of all treated samples before any ageing it is clear that the most effective polymer among all tested polymer is

suitable for conservation of wool is polymer V. While the least polymer (among all tested polymers) suitable for conservation of wool is polymer I.

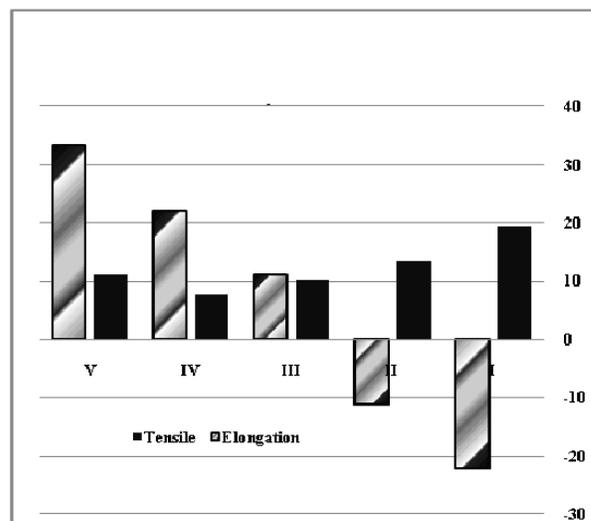


Figure (1): The changes in tensile strength and elongation of wool samples after the treatment with polymers

The results in Figure 2 show the loss % in tensile strength of both treated and untreated wool aged by heat and light. The results show that the loss % in tensile strength of both treated and untreated wool aged by light are more than the loss % in tensile strength of these samples aged by heat. This means that the light ageing is more dangerous on untreated and treated wool samples than heat ageing. The results show that the loss % in tensile strength of wool samples treated by polymer V is too little compared with the loss % in tensile strength of untreated wool samples and wool samples treated with all other tested polymers. This result indicates that polymer V is the best polymer among all tested polymers and can be used in conservation of wool on the long term.

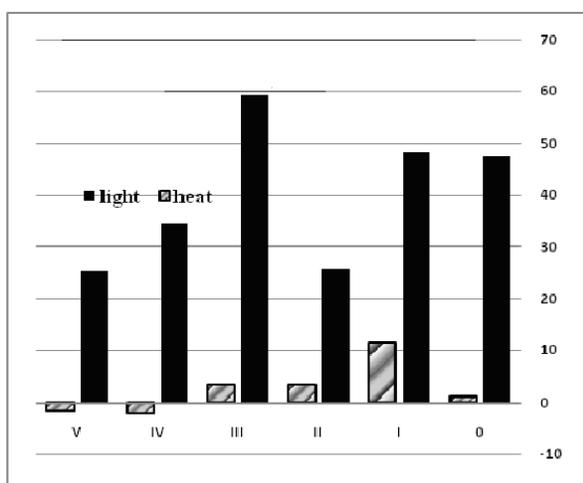


Figure (2): The loss % in tensile strength of untreated and treated wool samples after the aging.

FTIR spectroscopy

Figures (3&4) show the FTIR-ATR spectrum for both untreated wool and wool fabric treated with nanopolymeric copolymer V respectively. The two spectrums consist of many broad bands that are characteristic for the wool functional groups. Bands at 3262, 3060 and 2922 cm^{-1} are attributed to the O-H, N-H and C-H stretching modes, respectively. Moreover, major absorption bands at 1626 cm^{-1} for amide I, 1510 cm^{-1} for amide II and 1229 cm^{-1} for amide III are also observed in the spectrum. The band at 1446 cm^{-1} is caused by the C-H deformation of CH_2 and CH_3 bending modes. On the other hand, the presence of new characteristic band at 1730 cm^{-1} , is related to C=O groups of acrylate ester, in the spectrum of figure 4 (pre-treated wool sample) confirms the presence of the nano-sized copolymer in the structure of the wool fabric [13].

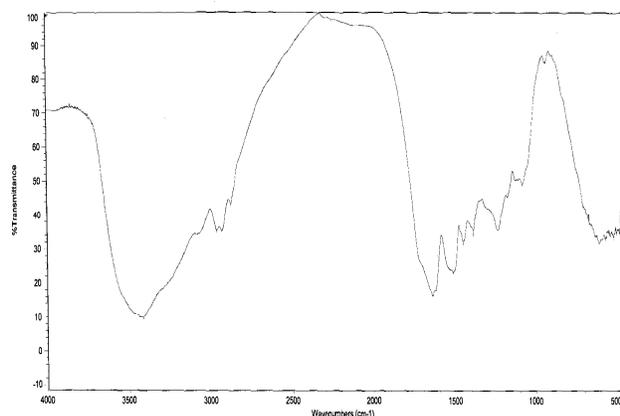


Figure (3): FTIR of untreated wool fabric

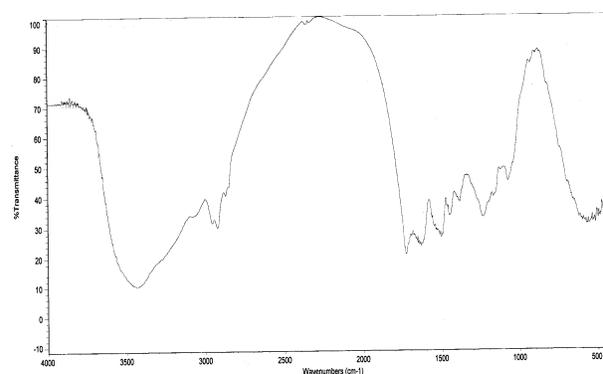
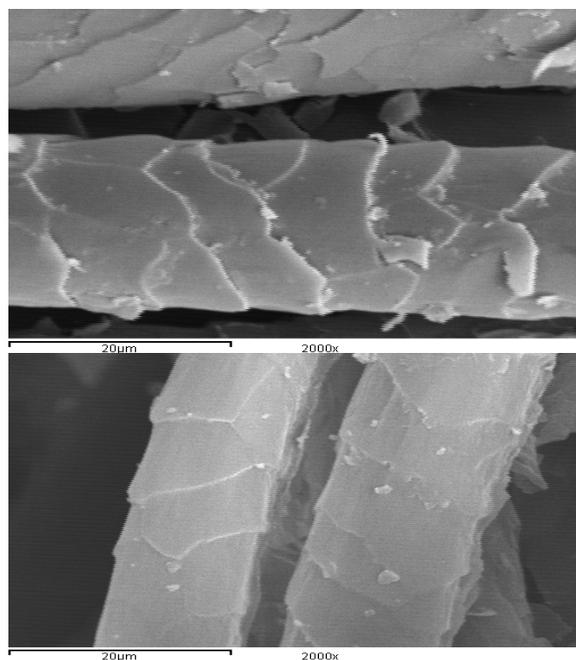


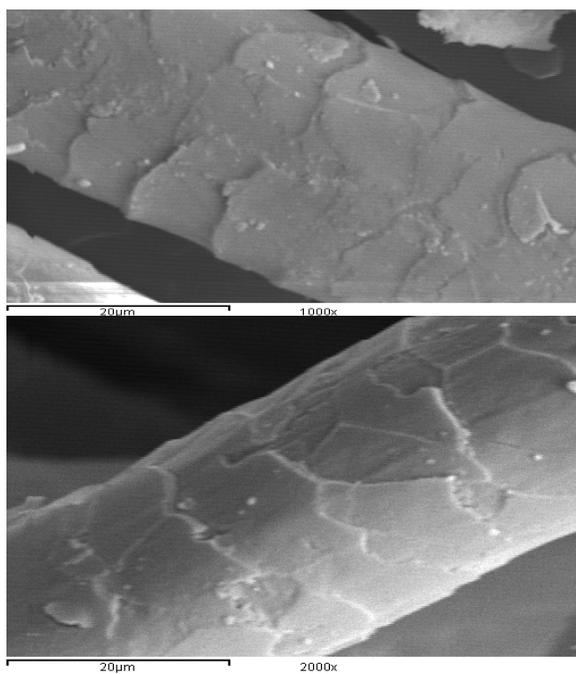
Figure (4): FTIR of treated wool fabric with nanopolymeric material (Copolymer III)

SEM investigation

The results of S.E.M. observation showed that all tested polymers do not cause noticeable changes in the morphology of the treated wool samples. It is clear that the surface morphology that is characteristic of wool fibers is too clear. These results indicate that the coating layer of all tested polymers on the wool surface is too thin and do not disappear the surface of wool. The results of SEM investigation show that the changes in surface morphology of wool samples treated with all tested polymers are less than the changes in the surface morphology of untreated wool samples after aging by both of heat and light. These results confirm that all tested polymers enhance the durability of surface morphology of wool against the light deterioration. However the results show that enhancing the long-term durability of wool depends on the used polymer. For example by comparing the results in Figures (5-7) it is clear that among all tested polymers the most polymers is polymer V while the least polymer is polymer I that can reduce the effect of light ageing on wool samples.



Figur (5): SEM images of untreated wool sample before and after light ageing, the uper is before ageing and the lower is after ageing



Figur (6): SEM images of wool sample treated with polymer I before and after light ageing, the uper is before ageing and the lower is after ageing

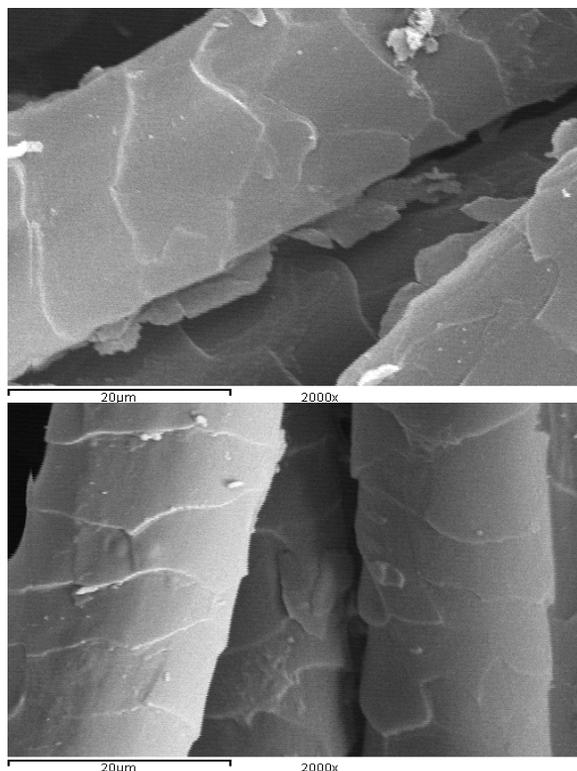


Figure (7): SEM images of wool sample treated with polymer V before and after light ageing, the upper is before ageing and the lower is after ageing

Thermogravimetric analysis

In this study the thermo-gravimetric analysis (TG) and derivative thermo-gravimetry (DTG) was carried out for three selected samples namely, (a) wool fabric treated with polymer V; (b) wool fabric treated with polymer V and deteriorated with light as well as (c) wool fabric treated with polymer III and deteriorated with heat. TG curves for the studied samples are shown in Figure (8). As it evident, regardless of wool sample type, the spectrum shows two characteristic stages for decomposition. The first stage starts at $35 \pm 5^\circ\text{C}$ and end at $91 \pm 5^\circ\text{C}$ with weight loss of $8 \pm 0.3\%$. This could be attributed to the moisture content of the untreated and treated wool fabrics. This observation is in accordance with other related work [22]. The second stage related to the main decomposition of wool macromolecules occurs in one step of decomposition. For wool sample pretreated with the nanopolymeric copolymer (sample a), the main decomposition starts at 238°C and end at 343°C with maximum decomposition temperature of 303°C and weight loss of 43%. On the other hand, for deteriorated pretreated wool fabrics by light and heat the main decomposition starts at $246 \pm 1^\circ\text{C}$ and end at $315 \pm 2^\circ\text{C}$ with weight loss of 52 & 59 % respectively. The remaining residue at 500°C was found to be 43; 52 & 59% for the three

studied samples (a); (b) and (c) respectively. These findings demonstrate the role of the pretreated nanopolymeric material with a film forming covering the wool thread to reduce the degradation process.

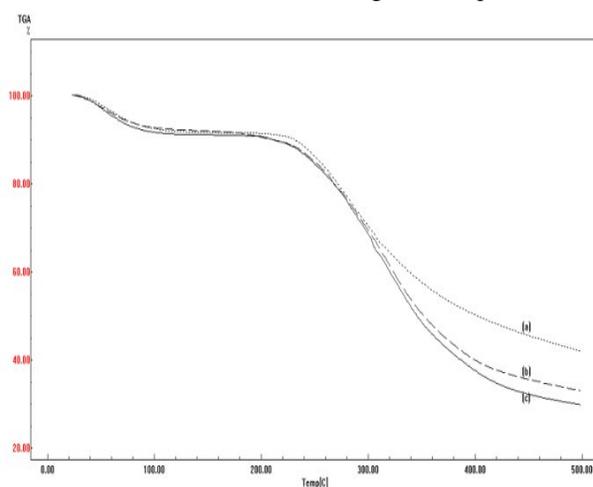


Figure (8): TG curves of wool samples treated with polymer III after ageing by different methods, (a) unaged sample, (b) sample aged by light, (c) sample aged by heat

XRD Results

The results of XRD show that the peak that indicates the polymer is too small in all treated samples. This result confirms that the coating layer of the polymer is too little. Also the results show that there are no noticeable differences in the amorphous areas in the wool fabrics before and after the treatment with all tested polymers (see Figures 9, 10). This indicates that the wool textile samples are still elastic after the treatment with the tested polymers. Also the results show that there is no change in XRD pattern of untreated and treated wool samples after the ageing by different methods.

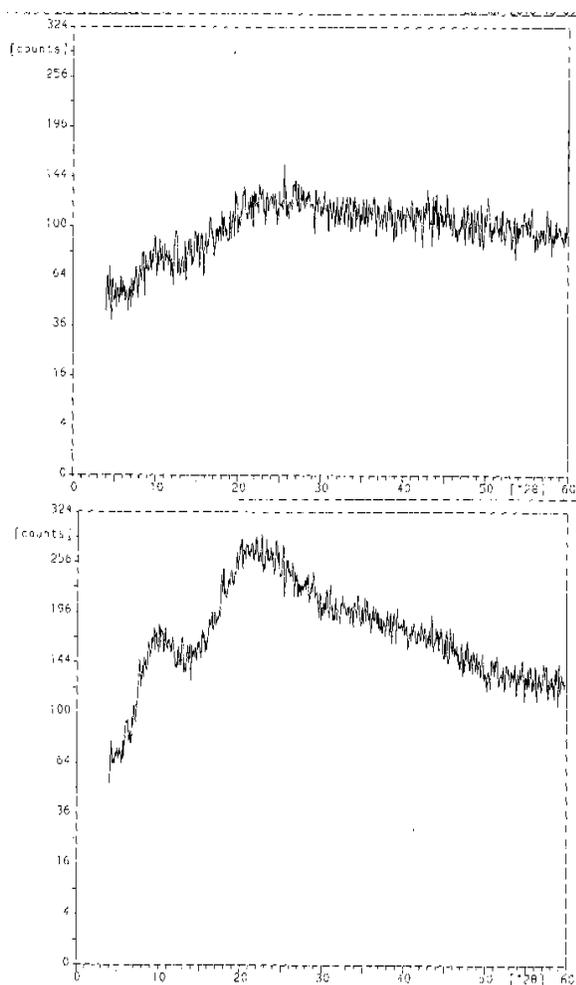


Figure (9): XRD pattern of untreated wool sample before and after light ageing, the upper is before ageing and the lower is after ageing

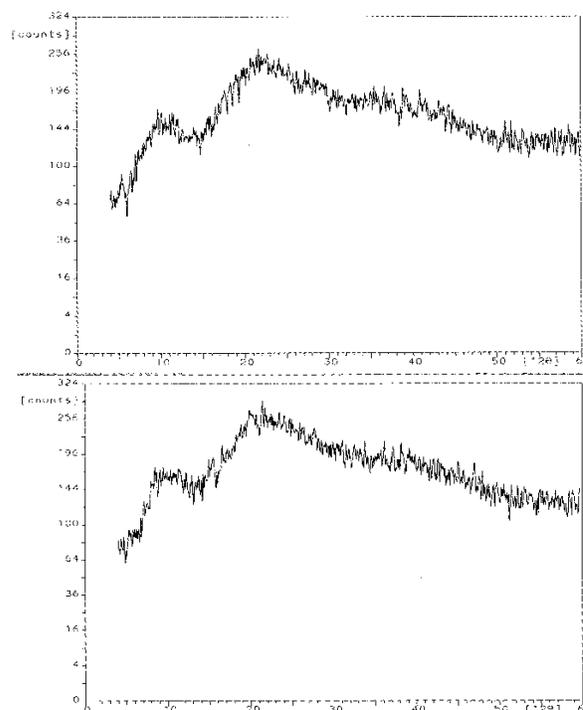


Figure (10): XRD pattern of wool sample treated with polymer V before and after light ageing, the upper is before ageing and the lower is after ageing

4. Conclusions:

All tested polymers were found to increase the strength of wool textiles. The elongation of the treated wool samples change according to percent of HEMA in the used copolymer. Polymer III is the most polymers among all the tested polymers that enhance the elongation of wool textiles. According to the results of the accelerated ageing techniques that are useful for detection if either the conservation materials adversely affected the normal degradation property rates of textile or the conservation materials act as a barrier to reduce the degradation rate. All tested polymers especially polymer III enhance the long-term preservation of wool textile. But there is not any polymer can completely prevent the deterioration.

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