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Thermal analysis and characterisation of cellulose grafted with acrylic monomers

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Abstract

An oxidative reaction of cellulose with sodium methaperiodate was performed in order to reproduce the natural ageing of textiles. The oxidised groups were transformed into free macroradicals by treatment with UV light. In presence of acrylic monomers in the vapour phase, these reactive sites become the starting point for the graft copolymerisation of methyl methacrylate and ethyl acrylate onto cellulose.

Thermal analysis is a convenient, useful and reproducible method for characterising complex organic materials from plants. In this research we have examined the thermal stability of oxidised and grafted flax and cotton using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) analyses, in order to evaluate the effect of the grafting on their thermal behaviour. In presence of acrylic grafted polymer, the thermal stability of the textiles increases.
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1. Introduction

Linen and cotton are cellulose based materials mainly used for manufacturing textiles; they have a structure consisting of monomeric units of β-D-glucopyranose, linked through 1,4-β-glucosidic bonds [1]. In linen is present about 2% of lignin, which is absent in cotton; thus the behaviour of the two textiles is very different [2].

The main reactions acting on the cellulose structure and causing its alteration are photodegradation, acid hydrolysis, oxidation and biodegradation. A complete analysis of them is quite complex, since these phenomena are all related to each other [3].

The oxidation reactions of cellulose have been already studied [4] and involve the primary and secondary hydroxyl groups of the pyranose ring leading to carbonyl and carboxyl groups. When the oxidation is prolonged, depolymerisation of cellulose and a general worsening of physical and mechanical properties of the material can occur.

Between various treatments used to improve the properties of natural fibres, the synthesis of graft copolymers [5] seems an interesting method to reduce the ageing phenomena of textiles, enhancing their mechanical properties, without modifying their appearance [3].

The properties of the grafted copolymer can be tailored by the chemical structure of monomers, the length of the grafted segment and the grafting level [1].

Graft copolymerisation of vinyl monomers onto cellulose has been widely investigated [6,7]; in particular the acrylic monomers can be used because of their physical characteristics (water-repellence, transparency, good filmability).

The creation of free radicals in the cellulose chain is necessary to initiate the grafting: the polymerisation can be induced by chemical method or, more conveniently, by radiation, as γ-rays, X-rays, UV light and electron beam. The selection of

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a particular type of radiation depends on the degree of penetration required. In literature several studies on photoinitiated grafting of cellulose by ultraviolet light are reported [2].

Because of the low energy, UV radiation-induced grafting offers advantages in the grafting reaction onto cellulose, such as a reduced degradation of the backbone polymer and a control over the grafting reaction [8–11,3].

In our research methyl methacrylate and ethyl acrylate in the vapour phase have been grafted by using UV light onto cotton and linen fabrics, previously oxidised with the intent to reproduce natural oxidative ageing.

Since natural fibres from plants, such as cotton and flax, when heated, decompose and totally degrade losing the main features, improving their thermal stability is highly advantageous.

Thermal analysis techniques are often used for characterisation of polymeric materials. Differential scanning calorimetry allows a rapid detection and measurement of the physico-chemical changes that a polymer undergoes when subjected to heating, whereas, thermogravimetric analysis provides a method for the determination of mass change in the polymer as a function of time and temperature. Thus, these techniques reflect reactions which occur at the molecular level of the materials.

Cellulose, hemicelluloses and lignin have been analysed by DSC by Camino and coworkers [12] and the effect of grafting cellulose on thermal properties has been also studied by Shukla et al. [13] and Fernandez et al. [14].

In a previous paper a detailed investigation about the thermal degradation of oxidised cellulose based materials, comparing them with the thermal degradation of the unaged ones, has been reported [15]. The main objective of the present research is to evaluate the effect of the grafting polymerisation on the thermal behaviour of linen and cotton.

The final aim of the whole research is the application of the grafting method as a new technique for the consolidation and the restoration of cellulose based textiles naturally oxidised, which belong to the field of cultural heritage.

2. Experimental

2.1. Materials

The cellulose substrates were linen Artemisia and cotton Ghinea, fabrics by Zecchi (Italy).

Sodium methaperiodate ($NaIO_4$) was obtained from Sigma–Aldrich and used without further purification. Methyl methacrylate (MMA) and ethyl acrylate (EA) from Aldrich were purified from the polymerisation inhibitor (hydroquinone monomethylether) with an Inhibitor Remover column. Acetone and methanol were laboratory grade products from Aldrich, used without further purification. Deionised water was used throughout the work.

2.2. Methods

2.2.1. Oxidation of cellulose

To investigate the cellulose behaviour at different level of oxidation, the samples have been treated in the dark with two different solutions of sodium methaperiodate: 0.1 and 0.4 M for different times. The ratio sample/solution was kept for all experiments 1 g/100 ml. At the end of the oxidation the samples were washed with deionised water up to neutral conditions and dried.

2.2.2. Grafting reaction

The photo-initiated grafting reaction was carried out on oxidised linen and cotton.

Cellulose samples, after drying in oven, have been swollen in deionised water for 24 h, because after a prolonged swelling the fibres became accessible to the vaporised acrylic monomer [16]. The suitable time of swelling for the textiles has been chosen after water absorption tests.

The wet samples were placed in the quartz reaction vessel (volume: 10 l), it was evacuated for a short time, so that the fabrics were still damp; then the liquid monomer was loaded, vaporised, and diffused into the reactor. The monomer/cellulose ratio has been varied between 1.5 and 3.3 mmol of acrylic per gram of sample. Subsequently the whole unit was exposed at room temperature to UV radiation from a mercury vapour lamp (400 W, with complete spectrum emission from 180 nm to visible light), placed at 60 cm so that no cooling system was required.

The polymerisation was stopped after 4 h by bringing the reactor up to room pressure. The non-reacted monomer was removed by washing the fibres with a mixture methanol–water (30/70 vol.%), a good solvent only for acrylic monomers, but not for the polymers. After this procedure the sample, containing grafted cellulose and homopolymer, was filtered and brought up to constant weight.

The drawback of the graft polymerisation is the simultaneous and inevitable formation of homopolymer; it is removed from the grafted material by extraction with acetone for 72 h at room temperature [1,17].

The percentage of synthesised polymer during grafting reaction is calculated as follows:

$$\text{polymer loading (PL) (\%)} = \frac{[(W_2 - W_1) \times 100]}{W_1}$$

where W_1 is the initial weight of the sample and W_2 is the dry weight of the polymerised sample before homopolymer extraction.

The quantity of grafted monomer is evaluated as the weight increase of the sample after extraction of the homopolymer:

$$\text{grafting yield (GY) (\%)} = \frac{[(W_3 - W_1) \times 100]}{W_1}$$

where W_3 is the grafted weight of extracted sample.

Table 1
List of oxidised samples and grafted with PEA and PMMA

Oxidation, time	EA			MMA		
	EA/cell	Grafting yield (%)	Grafting efficiency (%)	MMA/cell	Grafting yield (%)	Grafting efficiency (%)
Linen						
0.1 M, 2 h	2	43	63	1.5	22	49
	3.3	80	92			
0.4 M, 1 h	2	40	70		26	82
	3.3	89	91			
Cotton						
0.1 M, 4 h	1.5	54	95	1.5	37	61
	2	60	77			
	2.5	77	85			
	3.3	166	87			
0.1 M, 24 h	–	–	–		29	55
0.4 M, 4 h	–	–	–		27	61
0.4 M, 8 h	–	–	–		12	46

The grafting efficiency is defined as the ratio between the quantity of grafted monomer and the total polymerised monomer:

$$\text{grafting efficiency (GE) (\%)} = \left[\frac{W_3 - W_1}{W_2 - W_1} \right] \times 100$$

The amount of homopolymer is quantified according to the following relationship:

$$\text{homopolymer (\%)} = 100 - \text{grafting efficiency (\%)}$$

2.3. Thermal analysis

A DSC Mettler Toledo 821^e was used with oxygen flow (120 cm^3 min^{-1}); the analysis was performed between room temperature and 650 °C at heating rate of 5 °C min^{-1}, on 5–10 mg samples in an aluminium holder.

A Perkin Elmer TGA 7 was used with nitrogen flow (4 cm^3 min^{-1}). The samples were heated from 50 to 900 °C at the rate of 5 and 20 °C min^{-1}, on 3–5 mg samples. The weight loss (TG curve) and its first derivative (DTG curve) were recorded simultaneously as a function of time/temperature.

3. Results and discussion

3.1. Grafting reaction

Grafting polymerisation has carried out changing some parameters as the oxidation conditions of the sample and the
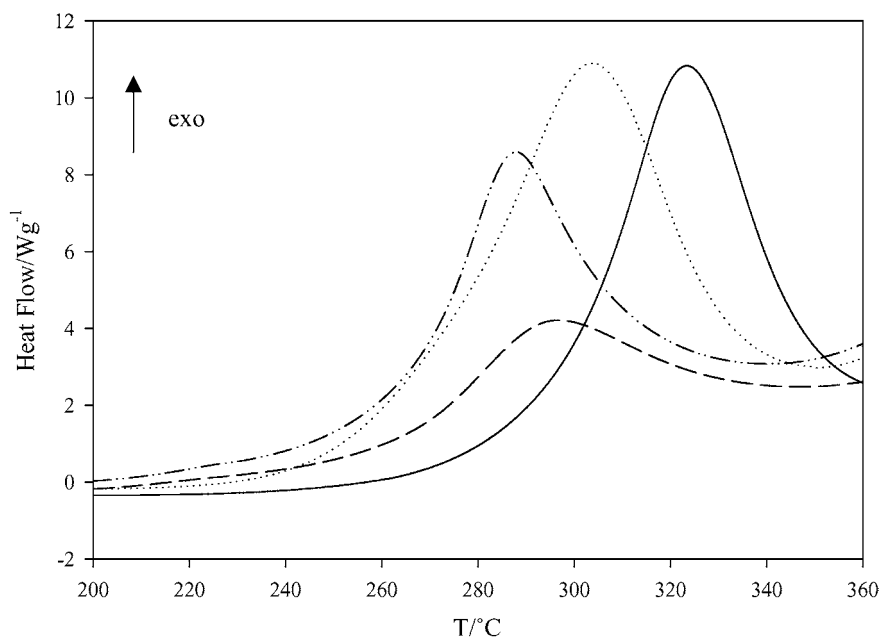

Fig. 1. DSC curves of untreated and oxidised ([NaIO$_4$] 0.4 M for 8 h) materials: (—) linen, (· · ·) cotton, oxidised linen (- - -) and oxidised cotton (-· --·-·).

monomer/cellulose ratio; in Table 1 the grafting yields with EA and MMA are reported. In the grafting with MMA, the ratio monomer/cellulose was fixed and only the oxidation conditions have been varied. Grafting EA, both the parameters (monomer/cellulose ratio and oxidation conditions) have been changed.

From data reported in Table 1, it is evident that PEA lead to a higher yield and a lower homopolymer percentage than PMMA and the grafting yields increase giving raise the ratio EA/cellulose.

When the cotton undergoes a strong oxidation, the grafting yield decreases, while on linen it does not change noticeably, by MMA results. This effect is not expected and is not easily explainable; it could be due to the termination step of the polymerisation.

The grafting on cotton and linen involves different results; in the same conditions, grafting yields for linen are lower than for cotton. This fact could be due to the presence of lignin in linen (2%) [15], which could act as inhibitor for the grafting process [18].

The grafting does not modify the aspect of the materials and this is important for objects of historical interest.

3.2. Thermal analysis: DSC

The thermal degradation of cellulose and modified cellulose has been extensively studied [12–14,19–21]; it involves a set of concurrent and consecutive reactions.

The strong exothermal peak at about 300–340 °C is attributed to the cellulose depolymerisation and to the charring and oxidation of the decomposition products [22]. The sec-

Table 2
Temperature of first peak of untreated, oxidised and grafted cotton with PMMA (MMA/cellulose: 1.5) in DSC curves

Untreated cotton, T_{peak} (°C)	Oxidised cotton		Grafted cotton, T_{peak} (°C)
	Oxidation, time	T_{peak} (°C)	
300	0.1 M, 4 h	298	305
300	0.1 M, 24 h	296	325
300	0.4 M, 4 h	290	312
300	0.4 M, 8 h	280	330

ond peak observed above 400 °C is likely due to the oxidation of the char.

In a previous paper the influence of heating rate on thermal decomposition has been investigated [15]. From experimental results, the suitable scanning rate to observe all the transitions is 5 °C min^{-1}; with faster rates the scanning is not meaningful.

The peak temperatures in the DSC curves of untreated materials are different; these differences become less evident in the oxidised samples (Fig. 1). The peak at 390 °C in the untreated cotton could be attributed to the starch: it is always used as finishing agent for textiles. During the oxidation the methaperiodate solution removes this additive and consequently the corresponding peak disappears.

For every oxidation performed on textiles, the first peak shifts to lower temperature and this effect is more evident when the textiles undergo a strong oxidation, as shown in Table 2, for cotton oxidised with methaperiodate 0.1 and 0.4 M for different times.
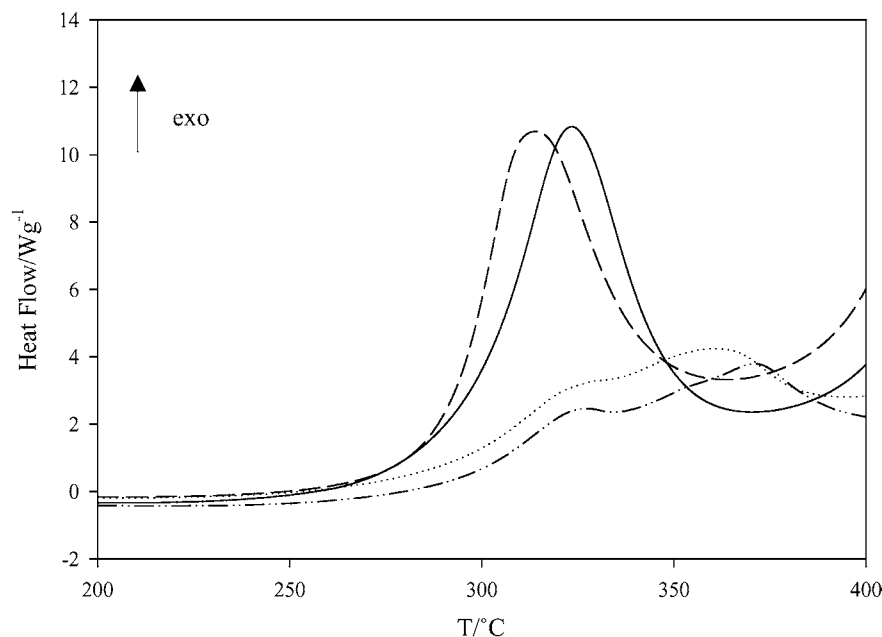

Fig. 2. DSC curves of untreated (—), oxidised ([NaIO₄] 0.1 M for 2 h) (- - -) and grafted linen with PEA (monomer/cellulose: 2) (···) and PEA (monomer/cellulose: 3.3) (-··-··-).
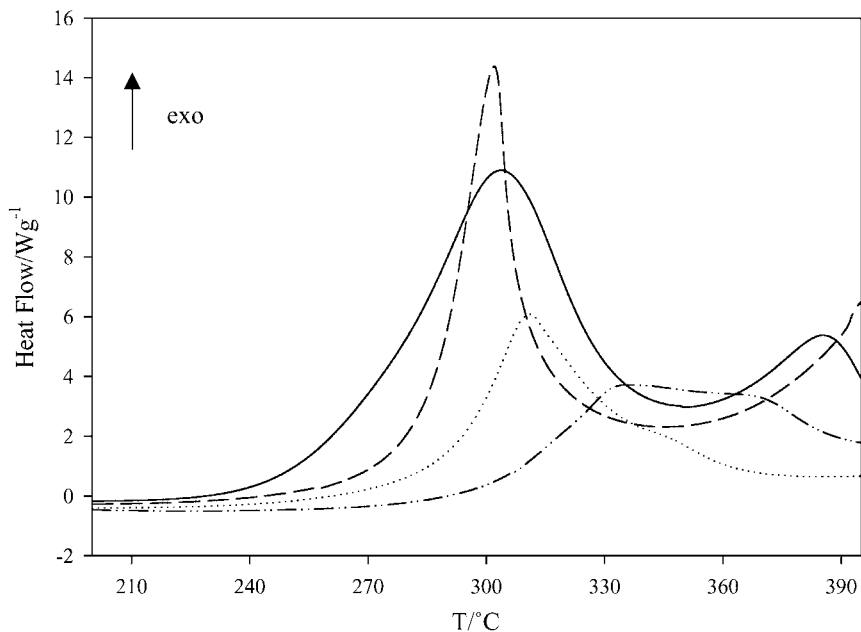
Fig. 3. DSC curves of untreated (—), oxidised ([NaIO₄] 0.1 M for 4 h) (- - -), grafted cotton with PMMA (monomer/cellulose: 1.5) (···) and PEA (monomer/cellulose: 1.5) (-·· -·· -·).

The shift can be explained assuming that the oxidised cellulose is already degraded with a large fraction of oligomers and therefore less energy is necessary for the thermal decomposition.

The DSC curves of the ungrafted and grafted linen are shown in Fig. 2. In the untreated material, the exothermic reaction starts at 300 °C with a peak at 340 °C, reflecting the thermal depolymerisation of cellulose. The curves of PEA grafted sample are different from that of ungrafted linen. The exothermic peak splits in two peaks; the first one corresponds to the decomposition of cellulose; the second one corresponds to the grafted PEA degradation and it is shifted towards higher temperature with the increase in grafting yields. When the ratio monomer/cellulose is increased from 2 to 3.3 (see Table 1), the grafting yields became the double and the peak attributed to the grafted polymer is shifted to higher temperature.

When the monomer/cellulose ratio is lower than 2, the splitting of the exothermic peak is not evident and the peak attributed to the polymer degradation becomes a shoulder of
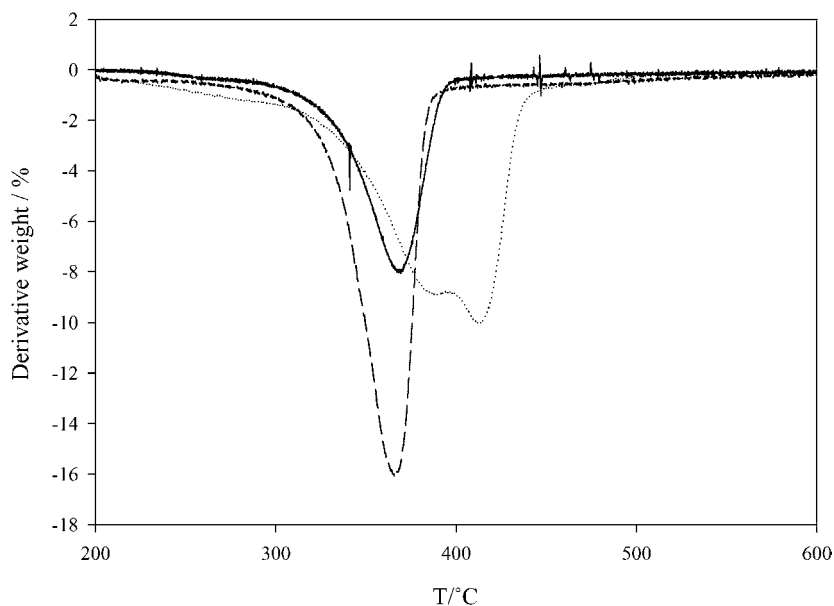

Fig. 4. TGA curves of untreated (—), oxidised ([NaIO₄] 0.1 M for 2 h) (- - -) and grafted linen with PEA (monomer/cellulose: 3.3) (···).
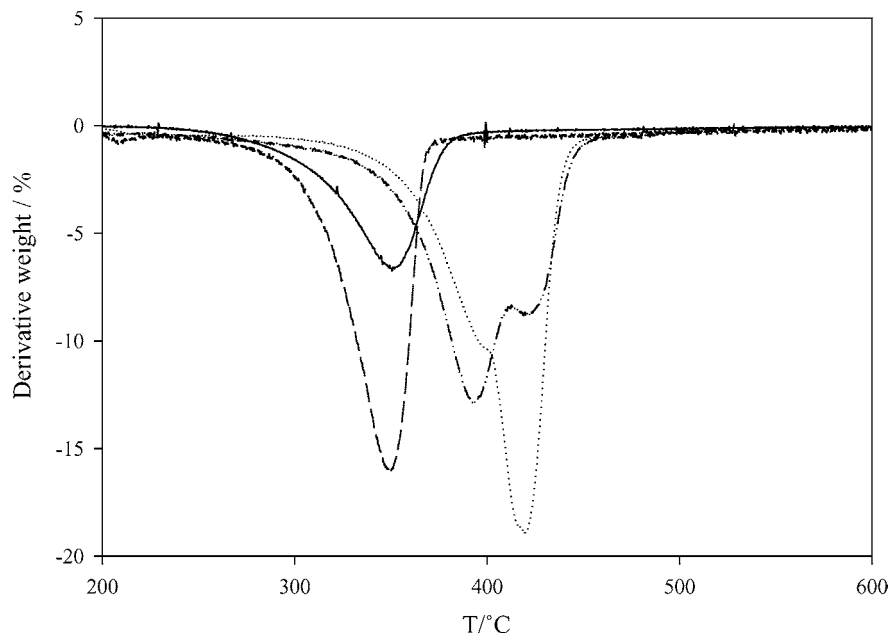
Fig. 5. TGA curves of untreated (—), oxidised ([NaIO$_4$] 0.1 M for 4 h) (- - -) and grafted linen with PEA (monomer/cellulose: 1.5) (-·-··-) and PEA (monomer/cellulose: 3.3) (· · ·).

the one corresponding to the decomposition of cellulose (see Fig. 3).

Comparing the thermal behaviour of PMMA and PEA grafted cotton (monomer/cellulose ratio: 1.5), the peak related to the cellulose decomposition shifts to higher temperature in comparison with the untreated and oxidised material, depending on the different amount of grafted polymer. The exothermic peak observed at 300 °C for the ungrafted sample shifts at 305 °C for 37% PMMA grafting yields (see Table 2) and at 335 °C for a sample containing 54% PEA grafting yields.

3.3. Thermal analysis: TGA

The results on the TGA carried out by determining the decomposition temperature (T_d) as the maximum of the derivative curve of ungrafted, oxidised and grafted linen with PEA have been shown in Fig. 4.

In accordance with the literature [23,24] it has been established that there is no degradation taking place until 200 °C. Above this temperature thermal stability is gradually decreasing and decomposition of the fibres occurs.

The effect of the degradation, due to the oxidation process, on the thermal stability of cellulose has been revealed with the shift of the derivative curve maximum to lower temperature, in comparison with the one of untreated linen. Grafted linen shows two different step: one peak below 400 °C and another one around 420 °C. The first peak is assigned to the decomposition of cellulose and it shifts to higher temperature in comparison with untreated and oxidised linen. The second peak is related to the degradation of grafted PEA; in order to

confirm this result, the acrylic homopolymer has been analysed by TGA analysis. In DTG curve the decomposition of PEA is evident at about 420 °C.

Therefore grafting polymerisation allows regaining the thermal stability.

The thermogravimetric curves of the ungrafted, oxidised and grafted cotton with PEA at different ratio monomer/cellulose are given in Fig. 5; they are similar to the curves of linen, as shown in Fig. 4. When the ratio EA/cellulose increases from 1.5 to 3.3, the second peak, related to the polymer degradation, becomes more evident. Data confirm the thermal stability of grafted cellulose increases and the grafting yields influence the decomposition of the substrates.

4. Conclusions

The studies here reported give an insight in understanding the structural changes occurring when cellulosic materials are oxidised and grafted with acrylic polymers.

Methyl methacrylate and ethyl acrylate have been grafted onto cotton and linen fabrics, previously oxidised by sodium methaperiodate, with the intent to reproduce natural oxidative ageing. In the same reaction conditions, cotton shows grafting yields higher than linen; in every experiment PEA leads to higher yield and lower homopolymer percentage than PMMA.

DSC and TGA curves of the oxidised samples show changes in respect to the starting materials. For every oxidation the first peak shifts to lower temperature, because the

oxidised cellulose is already degraded with a large fraction of oligomers and therefore less energy is necessary for their thermal decomposition.

In the grafted textiles two degradation steps, concerning cellulose and acrylic polymer, respectively, are observed and the key peak splits in two. Regarding the cellulose decomposition, the peak shifts to higher temperature than the untreated fabric. The shift can be explained assuming that the grafted cellulose has a better thermal stability due to the presence of acrylic polymer.

Therefore we can evaluate by thermal analysis the level of degradation and the effectiveness of the grafting polymerisation to improve the properties of cellulose based textile.

These observations suggest that the thermal analysis data contain information related to the structural properties of the different materials, and may be used to predict properties that are directly related to their physical performance as well as their thermal degradation parameters.

References

[1] F. Khan, S.R. Ahnad, J. Appl. Polym. Sci. 65 (1997) 459.
[2] S. Vicini, E. Princi, E. Pedemonte, Recent Res. Dev. Macromol. 6 (2002) 59.
[3] C.E. Butler, C.A. Millington, D.W.G. Clements, in: E.F. Hansen, W.S. Ginell, S.H. Zeronian, Historic Textile and Paper Materials, vol. II, American Chemical Society, USA, 1989, p. 34.
[4] U.J. Kim, S. Kuga, M. Wada, T. Okano, T. Kondo, Biomacromolecules 1 (2000) 488.
[5] M. Azam Ali, M.A. Khan, K.M. Idriss Ali, G. Hinrichsen, J. Appl. Polym. Sci. 70 (1998) 843.
[6] P. Gosh, D. Dev, Eur. Polym. J. 32 (1996) 165.
[7] F.E. Okieimen, D.E. Ogbeifun, Eur. Polym. J. 32 (1996) 311.
[8] P. Cremonesi, B. Focher, L. D'Angiuro, Cellulose Chem. Technol. 4 (1970) 497.
[9] P. Cremonesi, B. Focher, L. D'Angiuro, Cellulose Chem. Technol. 6 (1972) 145.
[10] P. Cremonesi, B. Focher, L. D'Angiuro, Cellulose Chem. Technol. 6 (1972) 277.
[11] M.L. Burstall, C.E. Butler, C.C. Mollett, J. Inst. Paper Conserv. 10 (1986) 95.
[12] S. Soares, G. Camino, S. Levchik, Polym. Deg. Stab. 49 (1995) 275.
[13] S.R. Shukla, G.V. Gopala Rao, A.R. Athalye, J. Appl. Polym. Sci. 44 (1992) 577.
[14] M.J. Fernandez, M.D. Fernandez, I. Casinos, G.M. Guzman, J. Appl. Polym. Sci. 39 (1990) 2219.
[15] S. Vicini, E. Princi, G. Luciano, E. Franceschi, E. Pedemonte, D. Oldak, H. Kaczmarek, A. Sionkowska, Thermochim. Acta 418 (2004) 123.
[16] S. Margutti, S. Vicini, N. Proietti, D. Capitani, G. Conio, E. Pedemonte, A.L. Segre, Polymer 43 (2002) 6183.
[17] C.E. Brockway, J. Polym. Sci., Part A 2 (1964) 3733.
[18] P. Goshy, G. Gangopadhyay, Eur. Polym. J. 36 (2000) 1597.
[19] F. Shafizadeh, A.G.W. Bradbury, J. Appl. Polym. Sci. 23 (1979) 1431.
[20] S. Lerdkanchanaporn, D. Dollimore, K.S. Alexander, Thermochim. Acta 324 (1998) 25.
[21] C. Flaquè, S. Montserrat, J. Appl. Polym. Sci. 42 (1991) 3205.
[22] R.K. Jain, K. Lal, H.L. Bhatnagar, J. Appl. Polym. Sci. 30 (1985) 897.
[23] A.K. Bledzki, J. Gassan, Natural Fiber Reinforce Plastics, Handbook of Engineering Polymeric Materials, Marcel Dekker Publishers, New York, 1997, p. 810.
[24] J. George, S.S. Bhagawan, S. Thomas, J. Therm. Anal. 47 (1996) 1121.