



## Colour Interceptions, Thermal Stability and Surface Morphology of Polyester Metal Complexes

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### Abstract

Chelating copolymers via grafting of acrylic acid (AAc) and acrylamide (AAm/AAc) comonomer mixture onto polyester microfiber fabrics (PETMF) using  $\gamma$ -radiation technique were prepared. The prepared graft chains (PETMF-g-AAc) and (PETMF-g-PAAc/PAAm) acted as chelating sites for some selected transition metal ions. The prepared graft copolymers and their metal complexes were characterized using thermogravimetric analysis (TGA), colour parameters and surface morphology measurements. The colour interception and strength measurements showed that the metal complexation is homogenously distributed. The results showed that the thermal stability of PETMF was improved after graft copolymerization and metal complexes. Moreover, the degree of grafting enhanced the thermal stability values of the grafted and complexed copolymers up to 25% of magnitude, on the other hand the activation energy of the grafted-copolymer with acrylic acid increased up to 80%. The SEM observation gives further supports to the homogenous distribution of grafting and metal complexation.

**Key words:** Radiation grafting, Acrylic acid, Acrylamide, Polyester, Polymer-metal complex.



## INTRODUCTION

High temperature polymers find extensive applications as matrix materials for rigid and lightweight fiber-reinforced structural composites, electrical insulations, etc. Aromatic polyesters are the main examples of this category. They show excellent thermal and oxidative stability.

Graft copolymerization of binary mixtures of vinyl monomers having different functional groups onto natural and synthetic polymers is of special importance with respect to grafting of individual monomers<sup>1-5</sup>. This is because grafting of monomer mixtures has the advantage of introducing different types of polymer moieties with different properties. In grafting of individual monomers, it is easy to control the process by controlling the factors affecting the graft yield. On the other hand, in the case of binary mixtures grafting, the graft yield of each monomer should also be controlled.

Polymer-metal complexes are expected to present a specific structure, in which central metal ions are surrounded by an enormous polymer chains. Based on this polymeric ligand, the polymer-metal complex shows interesting and important characteristics, especially catalytic activities, which is different from the corresponding ordinary metal complex of low molecular weight<sup>6-11</sup>. A study on the metal complex formation through radiation-induced graft copolymerization of acrylic acid onto poly (tetrafluoroethylene-perfluorovinyl ether) films was reported<sup>12</sup>. It was possible to determine the polymer-metal complexes for various applications as semiconductors beside their performances as cation-exchange membranes. Special cases of much interest are polymers containing metallic ions (either as a dopant or as complexes). These attracted the attention of researchers for a variety of reasons<sup>13-18</sup>. The catalytic properties of schiff base complexes of transition metal ions in a variety of organic reactions are known for a long time. However, when the metal ions were complexed with functional polymers the activity of the metal polychelates changes due to polymeric effect<sup>19</sup>. The organometallic polymers with different functional groups are found to exhibit good electrical conductivity<sup>20</sup>. The autooxidation of catalysts bound to polymer colloids has also been reported. The incorporation of metal ions in polymers not only affects its physical characteristics, like its strength, but also their chemical activity<sup>21</sup>. Recently, it is of interest to propose systematic methods to investigate the metal complex formation via radiation-induced graft copolymerization of vinyl monomers onto polyester micro-fiber materials.

In this respect, the present work deals with the radiation grafting of vinyl monomer onto polyester microfiber fabrics and metal complex formation by reaction of the grafted copolymers with some transition metals. In addition, characterization of the prepared copolymers and their metal complexes were studied. Also, the distribution of the different metals across the complexes was investigated by a colorimetric procedure.

## EXPERIMENTAL

### Materials

Polyester microfiber fabrics used throughout this work was kindly supplied by Trevira Gmbh & Co KG, Germany. The fabric was scoured, bleached and was not



subjected to any further finishing processes. The monomers of purity 98% were acrylic acid (Backer Chemical Co., England) and acrylamide (BDH Chemical Ltd., England). Copper acetate, cobalt acetate, nickel acetate and iron chloride (Sigma, USA) and methyl alcohol (Prolabo, France), were also used.

### Graft copolymerization

The polyester graft copolymers with individual or comonomer mixtures of vinyl monomers were prepared by using the direct method of radiation grafting. Strips of polyester fabrics of known weight were immersed in the different grafting solutions in glass - quick - fit tubes. The grafting solutions were composed of the individual vinyl monomer or comonomer mixtures at different ratios dissolved in the appropriate solvent composition. Ferric chloride salt at certain concentration (2%) was added to the grafting solution to minimize homopolymer formation. The reactants in the glass tube were then subjected to gamma irradiation. Irradiation to the required dose was carried out using cobalt-60  $\gamma$ -source at a dose rate of 7.75 kGy/h. The grafted samples were thoroughly washed with hot distilled water to remove unreacted monomers and surface homopolymer and air dried. Afterward, the grafted samples were extracted in reflux system using water as a solvent to reach a constant weight. The graft yield (in the case of individual monomer) or total graft yield (in case of comonomer mixtures) was determined by the percentage increase in weight as follows:

$$\text{Graft yield or total graft yield (\%)} = [(w_g - w_o) / w_o] \times 100$$

Where  $w_o$  and  $w_g$  represent the weights of the initial and grafted substrate, respectively.

### Synthesis of graft copolymer-metal complexes

The different graft copolymer-metal complexes of PET microfiber- grafted fabrics were prepared by refluxing with aqueous bath containing 3% metal salt (based on distilled water) from different metal salts under investigation.

#### 2.4. Colour distribution of metal complexes

The colour of the metal complexes of PETMF grafted fabrics was measured using a microcolour unit manufactured by Dr. Lang (Germany). The X, Y, Z system used throughout this work is based on the CIE-colour triangle (Commission International de E'claire units X, Y, Z). This system was applied to measure and specify the colours of the prepared metal complexes in comparison to the Bayer's standard samples widely used for C.I.E. system. The chromaticity coordinates x, y and z for the different metal complexes were calculated as follows:

$$x = \frac{X}{X + Y + Z}, \quad y = \frac{Y}{X + Y + Z} \quad \text{and} \quad z = \frac{Z}{X + Y + Z}$$

### Thermogravimetric Analysis (TGA)

The thermal behaviour of the copolymer metal complex samples was investigated by thermogravimetric analysis (TGA) which made under constant rate of nitrogen using a TG-50 instrument from Shimadzu (Japan) at a heating rate of 10 <sup>0</sup>C /min. The data obtained from TGA curves were used to determine the rate of thermal decomposition, activation energy and order of reaction.

#### 2.6. Scanning Electron Microscopy (SEM)

The surface morphology of different metal complexes of polyester microfiber fabrics was examined by SEM technique. The SEM micrographs were taken with a



JSM-5400 microscope made by Joel, Japan. A sputter coater was used to pre-coat conductive gold onto the surface before observing the microstructure at 30 kV.

## RESULTS AND DISCUSSION

In a previous work<sup>19</sup>, polyester microfiber fabrics was radiation grafted with acrylic acid (AAc) and acrylamide (AAM)/AAc comonomer mixtures. The  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Fe}^{3+}$  metal complexes of these grafts were formed and characterized by different techniques including differential scanning calorimeter (DSC), energy dispersive X-ray (EDX), tensile mechanical testing and electrical conductivity for practical applications. The results showed that the grafted chains acted as chelating sites for the different transition metals, in which the metal complexes were proposed to form by inter and/or intra molecular bridging in the polymer matrix. Also, the DSC thermogram showed that the glass transition temperature ( $T_g$ ) was greatly increased after metal complexation depending on the kind of the transition metal. The present work extends this study to illustrate the effect of metal complexation on the thermal stability and surface morphology.

### Colour distribution of metal complexes

The homogeneous distribution of the metal complexes along the surface and the entire bulk of the fabrics depend essentially on the homogeneous grafting and the length of the grafted chains. This state of affairs is of great importance for practical uses of these materials in the field of electrical conductivity, otherwise a deficiency in the material will come out. In this regard, the homogeneous distribution of the metals on PET grafted fabrics was investigated by a method suggested by the CIE to define the colour based on the spectral loci of colour on chromaticity chart as shown in Figure 1<sup>22</sup>. This colour triangle (right-angled) related to the X, Y, Z stimuli of colours. In order to plot colour values on a two-dimensional system it is necessary to have two co-ordinates, the combination of X, Y, and Z showed be unity. In Fig. 1, the wavelengths corresponding with various positions on the curve are marked in numerals. It is clear that the fully saturated colours are found on the spectral curve; in which the elliptic circle in the center represents the white position. A colour inside chromaticity chart can be determined by plotting x versus y.

As shown in Fig. 1, it is clear that the interceptions of x-y for the ungrafted PET or the grafted PET with AAc are located inside the white circle on the borders with the green and greenish blue positions, respectively. These finding may indicate that the colour of these substrates are not purely white due to the grafting process. On the other hand, the intercepts of the  $\text{Fe}^{3+}$  metal complex can be found on the border between the orange and the yellow colours positions, which are the natural colours of these ions. In a similar manner, the interceptions of the metal complexes of  $\text{N}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  were located in greenish blue, bluish green and bluish purple colour positions, respectively. These findings can clearly indicate that the metal complexes on the fabrics are homogeneously distributed along the fabric surfaces, taking in



consideration that x and y co-ordinates were measured in different positions across the samples.

The colour of PET metal complexes was also measured by L\*, a\* and b\* system, in which the a\* and b\* represent the red-green and yellow-blue axes, respectively. In this regard, the positive values of a\* and b\* represent the red and yellow, while the negative values represent the green and blue colour components, respectively. The measured a\* and b\* values for the metal complex of Co<sup>2+</sup> was found to be +86.1 and -45.0, respectively, which means it contains high proportion of red colour combined with a low proportion of blue colour component resulting in bluish purple in accordance with X, Y and Z co-ordinates. For the metal complex of Cu<sup>2+</sup>, the measured a\* and b\* were found to be -49.1 and -19.8, respectively, which means that the resulting colour is composed of a higher proportion of the green component (~ 2.5 times) and a low proportion of blue component resulting in the bluish green. Similar findings were observed in the case of the Ni<sup>2+</sup> metal complex.

On the basis of the above discussion, few points may be outlined: (1) the metal complexation is homogeneously distributed across the fabrics, in which the colour does not change from position to another. , (2) the proposed method can be used for identify precisely the colour, in which the X, Y and Z stimuli give the same results by using the L\*, a\* and b\* system and (3) Homogeneous grafting can be obtained by radiation grafting technique.

### Thermal decomposition behaviour

Thermogravimetric analysis (TGA) is widely used to investigate the thermal decomposition of polymers and to determine the thermal decomposition kinetic parameters such as activation energy and reaction order. These parameters can be used to have a better understanding about the thermal stability of polymers. Figure 2 shows the primary TGA thermograms of ungrafted PETMF, grafted PETMF with individual AAc, grafted PETMF with mixture of AAc and AAm, and their metal complexes with Cu<sup>++</sup>, Ni<sup>++</sup>, Co<sup>++</sup> and Fe<sup>+++</sup>. Also, the decomposition temperatures at which different percentage weight loss has occurred for these substrates are shown in Table 1. As can be seen, the introduction of the different grafted groups and metal ions into the macrostructure of polyester microfiber fabric decreases its thermal stability to some extents within the temperature range up to ~ 400 °C.

As shown above, the effect of grafting on the thermal stability cannot be confirmed unless the kinetics of thermal decomposition is determined. A method based on the rate of reaction proposed by Anderson and freeman was used to determine the different kinetic parameters<sup>23</sup>. The application of the Anderson and Freeman method can be described in the following steps: (1) The rate of conversion dw/dt or the derivative of thermogravimetric analysis curve (DTGA)-taken from the initial TGA curve - and the residual weight loss are plotted against the reciprocal of the absolute temperature (1/T) and (2) from this curve, the quantities (dw/dt) and w' were taken at an equal difference in (1/T) of 0.0025 X 10<sup>-3</sup> K<sup>-1</sup>. Figure 3 shows the plots of (dw/dt) against (1/T) for PETMF, PETMF-g-AAc, PETMF-g-AAc-AAm, and PETMF-g-AAc-Cu, PETMF-g-AAc-Ni, PETMF-g-AAc-Co, PETMF-g-AAc-Fe as well as PETMF-g-AAc-AAm-Cu, PETMF-g-AAc-AAm-Ni and PETMF-g-AAc-AAm-Co. It should be noted that only dw/dt is shown in these curves because the residual weight has been already shown in the TGA thermograms. It can be seen that these types of curves display similar trends; however, the temperature of the



maximum value of the rate differs from one copolymer metal complex to another. These temperatures for PETMF, PETMF-g-AAc, PETMF-g-AAc-AAm, PETMF-g-AAc-Cu, PETMF-g-AAc-Ni, PETMF-g-AAc-Co, PETMF-g-AAc-Fe, PETMF-g-AAc-AAm-Cu, PETMF-g-AAc-AAm-Ni, PETMF-g-AAc-AAm-Co were found to be 456, 473, 433, 427 - 447, 406 – 446, 429 - 470, 439, 416 – 436, 402 – 442 and 434 – 474 °C, respectively. These values indicate that PETMF copolymer metal complex with Co possesses the highest thermal stability while the PETMF copolymer metal complexes with Cu, Ni and Fe showed the lowest thermal stability.

When  $\Delta \log(dw/dt)$  was plotted against  $\Delta \log w$  for PETMF and PETMF copolymer metal complexes with different metal ions over the entire studied temperature scale, the data points do not fall on a straight line. Therefore, on the basis of Anderson and Freeman equation<sup>22</sup>, the thermal decomposition of these substrates does not depend on the residual mass but it does depend on temperature and follows a zero order reaction. In this case,  $\log dw/dt$  is plotted vs.  $1/T$  and the slope will equal to  $E^*/2.303 R$  from which the activation energy can be calculated. The calculated activation energies of the thermal decomposition of the different copolymer metal complexes are summarized in Table 2. On the basis of these data, it can be concluded that PET-g-AAc and PET-g-AAc-Ni showed the highest thermal stability associated with the highest activation energies. However, grafting PETMF with AAc monomer or the binary AAc and AAm comonomer mixture also improves the thermal stability, but to a relatively lower extents.

### Surface morphology of polymer-metal complexes

SEM technique was used to investigate the surface morphology of the different polymer-metal complexes before and after they had been grafted with PAAc and/or PAAc/PAAm mixture under the effect of gamma irradiation. Through SEM observation one can get direct information about the nature of grafting, the compatibility between the surface of fabric and the grafting and the distribution of the grafting along the surface. Figures 4 and 5 show SEM micrographs of the fracture surfaces morphology of different grafted fabrics and the corresponding metal complexes. A first observation showed that the thickness of the fibers forming the ungrafted and grafted fabrics differs from one to another. The average diameter of the fibers of PETMF, PETMF-g-AAc and PETMF-g-AAc-AAm were found to be ~ 17, 24 and 25  $\mu\text{m}$ , respectively as shown in Figs. 4 (a), 4 (b) and 4 (c). Therefore, the enlargement in fiber thickness does not go systematically with the graft yield, which indicates that there is a partial compatibility between the hydrophobic PET and the hydrophilic AAc and AAm monomers. Also, it is clear that there is no homopolymer is deposited between the fibers. Also, the texture of grafted PET with individual AAc seems smooth compared to the rough texture of the grafted PET with AAc/AAm comonomer mixture.

As shown in Fig. 4 (d), the complexation with  $\text{Cu}^{2+}$  metal seems to look like salt formation through the carboxylate groups covering the surfaces. On the other hand, the complex formation with  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  does not change the surface or the cross-section of the fibers indicating the formation of complexes rather than salt formation as shown in Fig.5.



## CONCLUIONS

The chelating copolymers of PETMF fabrics grafted with acrylic acid and/ or acrylamide mixtures were prepared using gamma irradiation technique. The grafted chains acted as chelating sites for some selected transition metal ions. Polymer-metal complexes showed a negative influence on the thermal stability. However, grafting individual AAc monomer was found to improve the thermal stability of polyester microfiber to some extent higher than the grafting with mixed monomers. On the other hand, The DTGA of ungrafted or grafted polyester microfiber with individual monomers displayed a two-stage mechanism, while in the case of grafting with mixed monomers, the two-stage mechanism no longer occurs. The thermal behaviour of both polyester microfiber metal complexes graft copolymers with individual or mixed monomers needs further investigation. However, the thermal stability of metal complex fabrics with different metal ions is of special importance. By colour measurements, it was able to investigate the metal complexes distribution on the grafted PET fabrics.

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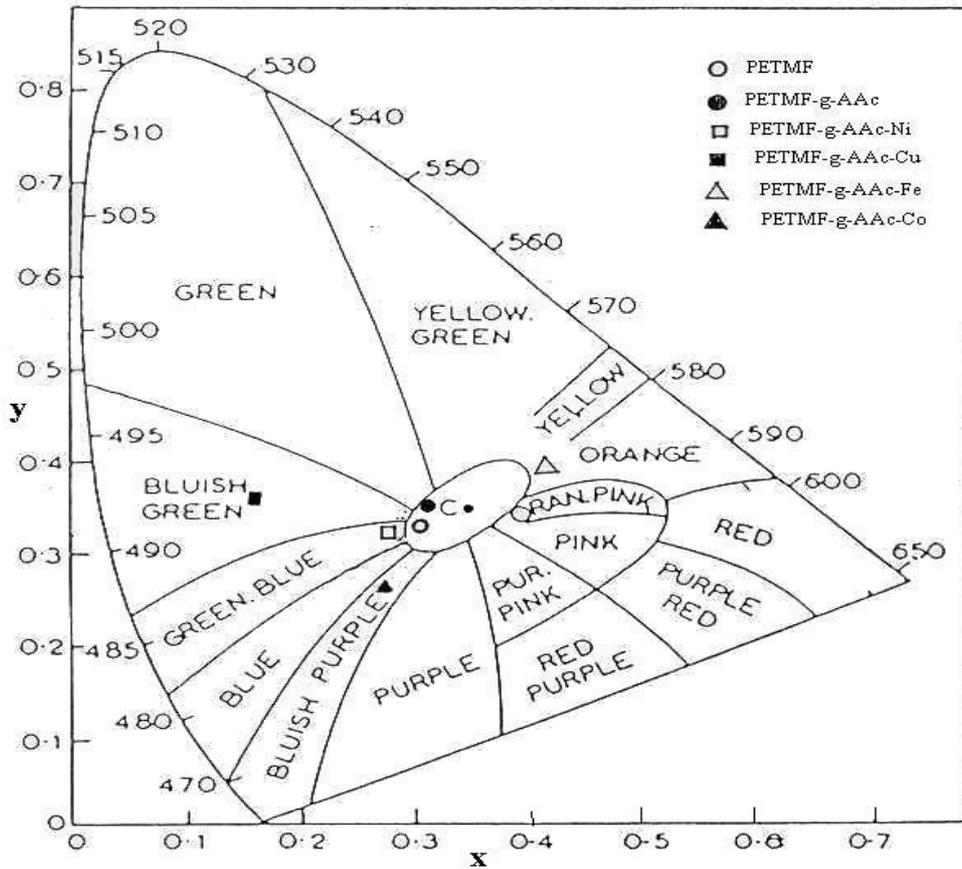
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**Table 1:** Decomposition temperatures at different percentage weight loss for polyester microfiber metal complexes

PETMF Metal complexes	Decomposition temperature, °C				
	10%	20%	40%	60%	80%
PETMF	395	415	435	455	476
PETMF-g-AAc	233	312	393	433	463
PETMF-g-AAc-AAm	252	372	412	452	532
PETMF-g-AAc-Cu	247	305	407	447	597
PETMF-g-AAc-Ni	164	365	405	445	546
PETMF-g-AAc-Co	149	368	409	449	509
PETMF-g-AAc-Fe	238	358	419	458	559
PETMF-g-AAc-AAm-Cu	195	336	396	436	596
PETMF-g-AAc-AAm-Ni	201	361	422	442	562
PETMF-g-AAc-AAm-Co	172	393	434	454	514

**Table 2:** Activation energies (E\*) of the thermal decomposition reaction of different polymer metal complexes

PETMF Metal complexes	Average activation energy, E* (kJ/mol)
TMF	226
TMF-g-AAc	411
TMF-g-AAc-AAm	169
TMF-g-AAc-Cu	240
TMF-g-AAc-Ni	301
TMF-g-AAc-Co	216
TMF-g-AAc-Fe	184
TMF-g-AAc-AAm-Cu	282
TMF-g-AAc-AAm-Ni	273
TMF-g-AAc-AAm-Co	181



The CIE chromaticity diagram

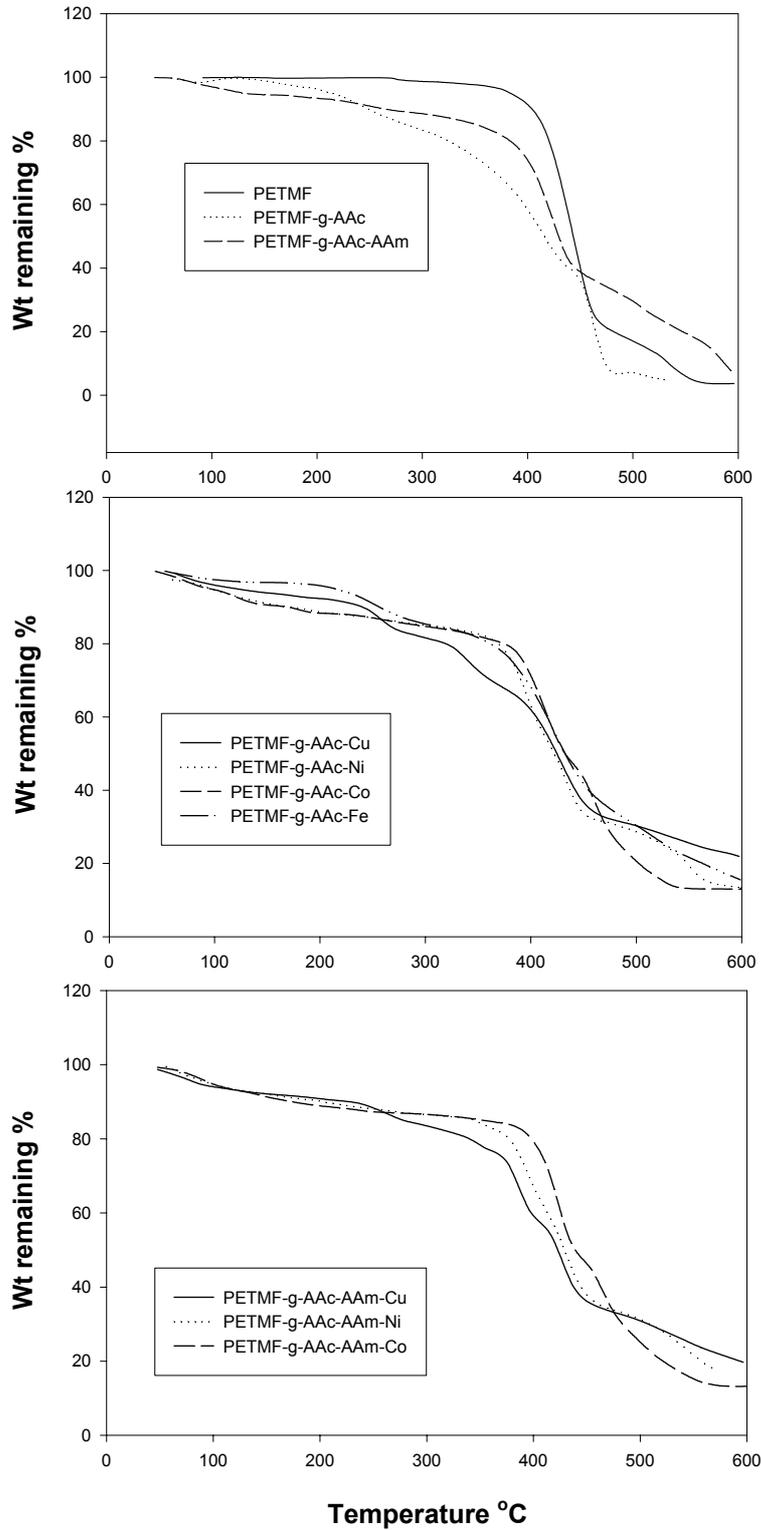
Fig. 1. The CIE chromaticity diagram of ungrafted PETMF fabric (o), PETMF-g-AAC (●), and metal complexes: (□) Ni<sup>2+</sup>, (■) Cu<sup>2+</sup>, (Δ) Fe<sup>3+</sup> and (▲) Co<sup>2+</sup>. The graft yield was constant at 74% in all fabrics.



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**Fig. 2.** Primary TGA thermograms of PET fabrics before and after graft copolymerization and metal complexation

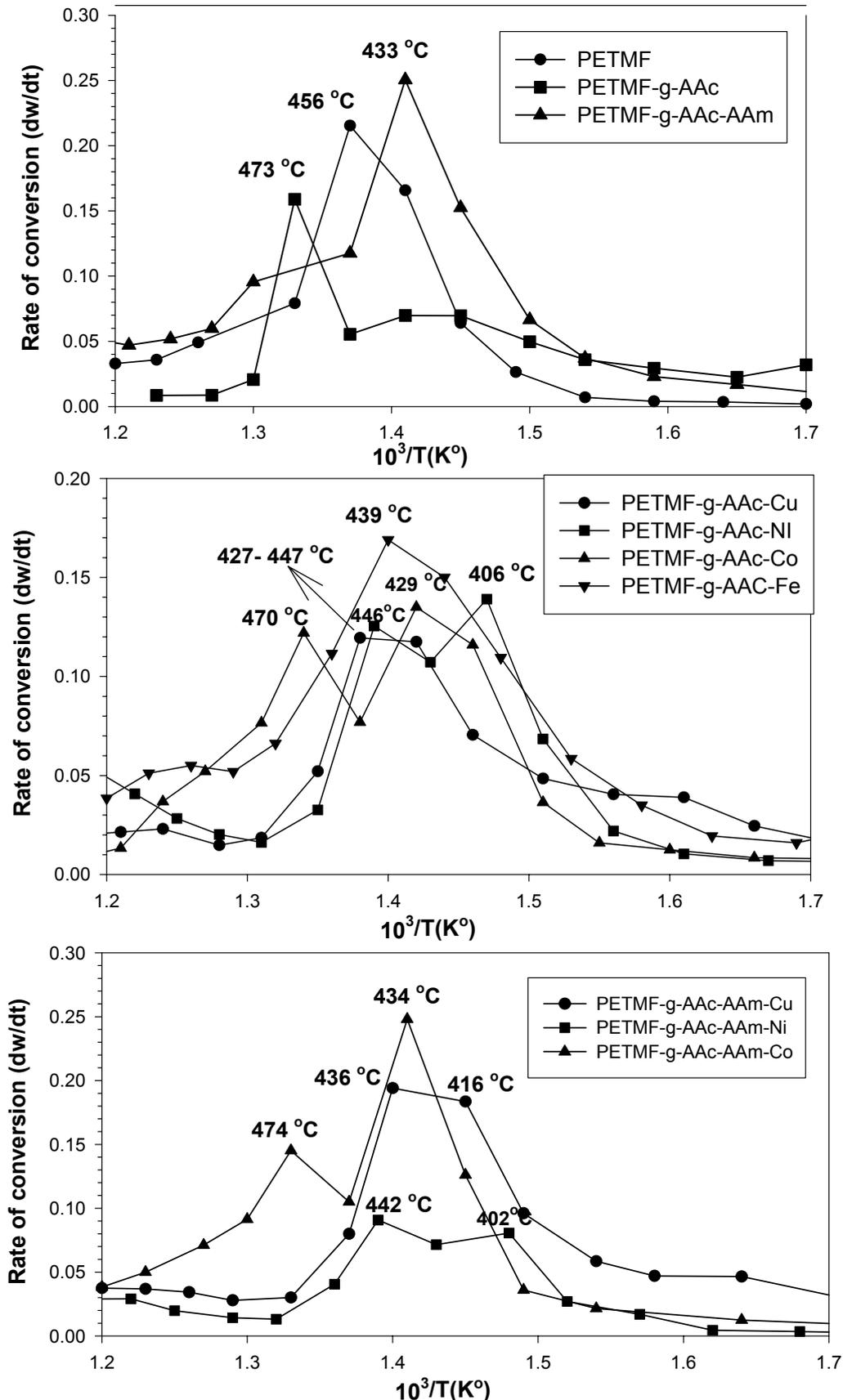
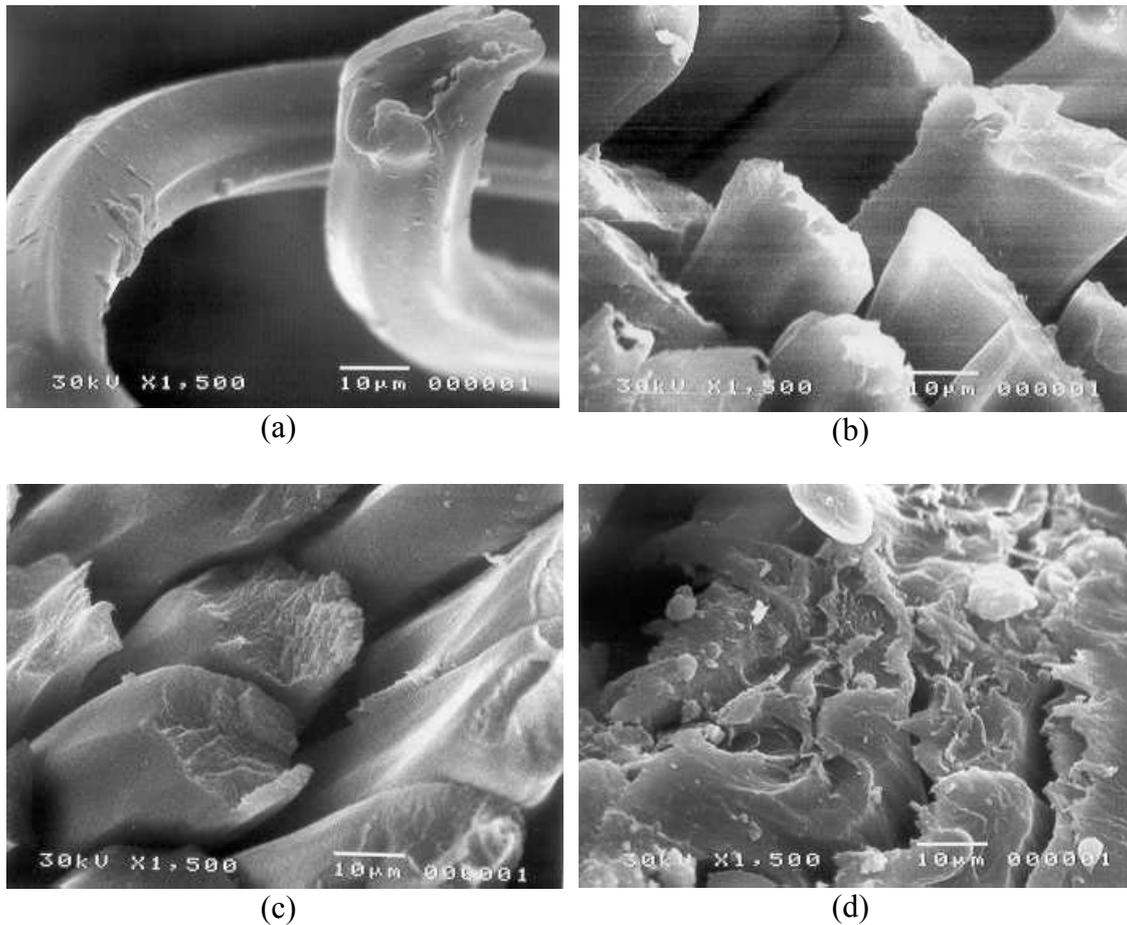
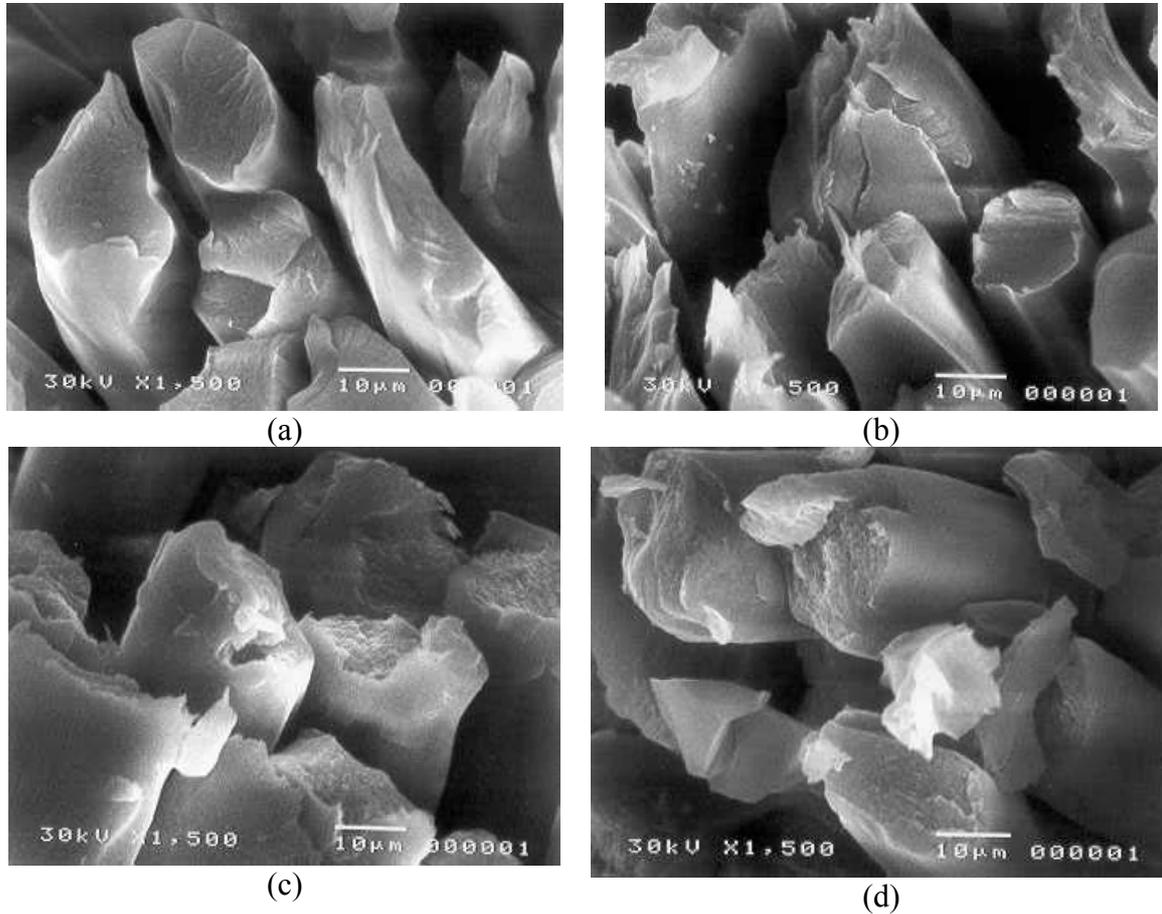


Fig. 3. Rate of conversion (dw/dt) against 1/T of PET fabrics before and after graft copolymerization and metal complexation



**Fig. 4.** SEM photographs of different metal complexes: (a) PETMF (b) PETMF-g-AAc (74%); (c) PETMF-g-AAc-AAm (76%) and (d) PETMF-g-AAc-Cu



**Fig. 5.** SEM photographs of different metal complexes: (a) PETMF-g-AAc-Ni; (b) PETMF-g-AAc-Fe; (c) PETMF-g-AAc-AAm-Ni and (d) PETMF-g-AAc-AAm-Co