Thermal Degradation of PET Fabrics Coated with Interpenetrating Polymer Network-Silica Fume Mixtures

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Abstract

Thermal degradation of polyester fabrics coated with interpenetrating polymer network (IPN) and silica fume (SF) was studied. Silica fume was modified with vinyltriethoxysilane (VTES) in order to improve its hydrophobicity and dispersibility in polymer matrix. Interpenetrating polymer network was prepared by sodium alginate (SA) mixed with 2-hydroxyethyl methacrylate (HEMA). Sodium alginate, HEMA, $K_2S_2O_8$, N,N'-methylenebisacrylamide, N,N,N',N'-tetramethylethylenediamine, and modified SF were mixed in aqueous solution with nonionic surfactant. In this condition, modified SF showed high dispersion ability in SA/HEMA solution. Additional, the application of 0.3 M $CaCl_2$ onto PET surface and dried at temperature of 80°C for 1 hr was conducted. The result showed that the thermal property of modified PET fabric occurred at low temperature. This caused by the thermal degradation of alginate. Also, the content of SF increased the char formation of treated polyester fabric.

Key words: Thermal degradation, Coating, Interpenetrating polymer network, Silica fume

Introduction

Polyester fibre has been successfully used in the production of garments such as apparel and curtains. This is due to its chemical and physical properties. It is light-weight, strength, resistance to photodegradation, and good colour retention.[1] However, thermal deterioration can still be found.

Thermal stability and flame resistance of polymeric matrixes can be enhanced by the addition of inorganic particles by blending, the blending of polymer with thermal resistant amorphous polymers or coating technique. However, the coating technique is lesser complicated, lower in production cost, and it can be applied to a wide range of textile materials.[2]

The modification of polyester fiber was widely studied by several researchers. Many methods has been successfully used for modifying the physical and chemical properties of polyester fiber such as blend with others polymers[3], modified with inorganic materials[4], and coating with tetraethoxysilane for thermal property improvement.[5]

A wide range of different inorganic compounds are introduced as flame retardants, or as elements of flame retardant systems in combination with bromine, phosphorus or nitrogen flame retardants. The inorganic compounds are based on every substances such as silica, metal oxide and other metal products (aluminium, zinc, magnesium) and aluminosilicate clays. Combination of inorganic and halogenated flame retardants increased a synergy effect and their efficiency.[6] Therefore, the use of biomaterial such as sodium alginate combined with inorganic compound such as silica fume is studied.

Silica fume, also known as microsilica, is a by product of ferro silica and silicon metal industry. The material is amorphous silicon dioxide which is generated in submerged electrical arc furnaces as a gas during the reduction of very pure quartz, with metallurgical coal. The gas vapour is then condensed in collector house as very fine spherical particles 0.1-0.3 microns. The silicon dioxide content can vary from 70-96%.[7] Kashiwagi et al. studied the effect of silica product on the flame retardant of polymers. The results showed that silica products increased

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the flame retardant property of various polymer. Silica products could contribute to flame retardancy by accumulating on the surface of burning materials, forming a non flammable char layer. [8]

Some biopolymer such as alginate is flame retardant materials. Alginate derived from marine algae is a linear copolymer of 1,4-linked β-D-mannuronate (M) and α-guluronate (G) residues. With one carboxy group in each M or G unit, it is a negatively charged polyelectrolyte at neutral or basic pH. Its gelling properties arise from the cooperative binding of divalent or trivalent cations (usually Ca^{2+}) between the homopolymeric sequence of G residues. Kong et al. studied the thermal degradation and flame retardancy of calcium alginate fibres. The results showed that calcium alginate fibres were inherently flame retardant with a LOI value of 34. Calcium carbonate and calcium oxide were formed during thermal degradation of calcium alginate fibres at different temperatures. The rigid combustion residue char acted as effective barrier to the outward diffusion of flam and heat. [9]

The study was then carried out in order to modify PET fabric with IPN-SF mixtures. The IPN was prepared from sodium alginate and HEMA. The PET fabric was then coated with alginate, HEMA, and SF. Also, the thermal property of modified PET fabric was investigated.

Materials and Experimental Procedure

Materials

Sodium alginate (SA) from brown algae was purchased as alginic acid sodium salt (Fluka; Singapore). Silica fume (SF) was purchased from Wacker (Thailand). Vinyltriethoxysilane (VTES) was purchased from Aldrich (Singapore) and used as received. 2-Hydroxyethyl methacrylate (HEMA), *N,N′*-methylenebisacrylamide (MBAM), and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), calcium chloride, were purchased from Fluka (Singapore). Potassium persulfate, from M&B Laboratory Chemical (England), was used as received. Nonionic surfactant was supported by Star Tech Chemical Industrial Co Ltd. (Thailand). The woven polyester fabric (PET) was obtained from Rajamangala University of Technology Krungthep (Thailand).

Surface treatment of silica fume with VTES

Silica fume was ball milled for 30 mins at room temperature. Then, VTES (2% and 5% (v/v)) in diethyl ether was applied onto the surface of SF (20 g). The mixture was reacted at room temperature for 24 hrs. The dried SF were washed with diethyl ether for three times and dried at temperature of 110°C for 2 hrs and subsequently cooled in desiccator.

Surface treatment on polyester fabric with IPN-SF

The solution used in the fabric surface treatments was prepared as follows. First, the aqueous solution of alginate (19 wt%) was mixed with HEMA (10% (v/v)), $K_2S_2O_8$ (4% by wt of HEMA), MBAM (4% by wt of HEMA), and TMEDA 1 ml. The solution was stirred at room temperature for 1 hour. And, the SF (1.5-7.5 % by wt of SA) was added into the solution with small amount of nonionic surfactant and stirred at room temperature for 30 mins. Then, the polyester fabric was impregnated with SA/HEMA/SF mixtures by using padder (Ernst Benz AG Type KLFV, Germany) with 95% pick up. It was kept at room temperature for 1 hour before the fabric was impregnated in 0.3 M $CaCl_2$ for crosslinking of SA and dried at 80°C for 1 hour and placed in a desiccator before measure the weight. The increase in weight was calculated on the basic of the oven dried weights before and after the surface treatment procedure.

Characterisations

Particle size measurement

The particle size distribution of silica fume and modified silica fume were measured by a laser particle size distribution Mastersizer S long bed (version 2.19, Malvern Instruments, Ltd., Worcestershine, England).

FTIR measurement

FTIR spectra of silica fume and modified silica fume were recorded in KBr pellets by using Perkin-Elmer FTIR Spectrophotometer System 2000 (Waltham, Massachusetts, United States of America).

Thermal analysis

The thermogravimetric analysis (TGA) was carried out by using Netzsch Simultaneous Thermal Analyzer STA 409 C Jupiter (Burlington Maryland, United States of America), which recorded the mass change as a function of temperature. The sample (17 ± 3 mg) was analyzed under nitrogen atmosphere from room temperature to 800°C at a heating rate of 20°C/min.

Microscopic studies

The samples were coated with gold in the Hitachi E 102 ion sputter. The surface morphology of sample was observed with a scanning electron microscope by using the accelerating voltage 15 kV (SEM, JEOL JSM-5410LV, Tokyo, Japan).

Results and Discussion

Modification of Silica Fume

Silica fume is amorphous silicon dioxide. Its surface is polar and hydrophilic. However, it is not dispersible in water due to its micron sized particle. Colloidal particle of SF in water may be enhanced with a surface modifying agent. Thus, SF is modified with VTES. VTES is a vinyl silane containing three alkoxy groups. Its chemical structure is $(CH_3\text{-}CH_2\text{-}O)_3\text{-}Si\text{-}CH=CH_2$.

The results showed that silanes reacted with substrate surface after their methoxy functional groups have been hydrolysed to form the corresponding silanol (Si-OH). These silanol species reacted with hydroxyl functional groups on the surface of the substrate and also neighbouring molecules. In addition, polysiloxane network is formed on the substrate surface, thereby changing the filler surface properties.

Figure 1 shows FTIR spectra of unmodified and modified SF with VTES. In the FTIR spectrum of unmodified silica fume (see Figure 1 (a)), the absorption band at 3,435 cm^{-1} attributed to the absorbance of -OH functional groups of Si-OH in silica; at 1118 cm^{-1} is due to Si-O stretching. The peak at 805 cm^{-1} is the absorption of Si-O in Si-OH, whereas at 478 cm^{-1} is the bonding vibration absorption of Si-O-Si.[10] The IR spectra of the treated samples showed all expected characteristic:

the peaks at 1135 and 1095 cm^{-1} were assigned to Si-O-CH$_2$-CH$_3$.[11] In addition the intensity of these peaks increased with increasing VTES concentration.
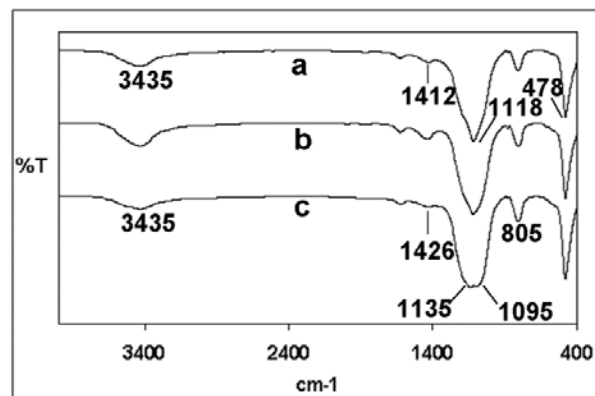

Figure 1. FTIR spectra of unmodified (a) and modified SF with VTES (b-c); (b) VTES 2% (v/v), (c) VTES 5% (v/v).

The particle size distribution of SF is shown in Figure 2. It can be noticed that increasing the concentration of VTES caused in decreasing in the particle size distribution of SF. The organic substitution in VTES has the hydrophobic property. It causes the decrease in the agglomeration of SF particles. Thus, VTES had an effect on the property of SF. The average diameter of modified particles was smaller than that of unmodified one (see Table 1). From this result, modified SF with VTES at concentration of 5%(v/v) was chosen for further experiment.
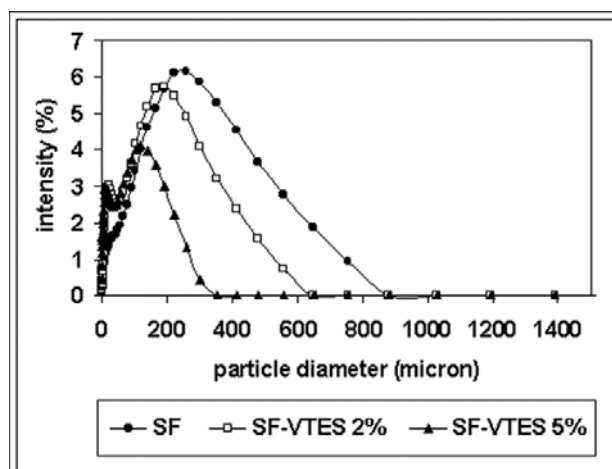

Figure 2. Particle size distribution of unmodified and modified SF.

**Table** 1. Mean particle size of unmodified and modified silica fume

| Type of silica fume	Mean diameter (micron)
Unmodified silica fume	20.00
Modified silica fume with VTES at various concentration(%v/v)	
2%	11.44
5%	5.43

Surface modification of polyester fabric with IPN-SF

In order to modify polyester fabric, SA/ HEMA mixed with modified SF was treated onto the surface of the fabric. The effect of SF content on the weight of polyester fabric was observed. The result (Figure 3) is showed that the content of SF had an effect on increasing the weight of polyester fabric.
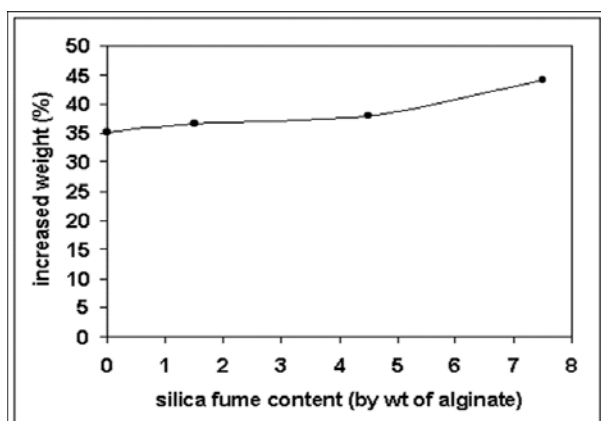
Figure 3. Weight of polyester fabric after being treated with IPN-SF.

The surface morphology of modified polyester fabrics was examined by using SEM analysis (see Figure 4). The result showed that modified fabric with IPN-SF had the particles of SF attaches on its (the SF particles were pointed in the SEM image).
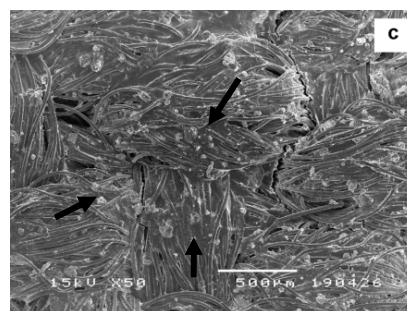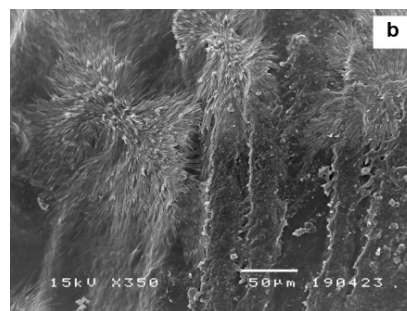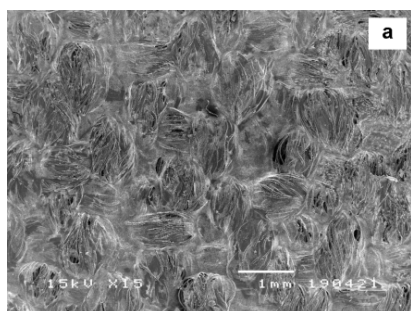
Figure 4. SEM micrographs of unmodified (a-b) and modified polyester fabrics with IPN-SF 1.5% (by wt of SA) (c).

The solution treated on polyester fabric composed of SA, HEMA and SF. The role of these components is described as follows. Alginate is biodegradable and flame retardant property.[9] The viscosity of alginate solution at concentration of 19 wt% is sufficient for suspension of modified SF in the solution. HEMA is hydrophilic polymer containing hydroxyl groups. From my previous experiment, it was found that the hydrophilic property of polyester fabric rapidly increased when HEMA solution at concentration of 10% (v/v) was coated on fabric. Therefore, HEMA at concentration of 10% (v/v) was used in this study. In the case of SF, it is inorganic material and flame retardant property similar to alginate. Modification of SF with VTES led to increasing its hydrophobic property. When it was added into the SA/HEMA solution mixed with small amount of nonionic surfactant, the suspension of mixtures then occurred.

In this experiment, SA was crosslinked with $CaCl_2$ while HEMA was polymerised and crosslinked with MBAM in the presence of alginate. An interpenetrating polymer network (IPN), defined as a combination of two polymers, has the two following characteristics: (1) one of the polymer must be synthesized, or crosslinked, in the immediate presence of the other; and (2) the combination must produce a multicomponent polymeric system, with a new property. The combination of SA and HEMA increased its hydrophilic property.[12] Thus, the IPN

was occurred. It expected that addition of SF in SA/HEMA solution had the synergistic effect for thermal resistance of polyester fabric. Also, the hydrophobic property of PET fabric was improved by HEMA in the IPN polymer.

TGA was used to study the thermal stability of polyester fabrics. The results obtained are shown in Figure 5-6 and Table 2. From Figure 5 (a), it is seen that for unmodified PET fabric the TGA curve showed the major weight loss at onset temperature of 414.5°C. A very complex mixture of product was produced, but the major product were carbon dioxide, acetaldehyde, and terephthalic acid.[1] The amount of char was 19.02%.
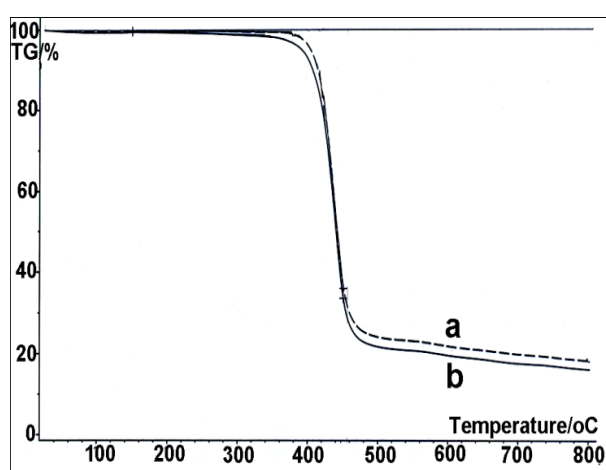

Figure 5. Thermograms of polyester fabric (a) and modified polyester fabrics with PHEMA (b).
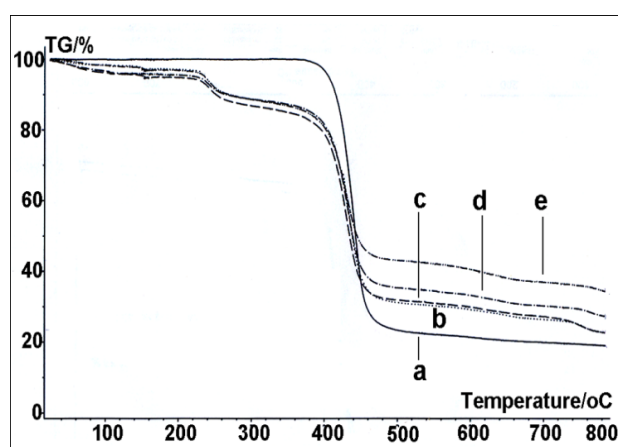

Figure 6. Thermograms of polyester fabric (a) and modified polyester fabrics (b-e); (b) PET/IPN, (c) PET/IPN-SF 1.5% (by wt of SA), (d) PET /IPN-SF 4.5% (by wt of SA), (e) PET/IPN-SF 7.5% (by wt of SA).

Table 2. Thermal degradation of polyester fabrics

Sample	Onset Temperature (°C)		Residual (wt%)
PET	414.5	-	19.02
PET/PHEMA	410.2	-	16.09
PET/IPN	225.7	405.0	22.71
PET/IPN-SF 1.5% (by wt of SA)	229.2	407.5	22.82
PET/IPN-SF 4.5% (by wt of SA)	228.1	405.5	27.58
PET/IPN-SF 7.5% (by wt of SA)	227.2	402.7	34.34

For coating of PET fabric with PHEMA (Figure 5 (b)), In the case of unmodified PET, it was found that the amount of char decreased from 19.02% to 16.09%. The mass loss of PHEMA began when temperature was reached at 322°C. The TGA curve of PHEMA homopolymer showed one reaction stage. The Initial degradation temperature of PHEMA was due to random chain scission.[13] Thus, the treatment of PET fabric with only PHEMA decreased its thermal stability.

For coating of PET with IPN or IPN-SF mixtures (see Figure 6), initial loss in weight can be noticed from TGA curves when temperature of specimens were in the region of 150-200°C. The loss in weight continues and rapidly increases when temperature reached 400°C. It can be seen from the result that the initial degradation of modified fabrics occurred at low temperature compared to unmodified one. The weight loss at low temperature is attributed assigned to the decomposition of calcium alginate. The one major region is related to the degradation of PET. Also, the result shows that coating of PET fabric with IPN or IPN-SF mixtures increased the amount of char from 19.02% in the case of original PET to 22.71-34.34% for modified PET. In addition, increasing of SF content increased the amount of char. The char formation resulted from the thermal degradation of the treated materials on PET fabric. Therefore, a way to stop spreading of the flame over the material is to create a thermal insulation barrier between the burning and unburned parts. Thus modified PET fabric with IPN-SF mixtures led to thermal shielding product. The char formation mechanism of IPN-SF mixtures on the thermal degradation of modified PET fabric is explained in the followings.

In calcium alginate, the weight loss from room temperature to 220°C was caused by the dehydration of calcium alginate. Also, calcium carbonate was formed

when calcium alginate was heated to 150°C. Calcium oxide and calcium hydroxide were found when heated to 700°C. The formation of calcium carbonate at low temperature played a key role for the flame retardancy of calcium alginate.[9] In the case of SF, it was reported that silica fume particles accumulated near the surface of burning material to act as thermal insulation layer and also acted to reduce the polymer concentration near the surface, creating a less flammable.[8]

Conclusion

IPN-silica fume mixtures were prepared, based on sodium alginate, HEMA, and silica fume. The combination between sodium alginate and HEMA produced IPN. The polyester fabric was coated with IPN-silica fume mixtures. The thermal behaviour of PET fabric was investigated. The modified PET fabric showed thermal degradation at low temperature which differed from unmodified PET. The char formation at high temperature of modified PET depended on the content of silica fume.

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