Studying the Effect of Phosphorylated Sol-Gel on Polyester Fabric as Flame-Retardant Coating

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ABSTRACT

This research was built to investigate the main role of phosphorylated sol-gel (PSG) to reduce the ignition problems of polyester fabric. Thermogravimetric analysis (TGA), Differential Scanning Calorimeter (DSC) and Fourier transform infrared spectroscopy (FTIR) of the un-treated and treated samples were investigated. PSG material was played as protective shielding coat and improved the thermal behavior. FTIR analysis of the treated sample showed that there is a sort of interaction between the molecules of PSG and the fabric. Limiting oxygen index (LOI) for the lowest oxygen concentration needed to start the ignition showed also an improvement in the ignition retarding behavior due to this treatment. To increase the affinity of fibers towards PSG, the fabric surface was exposed to UV/Ozone for different periods. Exposuring samples for 90 min showed the best results comparing to other samples (irradiated for UV/Ozone for 0, 30 and 125 min). Ignition behavior (UL/94) was also applied on samples by using the flame chamber for determining the rate of burning. The results of UL/94 (according to ISO 3795) confirmed the ignition behavior results produced from the LOI

Introduction

Polyester is a synthetic fabric, which is made from polyethylene terephthalate (PET) polymers. These polymers are composed of at least 85% by weight of ester, dihydric alcohol and terephthalic acid. There are two types of polyester; saturated and unsaturated ones. The first type can be defined as that the polyester which the backbones are saturated and hence non-reactive as compared to the more reactive, unsaturated ones. On the other hand, unsaturated polyester is consisting of alkyl thermosetting resins characterized by vinyl unsaturated. Synthetic fibers surpass the production of natural fibers with more than 55% of products in the textile industry [1]. It can be used in two ways; as a raw material by itself or as a blend because of its wrinkle its wrinkle-resistant property and its ability to retain its shape [2]. PET has several applications in industries as; electronic materials, automobile industries, packaging and household [3, 4]. PET fiber has the major advantages of high modulus and strength, quick drying, hardness, resistant to biological damage such as mold and mildew, stretch, wrinkle and abrasion resistances, relatively low cost and easy recycling [4, 5]. Besides many beneficial properties, synthetic fibers show various disadvantages such as is highly flammable, low dyeability, less wearing comfort, difficulties in finishing and insufficient washability associated with their hydrophobic nature [5, 6]. This research aimed to activate the PET fabric surface in order to produce free radicals to react with PSG [7]. For this purpose, many great studies have been carried out including, thermal analysis (TGA and DSC), which play an important role to study the flame-retardant of polyester. It supplies important information for the evaluation and the development of flame-retardant polyester via the profile of their thermal decomposition [8-11]. This indicates that, the sample irradiate to UV/Ozone for 90 min has the best results as

fire-retardant than the other. Secondly, the samples are exposed to flammability tests as; LOI and UL/94. The Fourier transform infrared is used to determine the peaks which appeared and disappeared in all samples. Also, the results of the optical properties such as; whiteness, yellowness and weight loss tests were followed.

Experimental

Materials

The following fabric was used throughout this study: Mill-scoured and bleached plane 1/1 weaved duck polyester fabric of 140 g/m^2 weight. It was provided by the Misr company for spinning and weaving, El-Mahala El-Kobra, Egypt. There are two kinds of this fabric; un-treated and treated samples with phosphorylated sol-gel coating as mentioned in part I [12].

Ultraviolet-Ozone Treatment

The studied Polyester fabric (100%) samples firstly was exposed to UV/Ozone [13] for different irradiation periods ranging from 30 to 125 min then immersed in the freshly prepared sol-gel solution for 2 min and finally padded under constant pressure for 100% uptake. The treated samples dried in furnace at 140° for 4 min [11].

Weight of Polyester Fabric

Five samples were cut to a specific area and weighed by Mettler Toledo of accuracy (0.1 mg). The weight was calculated for the square meter [14].

Color Measurements

Color parameters for all examined samples were determined using color Eye ® 3100 spectrophotometer SDL England in accordance with standard test method [15,16]. The instrument was used to measure the color parameters, e.g., L (lightness), a (red-green), b (yellow-blue), W (whiteness) and Y (yellowness) color components in accordance with the CIE-Lab color measuring system [17,18].

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR of 100% PET fabric samples (treated and un-treated) were recorded by means of Nicolet 380 Spectrometer – USA that is equipped with zinc selenide crystal, in the wavelength range 4000-400 cm^{-1}. To ensure reproducible contact between the crystal face and the fabric, a pressure of about 18 Kpa [19] is applied to the crystal holder. The FTIR absorbents frequencies for the treated samples are recorded with an average of 32 scans using a resolution of 4 cm^{-1}.

Limiting Oxygen Index (LOI)

The lower concentration of oxygen requires to sample ignition was measured by using a Rheometric limiting oxygen index instrument according to standard oxygen index test ISO 4589 [20]. Both nitrogen and oxygen were connected to the apparatus through pressure regulators (see Figure 1). Determined N_2/O_2 atmospheres were continuously sent through the glass chamber. Sample test was cut in dimension 150 * 50 mm^2, and then clamped in the holder vertically in the center of the combustion column. The top of the sample was ignited using a propane gas burner. Three or four replicates were tested for each sample to obtain the average LOI value.

Figure 1. Limiting oxygen index instrument

Flame Chamber (UL/94)

The fire-flammability of the samples was evaluated with the UL/94 (Figure 2). The samples are tested in a horizontal setting to determine the rate of burning according to ISO 3795 [21]. Sample with dimension 15 x 6 x 1 cm^3 is held at one end in the horizontal position. A burner flame with 3.8 cm is exposed to the free end of the sample for 15 Sec then remove it and studying the flammability properties of the samples. Five specimens are tested for each formulation.

Figure 2. Flam chamber (UL/94) instrument

Thermogravimetric Analysis (TGA)

It is an essential laboratory tool which used to determine the mass changes of a sample during thermal decomposition [22,23]. This TGA can be applied in many fields as; scientific research, petrochemical application, pharmaceutical, and food. The thermal stability of composites was studied using the Thermal Analyzer, TGA-50 Shimadzu Instrument-Japan. The analysis is performed under N_2 gas (flow rate: 30 ml/min) at a heating rate of 10°/min from ambient temperature to 750°. The

weight of testing sample was 6.2 mg that was placed in open platinum pans in the instrument.

Differential Scanning Calorimetry (DSC) [24]

It is used to provide information about thermal changes that do not involve a change in sample mass, characterize the thermophysical properties of polymers as; melting temperature (T_m), heat of melting, percent crystallinity (ΔH_m), glass transition (T_g). This test was performed with DSC-50 Shimadzu Instrument - Japan. The heating rate was 10°C/min and the nitrogen gas was used as; a carrier gas and at a flow rate of 30 ml/min. Samples were repeated three times to insure repeatability. Scans are started at temperature 30° to a final temperature of 650°.

Results and discussion

Weight Loss of Polyester Fabric

Figure 3 shows the effect of irradiation with UV/Ozone on weight sample (g/m^2). The data showed that the sample weights were decreased with the increasing of time for all studied ranges (0 to 125 min). Weight loss was affected by irradiating up to 90 min followed by insignificant decrement for extended irradiation time due to dry and photo-oxidation actions [25]. The changes in Figure 3 could be returned to the combined effect of UV and Ozone on the PET. Ozone action is always based on the effect of direct and indirect reactions with PET fibers. This is consequent to the disintegration of ozone ($O_3 \rightarrow O_2 + O^.$); oxygen free radical reacts with the water content producing OH-radicals and/or primary and secondary hydroxyl groups (R-OH) on the cellulose fibers. These radicals are very short-living compounds that have an even stronger oxidation mechanism than that of ozone [26].
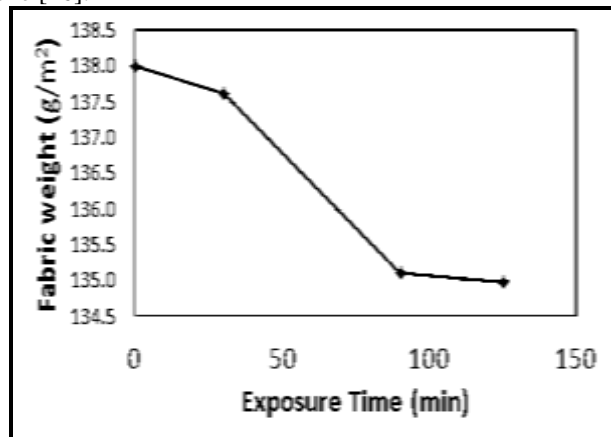

Figure 3. Effect of UV/Ozone exposure time on the fabric weight of polyester fabric

A good oxidative efficiency can be achieved by the coupling of UV radiation and ozone. UV/ozone treatment was essentially a photosensitized oxidation process in which surface molecules are excited and/or dissociated by the absorption of short–wavelength UV radiation. Generally when a polymer is exposed to radiant energy, physical and chemical changes may occur [27]. It is known that ozone is an excellent oxidizing agent for cellulosic, wool, and silk fabrics [28]. The possible interaction of UV in the presence of oxygen on the polymeric materials to produce many free radicals (P$^.$, POO$^.$, HOO$^.$, H$^.$ and HO$^.$) explained in Figure 4.

These free radicals on the polyester substrate were the responsible active sites for the attachment of treatment sole-gel to the PET substrate. These results are due to the action of UV/Ozone on the PET fabric due to the effect of irradiation in reducing elasticity and decreasing the average molecular chain

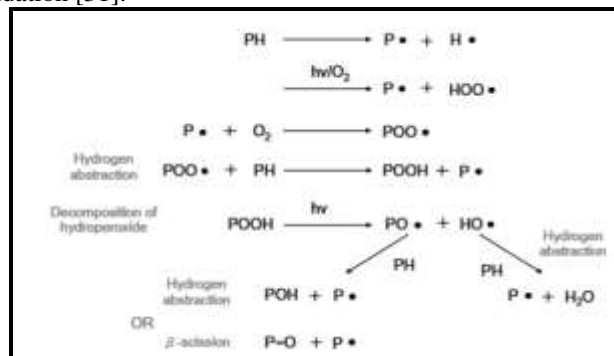of the treated fabrics, which may be due to the result of photo-oxidation [31].

Figure 4. Effect of UV/O₃ radiation on polymeric materials (PH) [29, 30]

These irradiated fibers reacted with phosphorylated sole-gel by either coating and/or cross linking due to the formed radicals resulted from the photo-chemical action of UV/Ozone.

Determination of the Color

Results in Table 1 show the effect of irradiation on the color parameters; L, a, b, W and Y in accordance with the CIE-Lab color measuring system [17,18]. Lightness of the PET samples slightly decreased with increasing the exposure time due to the photo-oxidation of the fabric surface. Red-Green component 'a' goes to the green side because all results have a negative value and the greenish color of the samples increased with irradiation up to 90 minutes followed by decreasing with extended time. The same tendency was found in the color component 'b' that goes to blue color because all results have positive values [32]. The change in yellowness and whiteness indices can be considered as; a sensitive indication of surface modification for the PET fabric under test during the different treatments. It is also clear from the data in Table 1 that, the yellowness value of AS-3P samples is higher than that of unexposed one to UV/Ozone and tends to increase with increasing irradiation time. This may be returned to the partially photo oxidation of UV/Ozone on the sample's surface.

Table 1. Effect of UV/Ozone exposure time on color components, yellowness and whiteness values of polyester fabric

Sample name	Exposed time /(min)	L	a	b	W	Y
AS-1P	0	92.19	-0.77	1.44	74.40	2.56
AS-2P	30	91.97	-0.80	1.79	72.22	3.25
AS-3P	90	91.20	-0.89	2.27	70.07	4.10
AS-4P	125	91.17	-0.71	2.91	65.10	5.56

L (lightness), a (red-green), b (yellow-blue), W (whiteness) and Y (yellowness

Infrared Spectroscopy

The FTIR spectroscopic analysis is used to identify and study the chemical composition of uncoated and coated samples with phosphorylated sol-gel after irradiating to UV/Ozone for different periods (30. 90 and 125 minutes) and the infrared of samples was shown in Figure 5. The main structure of the polyester fabric is ester, alcohol, anhydride, aromatic ring and heterocyclic aromatic rings. Alcohol was able to react with anhydride and produce ester groups [33]. That was the reason there was still alcohol and anhydride as; a residual reactants left in the polyester. The carboxyl, ester, anhydride and alcohol groups showed the polyester fabric was pure PET. It is clear from this Figure that, all samples of polyester exhibits broadband near 3425-3435 cm⁻¹ due to the OH-stretching vibration of free and hydrogen bonded groups (most probably

due to the humidity absorbed by KBr during the preparation of the pellets) [34,35]. The CH_2 anti-symmetric stretching is appearing at 2960-2980 cm⁻¹. The ester functional groups appeared in 1708-1720 cm⁻¹, 1260-1280 cm⁻¹ and 1090-1130 cm⁻¹, while the aromatic ring observed at 2960-2975 cm⁻¹, 1575-1585 cm⁻¹, 1500-1510 cm⁻¹, 1000-1020 cm⁻¹ and 720-730 cm⁻¹. Bands assigned for an ethylene CH_2 group of -O-(CH_2CH_2) -O- moiety are also observed at 1450-1465 cm⁻¹ and 840-855 cm⁻¹. The peak at 1410 cm⁻¹ corresponded to C-C stretching vibration of the benzene ring which was a stable group.
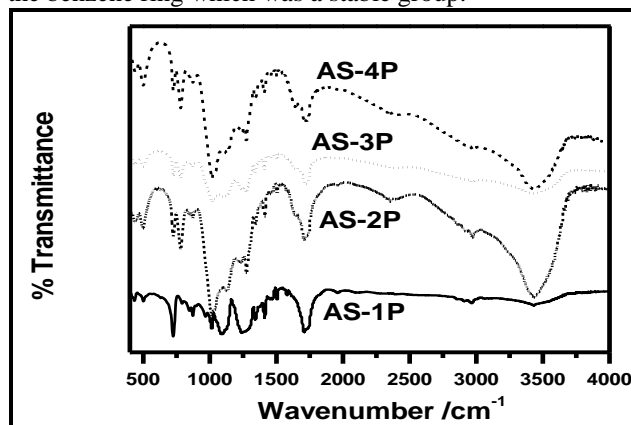

Figure 5. FTIR spectra of treated samples (AS 2P-4P) and un-treated one (AS-1P) after irradiating with UV/Ozone for different time periods

It was the characteristic absorption peak of PET. The presence of ester groups at 1709 and 1268 cm⁻¹ which preferred to break under certain conditions. In case of spectra (AS 2P-4P), the characteristic peaks of the sol-gel materials including the O-H stretching bands at 3500-3300 cm⁻¹. The band at 1630-1650 cm⁻¹ arose from the H–O–H bending of the absorbed water in case of coated samples only. Si-CH_3 bands give rise to a symmetric CH_3 bending band in the 1230-1245 cm⁻¹ range. At 1030-1045 cm⁻¹ the strong band of siloxane (Si-O-Si) is appeared. Phosphorylated coated materials (AS-2P to 4P) spectra show P-OH groups as; two broad bands in the 1030-1045 cm⁻¹ region. P=O group is present as a strong band near 1250 cm⁻¹. The characteristic absorption band of silanol groups (Si-OH) formed during the hydrolysis of the alkoxy groups in methyltrimethoxysilane (MTMS) could be enclosed in this band beside other OH groups. Given that the other characteristic band for Si-OH groups at 950 cm⁻¹ frequently appeared as; a shoulder, we presume that the poly-condensation reaction occurred to a very high degree [36].

In general when we are comparing the four spectrums of un-treated and treated samples we find the O-H stretching at 3425-3435 cm⁻¹ increased by UV/Ozone radiation and sol-gel coated samples because the phosphorylated sol-gel materials are rich with such groups, these band intensities decreased with increasing the exposure time due to partial drying and oxidation of the treated samples. C=O stretching band at 1708-1720 cm⁻¹ decreased due to treatment because most of phosphorylated sol-gel is attached to it.

Flammability Test

The flammability results are summarized in Table 2. Untreated polyester fabric is a flammable polymer as; shown by the LOI of 18.0%. It achieved class-3 classification in the UL/94 test. Irradiation the sample AS-2P to UV/Ozone for 30 minutes increased the LOI to 24.0% and improved the UL/94 rating to class-1 classification.

The LOI of AS-3P was more than doubled when coated with phosphorylated sol-gel after irradiating for 90 min and the

best UL/94 (class-1, RB = 0 mm/min) classification was obtained. Therefore, LOI and UL/94 show that AS-3P is flame-retarded well AS-3P is not as flammable as un-treated one (AS-1P) by far. It showed a high LOI (22.0% instead of 18.0%) and reached class-1 classification in UL/94.

Table 2. **It has the Flammability results (reaction to small flame) which determined by LOI and UL/94.**

Samples after treating with UV/Ozone for diff. times (min)	LOI (%)	UL/94 RB (mm min^{-1})	Classification of fabric
0	18	109	Class-3
30	24	0	Class-1
90	27	0	Class-1
125	22	0	Class-1

The sample can be classified class-1, when the fire not passing first line (after 2.5 cm from the free end), but when passing this line and stopped (not reached until the second line after 7.5 cm from the first one) it can be classified as class-2, and class-3 refers to the complete burning of the sample (fire will be reached to the second line, which found on 10 cm from the free end).

Thermal analyses

Thermogravimetric analysis

Thermogravimetry (TG) provided quantitative information on the weight change process. The amount of char residue formed in the thermal degradation of a polymer is a measure of its flame resistance. The amount of final residue provides quantitative information about the flame-retardants activity. Figure 6 shows TGA curves for coated (AS 2P-4P) and uncoated (AS-1P) samples after irradiating to UV/Ozone for different periods. It is illustrated that the AS-1P exhibit weight loss in three steps. The initial stage is observed up to 355.1°C and includes no sample loss. Up to 486°C the second step occurs.

The mass loss in this stage is due to thermal decomposition into CO and carbonaceous char [37, 38] whereas the third weight loss (486-750°) dehydration and charring reactions tend to be completed with lower thermal stability. It can be seen from Figure 6 that, the coated samples (AS 2P-4P), display weight loss in three steps as well. The first step is nearly up to 331° (0.3% in the case of AS-2P, 10.3% in the case of AS-3P and 9.7% in the case of AS-4P). In case of the second step, the second temperature range, actually exhibited one distinctive mass loss peak between 331-520°.

Mass loss in all coated samples may be explained as follows: Thermal degradation of phosphorylated sol-gel coating begins at a temperature well below that required for thermal degradation of polyester. Thus the coating acts as initial source of ignition in treateating polyester samples. Therefore, in a second step, the mass loss is mainly due to complete decomposition of the protective coating and partial decomposition of polyester.

At the third weight loss (520-750°) the dehydration and charring reactions tend to be completed and the weight loss is 72% (AS-2P), 67% (AS-3P) and 69% (AS-4P). This Figure and weight loss percent indicates that the AS-3P sample has more char (residue) than other samples because it is more bonded with the polyester layer than other coating, which plays an important role in protecting of polyester from the ignition as sacrificial layer, so it is indicative of an effective flame-retardant action.
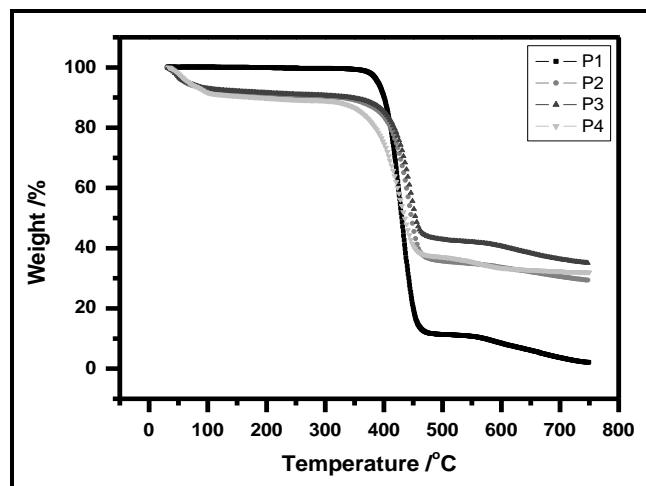

Figure 6. **Thermogravimetric studies of un-treated and treated samples with phosphorylated sol-gel coating after exposuring to UV/Ozone for different periods (P1 at zero min; P2 at 30 min; P3 at 90 min and P4 for 125 min).**

Differential scanning calorimetry

DSC traces for un-treated (AS-1P) and treated (AS 2P-4P) samples with UV/Ozone for different periods are shown in Figure 7. Table 3 indicates the values of the glass-transition temperature (T_g) and the melting temperature (T_m) of all the components of the samples. This data illustrate that, the T_g values are starting to increase in direction of coated samples to record the highest value (103.35°) in the case of sample irradiated with UV/Ozone for 90 min, and then started to decrease (90.76°) in case of AS-4P which irradiated for 125 min. On the other hand, the T_m is affected by irradiating periods with UV/Ozone. It is clear from Table 3 that a maximum increasing in T_m was achieved in case of AS-3P.
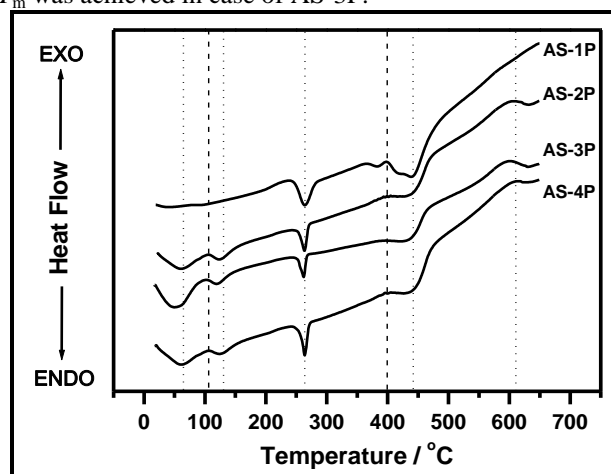

Figure 7. **DSC curves for un-treated sample (AS-1P), coated sample after irradiation with UV/Ozone periods, AS-2P (30 min), AS-3P (90 min) and AS-4P (125 min)**

The melting temperature of the coated samples ($T_{m.c}$) is considered the higher value in case of AS-4P than other coated samples, while in case of uncoated sample it has disappeared. These results were supported by oxygen index and UL/94 either. The difference in the shape and area under the peak was noticed in Figure 7 as well. Firstly, the effect of UV/Ozone on the polyester samples thermal stability was observed as endotherm at the range of 123-126°C, since the broader endotherm was formed in both of coated samples after treating with UV/Ozone for different periods. It is clear that, the area under the peak was decreased in case of AS-3P and became more sharply than that of the other coated sample.

Table 3. Values of transition temperature and heat of fusion for un-treated and treated samples

Samples Data	T_g /^{o}C	$T_{m.c}$ /^{o}C	ΔH /J g^{-1}	T_m /^{o}C	ΔH_m /J g^{-1}	T_{d1} /^{o}C	ΔH_1 /J g^{-1}	T_{d2} /^{o}C	ΔH_2 /J g^{-1}
AS-1P	77.95	--	--	260.02	-7.92	399.10	+7.13	440.47	-18.59
AS-2P	94.23	123.19	-6.62	262.09	-13.88	413.09	-25.46	607.41	+8.83
AS-3P	103.35	125.33	-5.17	262.50	-20.69	419.82	-23.50	618.81	+27.67
AS-4P	90.76	120.85	-4.73	262.01	-10.29	405.88	-13.39	603.29	+7.63

T_g is the glass-transition temperature, T_m is the melting temperature, $T_{m.c}$ is the melting temperature of the coated samples, ΔH is the heat of fusion, ΔH_m is the heat of fusion of melting temperature, T_{d1} is the temperature of the first decomposition, ΔH_1 is the first heat decomposition, T_{d2} is the temperature of the second decomposition and ΔH_2 is the second heat decomposition.

In case of un-treated sample, a broader endotherm appeared at 260°, which decrease toward AS-4P to form a sharp one than other coated samples. This variation in shape was attributed to the different degrees of crystallinity found in the samples with different irradiation periods of UV/Ozone treatment. The curve of un-treated sample (AS-1P) at 399° illustrated the presence of an exothermic peak, which disappeared in the case of the treated samples (AS-2P to 4P).

At 440° observed change in endothermic area, the area became larger and broader at AS-4P sample. This may have indicated the existence of PSG coating with polyester fabric. It is clear that heat flow changed as the samples exposed to UV/Ozone for different periods. These changes were attributed to a variation in crystallization, and are shown in Table 3. Finally, there is a new peak with broader exotherm found in all treated samples except untreated one at 612°. The highest area under the peak was recorded in case of AS-3P and started to decrease in the case of sample AS-2P then AS-4P. This new peak can be used to approve the decomposition of the residual components of the samples.

Conclusions

Thermal characterization gave a fairly good idea of the changes taking place in the PET polymer. The variation in shape and area of endothermic and exothermic peaks indicated changes in T_g, T_m and $T_{m.c}$ regions.

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