THERMAL CHARACTERISATION OF CELLULOSE BASED MATERIALS
Investigation of water content

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Natural polymers, as cellulose, with hydrophilic groups such as hydroxyl groups have various strengths of interaction with water. Cellulose is a structurally heterogeneous polymer, consisting of paracrystalline and amorphous domains. Water can interact with the amorphous domains, but it is excluded almost completely from the crystalline regions. The purpose of this study was to estimate the amount of bulk free water in cellulose based materials, as linen, cotton and paper, by measuring the heats of vaporisation. Moreover the amount of free water in oxidised and grafted samples has been determined by DSC and this quantity has been compared with that found in the corresponding native materials. In oxidised cellulose the water content increases with decreasing the degree of crystallinity; the oxidation, being a degradative reaction, modifies the amorphous content in the cellulose. In presence of acrylic grafted polymer, the free water content is reduced and this reduction is related to the grafting yields.

Keywords: cellulose, DSC, grafting polymerisation, water content

Introduction

Cellulose is the most abundant biopolymer present in nature; it has a strong interaction with water, both in the liquid and in the vapour phase, due to the hydroxyl groups in the glucopyranose ring. In presence of excess of water, hydrated polymers may swell and exhibit changes in mechanical and chemical properties. Actually, water can platicise the natural polymer or form stable bridges through intermolecular hydrogen bonds, as suggested from water absorption studies [1]. Also thermal properties of cellulose and water are markedly influenced through their interaction [2–4]. The behaviour of water can be transformed in presence of a polymer, depending on polymer characteristics and on the physical association between water and polymer.

Cellulose is a structurally heterogeneous polymer, consisting of paracrystalline and amorphous domains. Water can interact with the amorphous domains, but it is excluded almost completely from the crystalline regions [5, 6]. Water molecules, when they diffuse into the amorphous region, can break intermolecular hydrogen bonds among cellulose chains, increasing their intermolecular distance [7]. Therefore the absorbed water can cause an increase in cellulose chain mobility by opening the intermolecular space and allowing more water molecules to enter and to form hydrogen bonds with cellulose. At saturation, water absorption in the amorphous domains leads to swelling and to the formation of trapped water [8].

From a thermodynamic point of view, at least three states of water of hydration are recognised. Type I water, which corresponds to bulk free water, does not interact with the polymer and behaves as normal water in terms of its melting and freezing; it may be described as unbound water or freezing water. Type II water is loosely bound to the polymer, displays considerable supercooling and therefore freezes at lower temperature compared to bulk water (freezing bound water). Type III water is tightly bound to the polymer and it is incapable of freezing (non freezing bound water). The sum of Types II and III water may be defined as the bound water content [9].

In this article we reported the results of a study concerning the water uptake by raw and modified cellulose. The uptake of water vapour depends on the chemical structure and on the physical properties of the material, and on the ambient relative humidity, which determines the equilibrium moisture content. The main purpose of our research was to estimate the amount of bulk free water (Type I) in cellulose based materials including linen, cotton and Whatman paper, by measuring the heats of vaporisation during heating. The bulk free water content in the raw materials is compared to that present in cellulose modified by photoinduced grafting polymerisation of acrylic monomers [10, 11]. Results were correlated to the moisture regain values and to the crystallinity degree of the analysed samples.

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The first step of the investigation has been the preparation of the grafted samples. For the grafting process to occur, the presence of photo-sensitive agents onto cellulose chain is required. These are either created by an artificial ageing or by an oxidative reaction with sodium methaperiodate. In the presence of acrylic monomers in the vapour phase, these reactive sites become the starting point for the grafting reaction, induced by UV light. Methyl methacrylate and ethyl acrylate monomers have been used in this study.

Experimental part

Materials

The cellulose substrates were Whatman paper, linen Artemisia and cotton Ghinea; the fabrics are by Zecchi (Italy).

Reagents were commercial products supplied by Aldrich. Monomers (methyl methacrylate MMA, ethyl acrylate EA and 2,2,2-trifluoroethyl methacrylate TFEMA) contained an inhibitor (hydroquinone monomethylether), which was removed by passing each of them through an Aldrich Inhibitor Removers column; the purified monomers were subsequently stored at low temperature (4°C), in the dark. Sodium methaperiodate (NaIO$_4$), acetone and methanol were laboratory grade products from Aldrich and were used without further purification. Deionised water was used throughout the work.

Methods

Artificial ageing of cellulose

With the intent to form the photo-sensitive sites on cellulose [12, 13], an oxidative reaction with sodium methaperiodate was carried out on cellulose based materials before the grafting process. Periodate oxidation is a highly specific reaction that cleaves the C2–C3 bond of the glucosidic ring and converts the 2,3-dihydroxyl groups in two aldehyde groups, without significant side reactions [11]. To investigate the cellulose behaviour at different level of oxidation, the samples have been treated with different solutions of sodium methaperiodate and for different times:

- Cotton: [NaIO$_4$] 0.1 M for 4 h
- Linen: [NaIO$_4$] 0.1 M for 2 h and [NaIO$_4$] 0.4 M for 1 h
- Whatman paper: [NaIO$_4$] 0.1 M for 2 and 6 h and [NaIO$_4$] 0.4 M for 1 h

The ratio sample/solution was kept for all experiments at 1 g /100 mL.

Natural ageing of cellulose

Whatman paper and fabrics were undergone to a natural ageing. The natural weathering was conducted outdoor in Genova (Italy), in a green area close to the sea, where the local traffic is the only source of pollution. Samples were exposed to the south at an angle of 90° from horizontal, for 6 months (from March to September 2003), characterised by sun, no rain, high temperature and high humidity.

Grafting reaction

The photo-initiated grafting reaction was carried out on naturally and artificially aged cellulose based materials, as already described in a previous paper [11]. Monomers are used in the vapour phase; ethyl acrylate and two different monomers mixtures were employed: EA/MMA 75/25 mass% and EA/MMA/TFEMA 73/24.5/2.5 mass%.

The drawback of the grafting 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 [14, 15].

The quantity of grafted monomer is evaluated as the mass increase of the sample:

$$\text{Graft yields } (GY) \% = (W_2 - W_1) \cdot 100 / W_1$$

where W_1 is the initial mass of the sample and W_2 is the grafted mass of the sample after extraction of the homopolymer.

Moisture regain measurement

Moisture regain of ungrafted, aged and grafted cellulose based materials was determined by the desiccator method [16]. Samples were placed in a small weighting bottle and dried in vacuum oven at 70°C to constant mass (Wd). The dried samples were then placed in a desiccator for 24 h (Relative Humidity of 34%, $T = 18$°C). The moisturised samples were weighted again (Win) and the moisture regain was given by:

$$\text{Moisture regain (\%)} = (Win - Wd) / Wd \cdot 100$$

Moisture regain was measured also after 120 h in the same way.

Differential scanning calorimetry (DSC)

Samples were analysed by DSC, in order to detect the amount of bulk free water. The dried samples were placed in a desiccator for 24 h (to give a relative humidity of 34% at 18°C) before the scan. A TA Instruments DSC 2010 DSC was used, with a heating rate of 20°C min^{-1}; traces were recorded in the temperature range from –40 to 230°C under nitrogen atmosphere.

Results and discussion

Grafting reaction

Grafting polymerisation has been carried out onto naturally and artificially aged Whatman paper, linen and cotton. In Table 1 the grafting yields obtained by using two different monomers mixtures, EA/MMA 75/25 mass% and EA/MMA/TFEMA 73/24.5/2.5 mass%, are reported.

From data collected in Table 1, it is evident that the grafting reaction leads to the highest yield for Whatman paper. Comparing the textiles, higher yields for oxidised cotton with respect to linen are obtained, as already observed in previous studies [11]. When cellulose undergoes a stronger oxidation, more glucosidic units are oxidised to get the dialdehydic groups that act as radical sites for the polymerisation, after UV irradiation [17]. Notwithstanding more sites for the grafting process are present, the grafting yields does not increase; this effect is not easily explained and could be due to the termination step of the polymerisation.

Concerning naturally aged linen and cotton, the trend of grafting yields is similar to that of artificially aged; whereas naturally aged Whatman paper shows the lowest grafting yields.

By comparing the grafting yields obtained in all cases by using the two different monomers mixtures, EA/MMA and EA/MMA/TFEMA, it is evident there is a small decrease in presence of the fluorinated monomer.

Moisture regain measurement

Absorption and desorption of moisture are typical characteristics of cellulose based materials; their moisture content is always in equilibrium with the relative humidity of the environment; water molecules interact directly with the hydrophilic groups of cellulose chains. Every variation of the relative humidity involves a modification of the moisture of cellulose, with a rate depending on the material nature and shape. Moisture regain (MR) gives an indication of the accessibility of moisture in the fibres and of the Type I water. Since the water molecules penetrate in the pores of fibres only in the amorphous region, a high MR value in the sample means a low crystallinity degree of the material [18].

In Table 2 MR values for untreated, aged and grafted linen, cotton and Whatman paper are collected.

Untreated materials show a comparable MR, which increases after the oxidation treatment. As demonstrated in a previous work [19], after oxidation the crystallinity degree in cellulose based materials values decreases and this decreasing is correlated, at fixed time of oxidation, with the concentration of the oxidizing agent and, at fixed concentrations, with the oxidation times. Also the CP-MAS ^{13}C NMR analysis [19] confirms that, increasing the oxidation conditions, the amorphous phase in the cellulose progressively rises. Naturally aged samples show comparable MR value with the raw materials, because natural ageing induce a lower reduction of crystallinity. Therefore the ageing reduce the crystallinity of the cellulose and the moisture can penetrate in a larger amount in the material, increasing the MR value.

Concerning the grafted samples, MR value are low, because the presence of the acrylics, that have a hydrophobic character, reduces the water accessibility. The crystallinity of grafted sample is not influenced by the presence of the polymer and is similar to that of the aged materials [20].

Differential scanning calorimetry

Starting form the results of the moisture regain measurements, all the samples were analysed by DSC, in order to detect the amount of bulk free water (Type I) by measuring the heats of vaporisation during heating. The heat of vaporisation of bulk free water was calculated from an integration of the DSC peak. The amount

Table 1 Grafting yields for naturally and artificially aged cotton and linen grafted with EA/MMA 75/25 and EA/MMA/TFEMA 73/24.5/2.5

Sample	EA/MMA 75/25 Grafting yield/%	EA/MMA/TFEMA 73/24.5/2.5 Grafting yield/%
Cotton ox NaIO$_4$ 0.1 M 4 h	66	49
Cotton naturally aged	49	37
Linen ox NaIO$_4$ 0.1 M 2 h	36	26
Linen ox NaIO$_4$ 0.4 M 1 h	32	28
Linen naturally aged	45	35
Whatman ox NaIO$_4$ 0.1 M 2 h	96	84
Whatman ox NaIO$_4$ 0.1 M 6 h	88	71
Whatman ox NaIO$_4$ 0.4 M 1 h	64	57
Whatman naturally aged	23	20

Table 2 Moisture regain value for cellulose based materials

Sample	Treatment	MR 24 h/%	MR 120 h/%
Cotton	Untreated	2.39	3.10
	Ox NaIO$_4$ 0.1 M 4 h	2.51	3.24
	Naturally aged	2.57	3.29
	Ox 0.1 M. Grafted EA/MMA	1.49	1.49
	Ox 0.1 M. Grafted EA/MMA/TFEMA	1.70	1.70
	Naturally aged. Grafted EA/MMA	1.82	2.01
	Naturally aged. Grafted EA/MMA/TFEMA	1.74	2.16
Linen	Untreated	2.40	3.25
	Ox NaIO$_4$ 0.1 M 2 h	2.69	3.60
	Ox NaIO$_4$ 0.4 M 1 h	2.90	3.84
	Naturally aged	2.67	3.41
	Ox 0.1 M. Grafted EA/MMA	1.79	1.92
	Ox 0.1 M. Grafted EA/MMA/TFEMA	1.82	1.96
	Ox 0.4 M.Grafted EA/MMA	1.86	1.98
	Ox 0.4 M.Grafted EA/MMA/TFEMA	1.99	2.38
	Naturally aged. Grafted EA/MMA	1.69	1.77
	Naturally aged. Grafted EA/MMA/TFEMA	2.04	2.34
Whatman paper	Untreated	2.30	3.10
	Ox NaIO$_4$ 0.1 M 2 h	2.55	3.46
	Ox NaIO$_4$ 0.1 M 6 h	2.91	3.79
	Ox NaIO$_4$ 0.4 M 1 h	3.03	4.01
	Naturally aged	2.41	3.39
	Ox 0.4 M. Grafted EA	0.40	0.76
	Ox 0.4 M. Grafted EA/MMA/TFEMA	1.24	2.48
	Naturally aged. Grafted EA	0.90	1.47

of free water in oxidised and grafted samples has been compared with that found in the corresponding native materials. Free water is considered as unbound water in cellulose; its transition enthalpy and the peak shape in DSC curves are equal to those of pure water.

Initially for every sample two successive heating cycles were performed, in order to confirm that with the first heating the water was completely removed.

No glass transition appears for the cellulose in the scan temperature interval; it is well known that the glass transition detection for cellulose is very difficult and only with particular scan conditions it is possible to determine it [21].

By comparing the raw materials, an endothermic peak corresponding to the water vaporisation appears at about 70–80°C for textiles and at about 100°C for Whatman paper. The heats of vaporisation are comparable and vary in the range from 12 to 15 J g^{-1}.

Natural ageing of cellulose based materials does not significantly modify the water content, as demonstrated from the value of vaporisation enthalpies. As shown in Fig. 1 naturally aged Whatman paper has a vaporisation enthalpy of 13 J g^{-1}.

In oxidised cellulose the water content increases with decreasing the degree of crystallinity. This fact is explained by considering that the oxidation, being a degradative reaction, enhances the amorphous content in the cellulose. For cotton, vaporisation enthalpy increases to 24 J g^{-1}(Fig. 2). For linen, we can observe
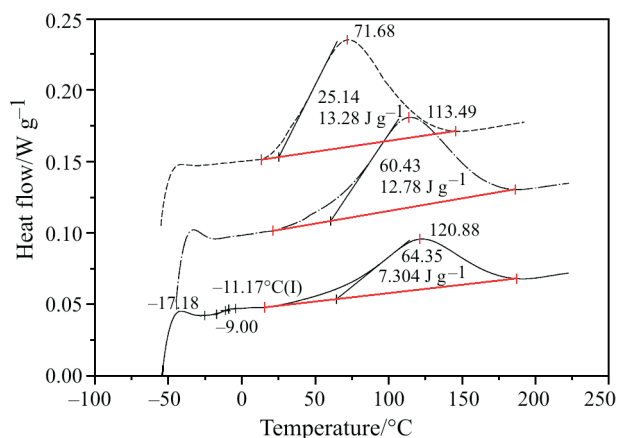
Fig. 1 Water vaporisation curves of raw, naturally aged and grafted (with PEA) Whatman paper
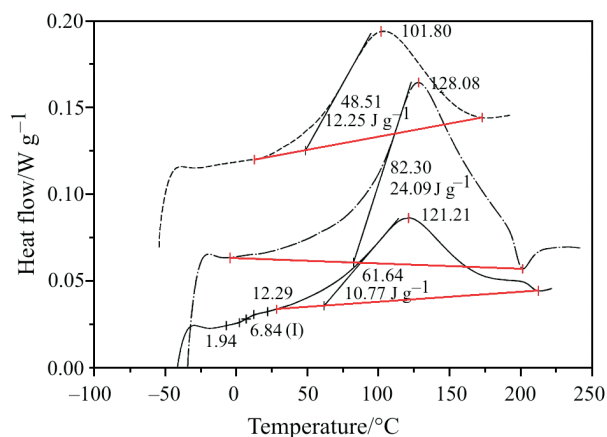
Fig. 2 Water vaporisation curves of raw, artificially aged and grafted (with EA/MMA 75/25) cotton

a rising of enthalpy when the oxidation conditions become stronger: 26 J g^{-1} for [NaIO$_4$] 0.1 M and 38 J g^{-1} for [NaIO$_4$] 0.4 M. In the case of Whatman paper, vaporisation enthalpy is about 27–30 J g^{-1} for the oxidations with [NaIO$_4$] 0.1 M and it gets to 35 J g^{-1} using [NaIO$_4$] 0.4 M.

In presence of grafted polymer the free water content is reduced in respect to the raw materials, because of the hydrophobic nature of acrylics, as shown in Figs 1 and 2 for Whatman paper and cotton respectively. During the heating it is also possible detect the glass transition temperature of the grafted polymers: –9°C for polyethyl acrylate, about 8°C for the copolymer EA/MMA and the terpolymer EA/MMA/TFEMA.

Conclusions

The amount of free water in oxidised and grafted samples has been determined by moisture regain measurement and by DSC analysis; this quantity has been compared with that found in the corresponding raw materials. DSC data confirmed the MR results, obtained by a gravimetric technique.

In oxidised cellulose the water content raises with decreasing the degree of crystallinity, because the oxidation increases the amorphous phase.

In presence of acrylic grafted polymer, the free water content is reduced and this reduction is related to the water repellence properties of acrylics.

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