Effect of the macro-structure on the flammability of the oxidized PAN fibre based woven textiles

Dr. **Zsuzsanna Kerekes,** Ph.D
Dr. **László Beda,** Ph.D
Szent István University, Ybl Miklós Faculty of Architecture and Civil Engineering
Institute of Fire Protection and Safety Engineering
Budapest, Hungary
e-mail: Kerekes.Zsuzsa@ybl.szie.hu
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In this work, the micro- and macro structure properties which determine the flammability of the end products (woven textiles) produced from 100 % oxidized PAN fibres, based on their micro structure properties were examined. The conclusion was that the flammability of an end product can be defined and tested in two forms: one form is the oxidized PAN fibre as main product (micro structure) and the other is the woven fabric made from these fibres (macro structure). A textile produced from a certain oxidized fibre shows different flammability and oxygen index if the types of woven fabrics are different. The authors also concluded that the oxygen index, which characterises the flammability of an end product, is in correlation with the main parameters (e.g.: density) of the macro- and micro structures. Based on the results obtained it seems, that to characterise the flammability of the end products it is not enough to give only the standardized oxygen-index and it is not enough to give only the LOI parameter of the base material.
***Key words**: flammability, fire resistance, oxygen index, oxidized PAN fibre, areal weight*

1. Introduction

Carbon fibre based products, due to their special properties, are used in applications where heat and fire resistance need to be ensured, e.g.: protective clothing including protective gloves, fire blankets, automotive industry including thermal insulations and internal lining of vehicles [1-3]. Advantages of uses of oxidized fibre come from its unique heat stabilized molecular structure. Non-flammability is ensured by a partly homogenous and partly heterocyclic structure with high carbon-content (greater than 60 %).

The final chemical structure of the oxidized PAN fibres are formed during the production process and the micro structure of the fibre works out [4]. The fibre parameters of the micro structure are the fibre density (g/m^3) [5], the carbonisation index, the cyclization index [6], the stabilization index [7] and the chemical composition (carbon, nitrogen, oxygen content).

It was shown in our previous work that there is a correlation between these parameters, so in recent work we highlight the fibre density – that can easily be measured during the manufacture - and consider it as a primary micro parameter.

The macro structure of the textiles made from fibres is developed in the textile manufacturing process. The flammability of a product is determined both by their micro- and macro structure [8]. The macro structure parameters of the woven textiles are the areal weight (g/m^2), the weave density and the type of construction. The areal weight is determined by the fibre density, the size of yarn, the yarn density and the weave type together. The carbon-based products and the carbon fibre itself are qualified, beside their mechanical and physical properties (fibre density, fibre diameter, tensile strength) by supplying their oxygen index [9].

There are several methods to describe the flammability of various materials, such as the ignition temperature, smoke production, heat generation, the ease of ignition, the flame propagation in different directions. The flammability of materials can also be characterized by their minimal oxygen concentration required to maintain of burning. The majority of flammable materials are capable of combustion at normal oxygen levels (21 vol %.), but there are materials that burn at lower or higher oxygen concentration in comparison. The Limiting Oxygen Index (LOI) measures how much oxygen is needed to sustain combustion. In other words, it is the minimum concentration of oxygen, expressed as a percentage that will support combustion of a material.

The LOI parameter can also be used for fire protection qualification of carbon fibres, oxidized fibres and materials made from those.

A material with LOI of greater than 21 % but less than 28 % would be considered "slow burning", with LOI of greater than 28 % would be considered "self-extinguishing" and LOI =100.00, "non-flammable" material. A self-extinguishing material is one that would stop burning after the removal of the fire or ignition source [10, 11].

In one of our earlier work it was shown that as the temperature rises during the manufacturing process, the fibre density and also the oxygen index is growing [8, 9, 12].

The Limiting Oxygen Index test is a widely used research and quality control tool for determining the relative flammability of polymeric materials, although in principle it is applicable to all combustible solid materials. LOI is measured by passing a mixture of oxygen and nitrogen over a burning specimen, and reducing the oxygen level until a critical level is reached. The test is a standardized and can be carried out using ISO 4589 or ASTM D2863 [13].

Numerous works and experiments deal with methods to improve the oxygen index of different types of textiles by specific treatment or additional materials. Weidong Wu and collaborators found correlation between Limited Oxygen Index (LOI) and the different finishing processes [14,15] and also there are new methods in the literature for modifying the textile properties [16-19].

2. The instrument for determination of LOI

In our work we used FIRE type oxygen index test apparatus, equipped with paramagnetic oxygen analyser according to ISO 4589. The accuracy of measurement: 0.1

The main part of the instrument is shown in Fig.1. The sample holder is a 6 x 16 cm, U shaped, double layered vertical metal frame, secured in a glass cylinder with its top end open. The source of ignition is a 4 cm long gas-flame as prescribed by standards. The specimen is ignited along the upper edge applying the flame for maximum of 15 seconds. Burning proceeds downwards against the flow of the pre-adjusted gas mixture. Nitrogen and oxygen content are adjustable as required [13].

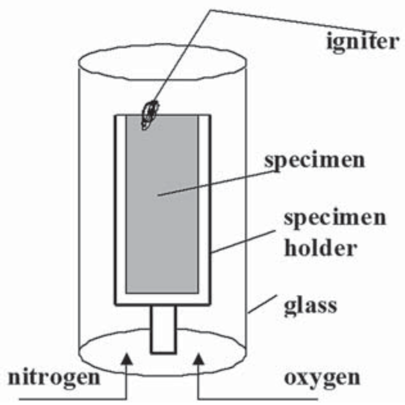

Fig.1 Diagram of the apparatus for determination of oxygen index

3. Parameters of the samples

The samples were tested as finished industrial products; therefore the raw materials and the surface density were defined *a priori* by the production technology. The density of the tested fibres was between 1.35 and 1.42 g/m^3 according to industry data. The testing samples and their parameters are summarized in Tab.1. The notations used in the Table refer to the type of construction, the numbers refer to the groups of parallel samples.

PW - plain wave,
SW - satin wave,
TW - twill herring bone,
AS - textile from Japan,
KF - knitted fabric.

The samples were made from 100 % oxidized PAN fibre. In the present paper the overall effects of the textile parameters on the oxygen index, including the type of construction, are examined.

4. Results and discussion

4.1. Effect of area weight on the oxygen index

The surface density is determined by the fibre density and the weave density. We examined how they affect the oxygen index of the final product. The measured values can be seen in Fig.2. In the range of 300 and 400 g/m^2 surface density LOI values significantly vary between 30 and 54. Deviation of the values can be attributed to the differences in the fibre density.

Depicted the LOI vs. fibre density close relationship can be realized (Fig.3). The samples with low LOI values typically have low fibre density, 1.37 g/cm^3 or below. The LOI of a product made from fibres having a density more than 1.4 g/m^3 is significantly higher.

The fibre density looks to be the determining factor. This statement will be confirmed, if two textiles with the same fibre density are compared (1.37 g/cm^3), one is the SW01 which area weight is 460 g/m^2 and the other

Tab.1 The testing samples and their parameters

Type of fabric	Sample identity	Type of construction	Areal weight (g/m²)	Fibre (dtex)	Fibre density (g/cm³)	LOI
Woven fabric	PW01	Plain	360	1.7	1.35	29.9
	PW02	Plain	340	1.7	1.37	30.2
	PW03	Plain	310	1.7	1.35	32
	PW04	Plain	190	1.7	1.4	50
	SW01	Satin Weave	460	1.4	1.37	31
	SW02	Satin Weave	470	1.7	1.39	35.4
	TWH	Twill herring bone	420	1.7	1.395	43.3
	TW*	Twill herring bone	980	1.7	1.4	58
	TWC	Twill	410	1.7	1.4	53
	AS	Plain	400	1.7	1.42	54
Knitted fabric	KF01	Double Interlock	340	1.7	1.35	31
	KF02	Double Interlock	340	2.2	1.37	32.1
	KF03	Double Interlock	330	1.7	1.37	33.5

TW*edge of the fabric, where the weave is very dense: LOI: 52, while inside: LOI: 43,3

is the PW02 which area weight is 360 g/m², both LOI value is nearly 30 (Tab.1).

In case of TWH samples with high fibre density it was observed as well, that at the edge of the textile where the areal weight is higher because of the technology, the value of the oxygen index is higher (LOI = 52), while inside a lower value (LOI = 43.3) could be measured. The difference is significant, 8-9 units. The edge of the sample is not flammable in 43.3 % oxygen content, while the middle of the sample is flammable.

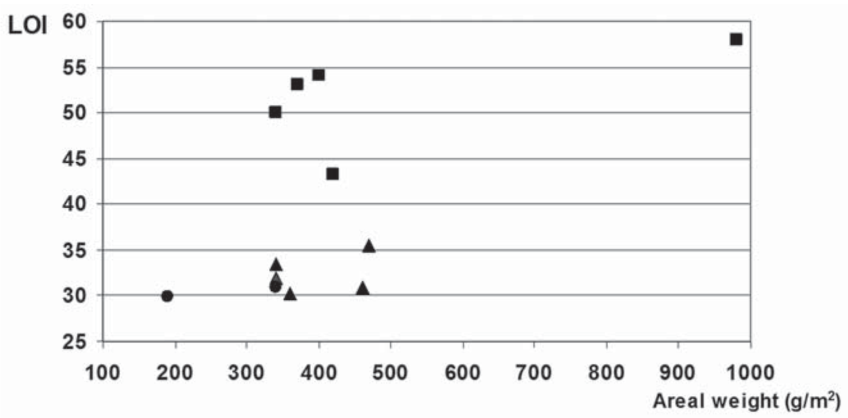

Fig.2 LOI vs. areal weight at plain and twill textiles (based on data of Tab.1)

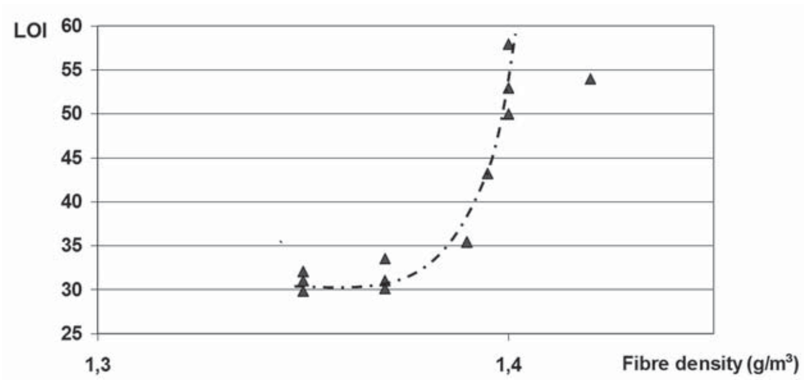

Fig.3 Effect of fibre density on the LOI of the macro structure

Difference could be observed between the low and high area weight textiles regarding their burning phenomena. The samples with LOI < 29-30 were carbonised after burning and fragile frame remained, while the dense textiles even kept their woven pattern and in some cases they kept their tear resistance too. This is also true for knitted fabrics, for which the oxygen index in elastic (weft) direction is LOI = 33.0, in inelastic (warp) direction is LOI = 33.3. 2-3 mm flame length is typical for their burning. They keep also their elasticity after burning despite their thickness.

Summarized: the changing of oxygen index is not linear with the macro structure parameters however a micro structure parameter, the fibre density is determining. Another finding in case of woven fabrics is that LOI higher than 50 can only be achieved if the fibre density higher than 1.39. On the basis of LOI values the burning behaviour of the material can be predicted, for example if LOI greater than 50 there is no flaming combustion.

4.2. Effect of weft yarn density on oxygen index

The areal weight of textiles includes the density of warp and weft yarns

Tab.2 Effect of yarn density on oxygen index in case of plain fabric

Sample	Areal Weight g/m²	Warp yarns /10 cm	Weft yarns/10 cm	Thickness mm	LOI, %		Fibre density, g/cm³	
					L	T	L	T
PW011	365,55	**97,0***	**95,0***	0,76				
PW012	366,43			0,78				
PW013	365,45			0,75				
PW014	363,23			0,74				
PW015	368,02			0,76				
PW01*	**365,74***			**0,76***	**31,9**	**32**	**1,37**	**1,37**
PW021	343,76	**95,0***	**82,0***	0,76				
PW022	344,01			0,76				
PW023	345,37			0,74				
PW024	338,12			0,78				
PW025	334,87			0,72				
PW02*	**341,23***			**0,752***	**32,4**	**32**	**1,37**	**1,37**
PW031	309,00	**94,0***	**70,0***					
PW032	307,29							
PW033	310,19							
PW034	314,77							
PW035	317,18							
PW03*	**311,69***			**0,75***	**32,4**	**32**	**1,38**	**1,38**

L - Longitudinal, T - Transversal
* averages

(warp or yarn/10 cm). The examined sample was such a PW type, which average areal weight is 360 g/m², so regarding the oxygen index it laid in the low LOI range (Tab.2). The weft density was modified in order to reduce the area weight. The weft density was reduced from 95/10 cm yarns to 70/10 cm, meanwhile the LOI of the textile changed from 31.9 to 32.4. This change is not considerable, the LOI values stayed in the lower range. There was no possibility for more rarefaction of the yarns because of the set of the producing machine. This result confirms that the flammability of loose structure fabric textiles with low areal weight is determined firstly by the oxygen index of the fibres and not by the macro structure of the textile.

4.3 Effect of warp and weft fibre density on the oxygen index

In these tests also the effects of the macro structure parameters were examined. The effect of the weft and warp was tested meanwhile the structure of the textile was not modified and the textile density was even. We examined whether the oxygen index of the textile would change if the fibre density of the weft and warp is different (and so the LOI as well), but their average is the equal. The results show that the oxygen index of the textiles will also be equal. So when in a textile the fibre density of the weft or warp modifies, but their average is the same, there will be no difference between the oxygen indexes (Tab.3).

4.4. Effect of heat treatment on the oxygen index

During the utilization, it can happen that a product is not appropriate by the view of combustibility. In these cases, they try to burn down adsorbed materials from the surface with posterior heat treatment. This kind of treatment causes modification on the surface of the fibres. The samples exposed to the heat treatment had different macro structure (Tab.4).

The heat treatment took for a maximum one hour on 200 and 250 °C. We compared the samples' oxygen indexes before and after the heat treatment. The PAN does not contain oxygen chemically, but the stabilization step of the producing technology goes through in oxygen atmosphere, in which on the surface of the fibre the oxygen binds by chemisorption. This kind of fibre is burning with flame when the function groups bonded on the fibre surface are burning down. This phenomenon is characteristic mostly for low-density fibres. When the fibre density is higher than 1.4 g/m³, both the fibres and the fabrics is only glowing without flame. The result shows analogy with the relationship of the fibre density and area weight), here could also be observable changes in LOI values that were caused by the fibre density alterations. When the fibre density is lower than 1.4 g/m³ the heat treatment would not modify the LOI value. The same results can be considered as at areal

Tab.3 Determination of the weave homogeneity of the plain woven fabric by oxygen index (Sample area weigh: 190 g/m^2)

Plain woven fabric	Fibre density (g/cm^3)			LOI (%)
	Warp	Weft	Average	
PW041	1.375	1.373	1.374	30.7-30.8
PW042	1.380	1.371	1.375	30.1
PW043	1.380	1.373	1.376	30.7-30.8
PW044	1.376	1.376	1.376	30.0
PW045	1.375	1.375	1.375	30.6-30.7
PW046	1.376	1.376	1.376	30.9-31

Tab.4 Oxygen index of heat treated samples

Sample	Fibre density (g/cm^3)	LOI before heat treatment	LOI after heat treatment at 200 °C
PW01	1.35	32.7	33.4
TWH	1.4	43.3 - 44	44
TW	1.402	44.6	47.8
TWK	1.406	44.2	50.1
TWC1	1.4	52.8	5,28
TWC2	1.4	52.8	53-54 (250 °C)
AS	1.42	54.0	53.6

weight (Fig.2) i.e. at the range of low-density fibres no LOI increase can be seen. Increasing the fibre density the difference between the oxygen index of the treated and not treated samples was increasing as well, but this change cannot be noticed in the case of LOI > 50.

For example: in the case of PW01 samples (fibre density 1,37 g/m^3), the LOI value changed from 32.7 to 33.7, so the increase is lower than 1. At the not-treated TWILL samples (fibre density more than 1.4 g/m^3) the LOI changes from 44.6 to 47.8, the growth is more than 4 (Fig.4).

Remark: as a result of heat treatment the area weight of textiles have grown in low degree in the case of TWC samples. Before heat treatment it was 370 g/m^3, after treating on 200 ^{o}C it was 390 g/m^3, and after heat treatment on 250 ^{o}C it has changed, as a result of the shrinkage, to 396 g/m^3, which was accompanied with a low degree LOI growth as well.

5. Conclusion

The micro and macro structure properties that determine the flammability of fabrics made from pure oxidized fibres were investigated in our work. The flammability tests were based on the measurement of limited oxygen index. It was shown that the flammability of a fabric is determined by both the oxidized fibre as raw material (micro structure) and the woven structure of the knitted textiles (macro structure) made from them.

Textiles made from the same oxidized fibre but with different woven show different flammability and different oxygen index. In case of woven textiles the oxygen index of the macro structure is always lower than the LOI of the oxidized fibre used as raw material. If the oxidized fibre used as raw material, has fibre density less than 1.4 g/cm^3 and the areal weight of a loose structure fabric is less than 370 g/m^2 the value of the oxygen index of the fabric is constant around 30-33. A textile LOI value above 45 can be reached only by using high density fibres higher than 1.4 g/cm^3. We also concluded that if the fibre density of the warp and weft yarn is different but their average is the same, the oxygen index of the textiles will also be the same. It was also investigated that what is the lowest level of the weft yarn density where the oxygen index of the textile will not change. A 25 % decrease of the weft yarn density will not result in a remarkable change of LOI.

The fabric shows different burning phenomenon in the function of the oxygen concentration. If the LOI is lower than 30 the textile burn with flame and the material loses its structure: carbonizes and crumbles. They glow if LOI is higher than 48-50. It means that only those woven textiles are safely inflammable that have LOI value higher than 50. Considering the raw material, if the oxidized fibre has the LOI value higher than 50 it can be kept as thermodynamically stable against burnings and flames.

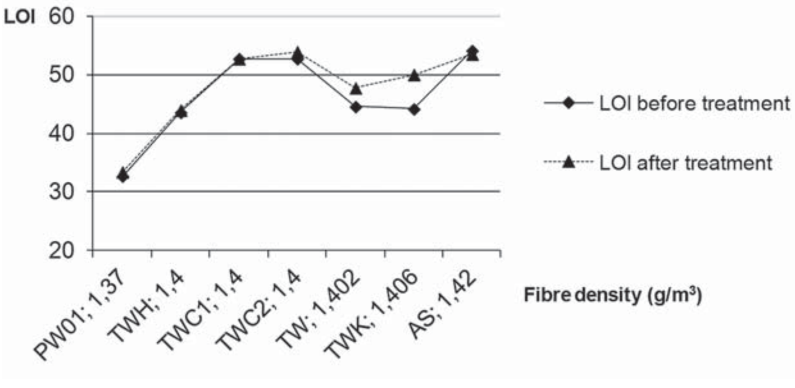

Fig.4. Change of LOI of fabrics with various macro structure after heat treatment

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