Determination of the Factors Influencing the Flame Retardant Efficiency of the Protection - Dyed Cellulose Materials Using the Analysis of Variances

VASILICA POPESCU*, LILIANA ROZEMARIE MANEA, NICUSOR AMARIEI
"Gh. Asachi" Technical University, Faculty of Textile and Leather Engineering, 53 D-trie Mangeron , 700050, Iasi, Romania

The influences of the concentration of the Pekoflam DPN 1 (active flame retardant reagent), of the cure temperature, of the neutralization efficiency and of the samples final washing after the flame retardant treatment have been studied. By using the analysis of variances there has been proved that all studied factors have significative influences on the length of the carbonization area, on the rate of spread of the flame and on the weight increasing after the flame retardant treatment.

Keywords: efficiency, flame retardant reagent, pad-dry-cure technology

The treatments whose aim is the protection against ignition and burning are known as "flame retardant or fireproofing".

The fireproofing of the cellulose materials are especially applied to the following items: protection clothing, children garments, bed linen, decorative items, furniture fabrics, etc [1-5].

Depending of their nature and structure, textile fibres are behaving differently during the ignition and burning processes [6 – 10], as follows:

– asbestos, glass fibres and some polyvinyl chlorides fibres are non-flammable fibres;

– polyamides, polyesters, polyethylenes, cellulose acetates and wool are hard flammable fibres;

– viscose, cotton, jute, flax, hemp and natural silk are easy flammable fibres;

– acrylic fibres and kapok are very easy flammable fibres.

The efficiency of any flame retardant treatment depends on the flammability of the textile product [1–10], on the combustion as well as on the post-incandescence. The flammability refers to temperature and to the heat amount necessary to ignite a textile material with a certain chemical composition and a given configuration [11-14]. The combustion indicates the development of burning after ignition while the post-incandescence is the phenomenon of burning without any flame, often being accompanied by noxious gas and vapour delivery.

This paper aims to establish the qualitative and quantitative factors influencing the efficiency of a flame retardant treatment.

Experimental part

Materials

Four identical series of 100% cotton material dyed with a Direct Blue A dyestuff, having a 0.200 Kg/m specific weight, a 35 cm length and a 3 cm width, respectively, have been subjected to the flame retardant process.

The following substances have been used for the flame retardant treatment:

- Pekoflam DPN 1 an organic phosphorous compound with a 455°C ignition temperature, a 1.24 g/cm^3 density and a 37 mL viscosity at 20°C. It is applied at room temperature and at *p*H = 4;
- ortho-phosphoric acid, the catalyst and the accomplisher of the acid medium required by the Pekoflam DPN 1 ignifugation active substance;
- Cassurite HML 1,3,5 trazine-2,4,6 – triamine, an etherified methylol-melaminic compound with 50% concentration and 1.15 g/cm^3 density;
- urea;
- Kerallon JET, a mixture of non-ionic surfactants.

Experiments

The flame retardant finishing is based on the pad-dry-cure technology which involves the following phases: pad–squeezing – drying – cure – neutralization – washing (rinsing). The efficiency of a flame retardant treatment can depend on many factors, among them being:

– concentration of the active flame retardant reagent;

– cure temperature;

– conditions of the neutralization (carbonate concentration, temperature, time period) and of the rinsing;

– pad time period;

– time period of the cure treatment.

This paper deals with the effects produced by the first three above mentioned factors.

The employed working formulas are the following:

– padding with:
X_1 g/L Pekoflam DPN 1; $X_1 \in [100 \div 600$ g/L];
40 g/L Cassurite HML;
20 g/L ortho-phosphoric acid;
5 g/L urea; 2 g/L Kerallon JET.

– squeezing at DS= 75%;

– drying at 120°C for 2 min;

– cure at X_2 °C; $X_2 \in [150 \div 180$°C] for 2 min;

– neutralization with 2 g/L Na_2CO_3 for 15 min at 30 °C.

After the flame retardant finishing, two series of samples have been subjected, without a preliminary washing after the cure treatment, to the flammability-determining test according to the STAS 8025-84, the other two series of samples passing through all five phases of the pad-dry-cure technology. The lengths of the carbonization and non-carbonization areas,

* *email: vpopescu@tex.tuiasi.ro*

respectively, the time period of the flame propagation, and incandescence as well as the loss in weight after burning have been determined.

To study the qualitative and quantitative effects exerted by the above mentioned influence factors, a mathematical method for the results analysis, namely, the bifactorial analysis of variances with systematic effects, has been employed. The following steps have been carried out for a correct usage of this method:

-a rigorous planning of the experiments so that with any of the mentioned concentration of Pekoflam DPN 1, flame retardant finishings at 150, 160, 170 and 180°C temperatures, respectively, should be accomplished;

-in fact, each experiment has been done twice, a fact justified by the existence of two identical series subjected to the analysis, with a view to obtain two readings for each cell in the analysis of variances.

Results and discussions

Mechanism for the Ignition, Burning and Combustion of Cotton

The burning and the combustion of cellulose is based on a mechanism of pyrolysis and burning in more phases. At temperatures higher than 300° C, the cellulose starts decomposing quickly with the formation of vapours and gases (flammable and non-flammable), liquid products (tars) and carbon residues. Some of these products, i. e. gases and flammable vapours, ignite around 350°C; on starting from this point, there is a spontaneous combustion with the elimination of considerable amounts of heat up to the complete carbonization (fig. 1)

In fact, the burning and the combustion of cellulose result from a pyrolysis and burning mechanism, respectively, which is based on heat accumulation phases (at 300-350°C temperature) and heat elimination ones (at 600 – 700°C). Under the influence of heat, a process of cellulose depolymerization takes place, breaking the glucosidic bonds while the glucopyranoses fragments are changed into anhydro-glucopyranose (levo-glucosane). Igniting volatile organic products as well as carbon residues result from the cracking process of the levoglucosane.

Acting mechanism of the flame retardant reagents

A flame retardant reagent can act as a rule according to two directions, namely, by decreasing the quantity of energy which is eliminated during the burning process or by increasing the quantity of energy necessary for the fibre to attain the burning stage [2]. A first method of decreasing the quantity of energy eliminated during the pyrolysis process is the burning control so that lesser flammable products should be formed; thus the quantity of heat eliminated during the burning process is being decreased [3, 4]. This is the way the fireproofing substance called Pekoflam DPN 1, a phosphorous-based organic substance, is also acting.

In what the cellulose is concerned, an ideal fireproofing should lead the pyrolysis to a complete dehydration according to the reaction (1):

$$(C_6H_{10}O_5)_n \rightarrow 6n\ C + 5n\ H_2O \quad (1)$$

Volatile substances and tars which propagate the burning with flames should not be developed. The resulted coal can propagate only smouldering with CO_2 formation.

Influence of the Pekoflam DPN 1 Concentration and of Cure Temperature

The following values have been obtained by burning the control sample (witness):

– a propagation time period of the flame of 13.75 seconds;

–an incandescence time period of 1 s;

– the length of the carbonization area L = 35 cm (the sample burnt entirely);

– the mass after burning = 0.037g.

By burning two series of flame retardant treated samples under the same conditions, but un-washed, the time periods necessary for the flame propagation have varied between 0.2 and 3 s while the incandescence time period = 0 – 0.5 s; the values for the length of the non-carbonization area are shown in table 1. The calculus for the length of the non-carbonization area is:

$$\textit{Length of the non-carbonization area} = L_{initial} - L_{carbonization\ area} = 35 - L_{carbonization\ area} \quad (2)$$

By applying the bifactorial analysis of variances with systematic effects the information shown in table 2 have been obtained.

According to the bifactorial analysis of variances both the Pekoflam DPN1 concentration and the cure temperature influence the magnitude of the non-carbonization area, i.e. the fireproofing efficiency. One knows that a great length of the non-carbonization area is equivalent with a good fireproofing effect of the applied treatment.

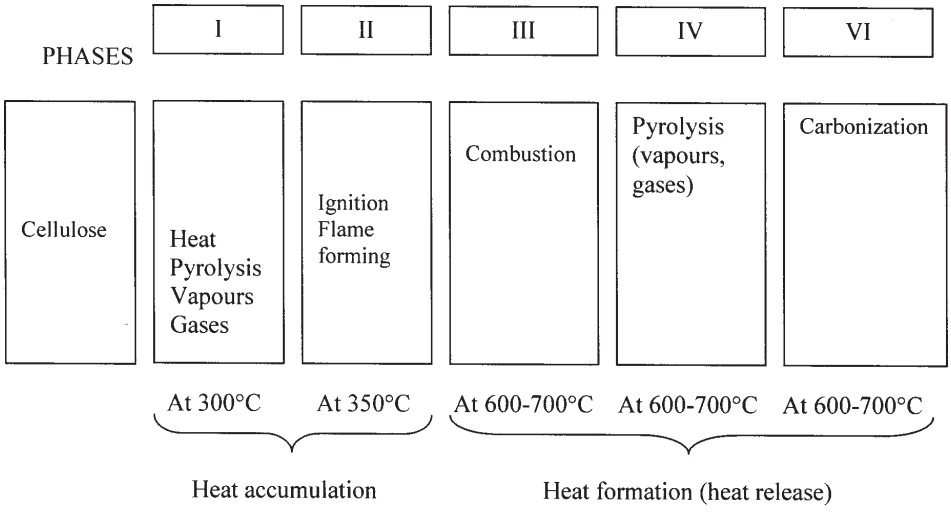

Fig. 1. Preliminary phases for the cellulose carbonization

Concentration / T_{cure} [°C]	Variation levels of the Pekoflam DPN 1 concentration					
	Level 0 *100g/l*	Level 1 *200g/l*	Level 2 *300 g/l*	Level 3 *400 g/l*	Level 4 *500 g/l*	Level 5 *600 g/l*
Level 0 *150°C*	27.5 27.6	24.4 24.7	25.8 24.5	24.7 24.9	31.4 31.7	30.5 30.9
Level 1 *160°C*	26.0 25.8	23.0 22.5	23.5 23.9	29.3 29.5	30.4 30.9	30.4 30.9
Level 2 *170°C*	23.0 22.9	24.2 24.0	24.1 24.6	25.2 25.7	30.4 30.9	33.7 34.0
Level 3 *180°C*	24.5 24.2	22.9 22.4	24.6 24.8	32.0 31.2	31.6 31.2	33.0 32.2

Table 1
THE LENGTH VALUES OF THE NON-CARBONIZATION AREA (cm)

Sourse of variation	Sum of squares	Number of degrees of liberty	Average value of squares	Fischer function	Estimation of dispersion
Line (*A=Cure Temperature*)	SP_L = 56.4206	ν_L=3	S_L^2=18.807	F_L=274.38	S^2_{Amin}=18.9356 S^2_{Amax}=18.9959
Column *(B=Pekoflam concentration)*	SP_C = 6821.90	ν_C=5	Sc^2=1364.38	F_C=19905.85	S^2_{Bmin}=852.8463 S^2_{Bmax}=852.9066
Interaction A with B	SP_{LC} = 114.45	ν_{LC}=15	S_{LC}^2=7.63	F_{LC}=111.319	S^2_{Abmin}=7.7036 S^2_{Abmax}=7.7639
Errors inside the cells	SP_{REZ} = 1.645	ν_{REZ}=24	S_{REZ}^2=0.0685	$F_{95,3,24}$=3,01 $F_{95,5,24}$=2,62 $F_{95,15,24}$=2,11	σ^2_{min}=0.03354 σ^2_{max}=0.09387
Overall error	SP_G = 6994.42	ν_G=47	.....	.....	.....

Table 2
INFORMATION REFERRING TO THE BIFACTORIAL ANALYSIS OF VARIANCES APPLIED FOR THE STUDY OF THE VARIATION OF THE NON-CARBONIZATION AREA LENGTH

According to the multiple comparison which certifies the accuracy of the analysis of variances, all concentrations of Pekoflam DPN 1 lead, with 99% probability, to a certain degree of flame retardant treatment; the greater the concentration is, the stronger this effect will be. In exchange, in what the "cure temperature" factor is concerned, the method of the multiple comparison shows the fact that only two temperatures influence the flame retardant efficiency, namely, T=160°C and T=180°C. From these two factors, i.e. the Pekoflam DPN 1 concentration and the cure temperature, the greatest effect is brought about by the concentration of the flame retardant reagent, a fact also revealed by the values S^2_{Bmin} and S^2_{Bmax} which are much higher than S^2_{Amin} and S^2_{Amax}. The interaction of these two factors also has a certain contribution in accomplishing the flame retardant effect, but the exerted influence is much smaller as compared to those produced by each factor taken separately.

The relative overall error is extremely small, namely 0.458114%.

The efficiency of the flame retardant treatment due to both the Pekoflam DPN 1 concentration and the cure temperature factors, respectively, is also evident from the variation of the weight, of the thickness of the samples (after the pad-dry-cure treatment) (figs. 2 and 3), of the length of the carbonization area (fig. 4) as well as from the decrease of the fireproofing treated samples weight after burning (fig. 5). The irregularity of the burnt area from an fireproofing treated sample has imposed the finding of a solution for a flame retardant efficiency as high as possible; that is why the decrease of the mass of the sample treated and subjected to burning has been studied; this decrease should be as small as possible to

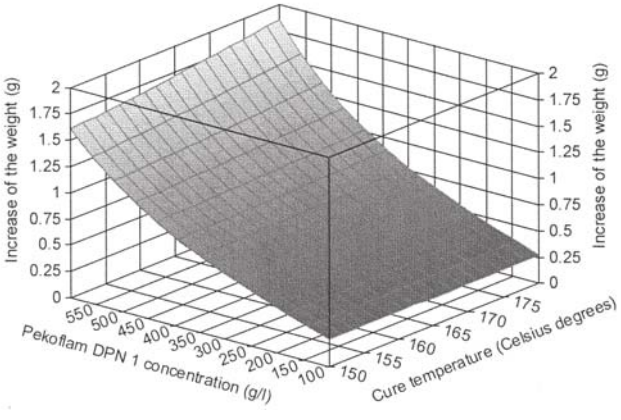

Fig. 2. Increase of the samples weight after fireproofing treatment

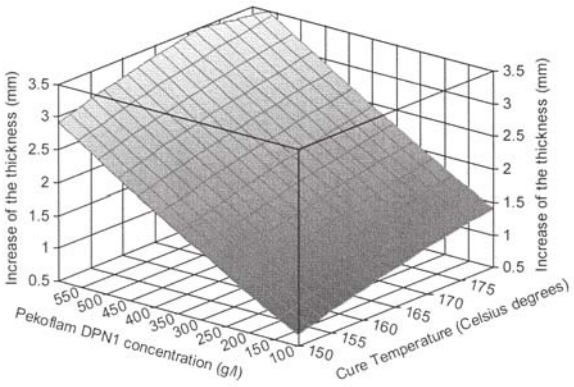

Fig. 3. Increase of the samples thickness after fireproofing treatment

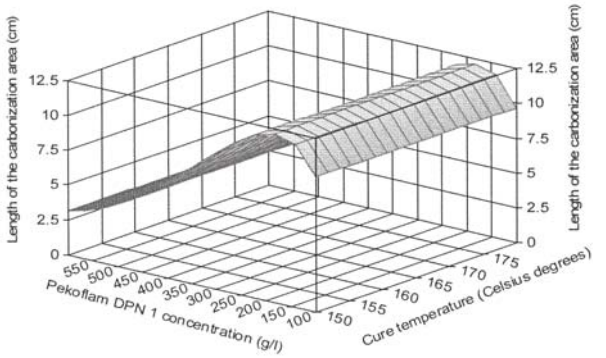

Fig. 4. Length of the carbonization area at the non-washed samples

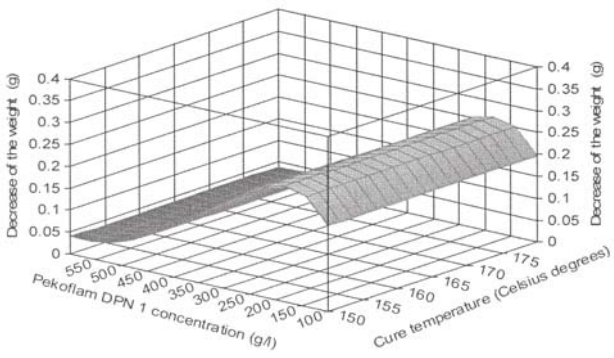

Fig. 5. Decrease of the samples weight after burning

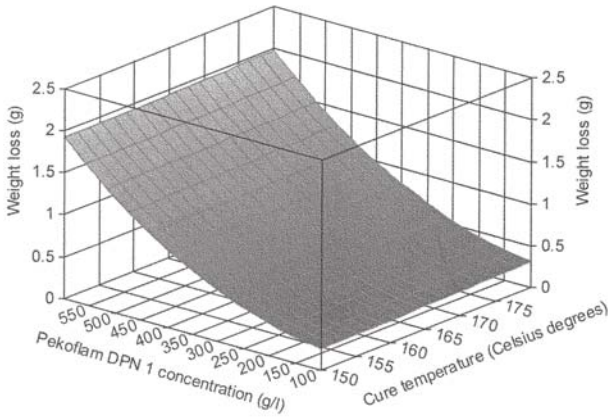

Fig. 6. Loss in the samples weight after neutralization and washing

Effect of flame retardant treatment on difference of colour

To estimate the difference of colour as a result of a flame retardant treatment, the colour intensity (colour strength) of the samples has been determined with a Data colour – 2004 spectrophotometer.

Referring to the standard sample (without flame retardant treatment), some significant colour values, i.e. DE, DL, Da, Db, DC and DH have been determined.

Analysing these values on the series of samples subjected to the entire pad-dry-cure technology, we have inferred that an increase in blue appears at the same time with the increase of the Pekoflam DPN 1 concentration, probably because it has an increased absorption coefficient. This is also due to the great value of the DE >5 AN units.

Another tendency shows a marked diminishing of the blue colour for any Pekoflam concentration but only at 180°C temperature. It is possible that this temperature should be outside the optimum domain.

Influence of Neutralization and Washing on the Flame Retardant Efficiency

The neutralization is necessary to annihilate the phosphoric acid from the textile material, an acid which in time will generate a destruction with the formation of hydrocelluloses.

The subsequent washing with water (rinsing) is necessary for the elimination of all residual substances existing on the textile material.

One can notice that these treatments are more than necessary but they influence in a certain way the keeping in time of the character obtained by the flame retardant treatment. To render this fact evident, the other two sets of samples have been subjected to flame retardant teatment, observing the same flame retardant formulas, but in the end they have been neutralized and rinsed out with plenty of water. As a result of these operations, a decrease in the samples weight has been noticed, as shown in figure 6.

The fireproofing treated and washed out samples (2 series because the analysis of variances needs two readings per cell, for the same treatment) have been subjected to burning according to STAS 8025-84. For the application of the bifactorial analysis of variances with systematic effects given both by the flame retardant reagent concentration and the cure temperature during the period the flame propagation (rate of spread of flame) the have been found out the values from the table 3.

These values indicate the following aspects:

– the greatest influence is given by the Pekoflam DPN 1 concentration;

– all the six levels of the flame retardant reagent concentration significantly influence the rate of spread of flame with 99% probability;

– the Pekoflam DPN 1 concentration (table 4) presents the same effect as value (given by the difference between the maximum and the minimum effect, respectively) for all six flame retardant reagent concentrations, the only difference being in the way this influence is shown, i.e. positive or negative. One can infer, from table 4, the fact that the first concentrations (from 100÷400 g/L inclusively) show positive influences rendered evident by the (+) signs for each minimum or maximum effect. The exceeding of the 400 g/L concentration leads to strong negative influences made

Table 3

INFORMATION REFERRING TO THE BIFACTORIAL ANALYSIS OF VARIANCES APPLIED TO STUDY THE VARIATION OF RATE OF SPREAD OF FLAME FOR THE FIREPROOFING TREATED AND WASHED-OUT SAMPLES

Sourse of variation	Sum of squares	Number of degrees of liberty	Average value of squares	Fischer function	Estimation of dispersion
Line (*A=Cure Temperature*)	SP_L= 31.158	ν_L=3	S_L^2= 10.386	F_L=121.8478	S^2_{Amin}=10.546191 S^2_{Amax}=10.621173
Column *(B=Pekoflam concentration)*	SP_C = 5868.41	ν_C=5	Sc^2= 1173.68	F_C=13769.57	S^2_{Bmin}=733.687529 S^2_{Bmax}=733.76251
Interaction A with B	SP_{LC} = 740.51	ν_{LC}=15	S_{LC}^2= 49.367	F_{LC}=579.176	S^2_{Abmin}=49.459086 S^2_{Abmax}=49.534068
Errors inside the cells	SP_{REZ} = 2.045	ν_{REZ}=24	S_{REZ}^2= 0.0852	$F_{95,3,24}$=3,01 $F_{95,5,24}$=2.62 $F_{95,15,24}$=2.11	σ^2_{min}=0.041712 σ^2_{max}=0.116694
Overall error	SP_G = 6642.1374	ν_G=47	.....	.....	.....

The relative overall error is 0.567643%.

Table 4

EMPHASIZING THE SIGNS ACCOMPANYING THE MINIMUM AND MAXIMUM EFFECTS

	The levels of the *Pekoflam DPN 1 concentration* factor, coded with j					
	j=o *100g/l*	j=1 *200 g/l*	j=2 *300g/l*	j=3 *400g/l*	j=4 *500g/l*	j=5 *600g/l*
Minimum effect	+12.5196	+3.8634	+5.1459	+7.9946	-15.3579	-15.3579
Maximum effect	+12.9171	+4.2608	+5.5433	+8.3921	-14.9604	-14.9604

evident by the (-) signs which accompany the minimum and maximum effects.

– by applying the multiple comparison referring to the levels of the A factor (the cure temperature) there has been found out, with 99% probability, that only the level 1, i.e. T=160°C, leads to a rejection of the null hypothesis, that is, it shows a significant influence on the rate of spread of flame.

As a result of burning, there has been noticed that the length of the non-carbonization area is smaller than that corresponding to the fireproofing treated, but not washed out, samples (for the same flame retardant treatment); however, the non-uniformity of these areas has imposed, for greater accuracy, the study of the decrease in weight by burning; the smaller the weight decrease is, the more significant the flame retardant effect has been (fig. 7).

The way of accomplishing the neutralization and washing out treatments can significantly influence the flame retardant efficiency. If the neutralization is done at a ≥ 40°C temperature, t = 20÷30 min, then the flame retardant efficiency is considerably diminished.

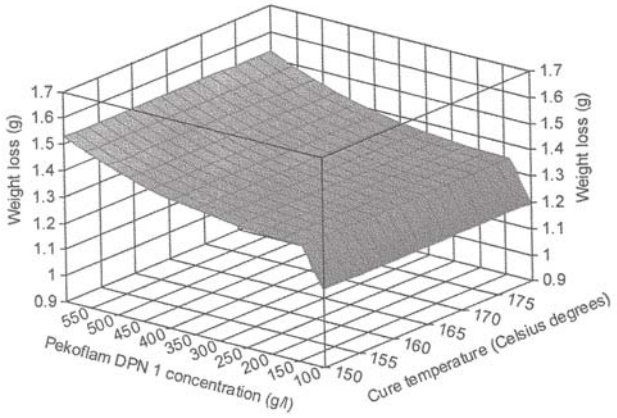

Fig. 7. The loss in the samples weight after burning

Conclusions

As a result of the flame retardant treatment carried out with a phosphorus-based compound, i. e. the Pekoflam DPN 1, the following conclusions can be stated:

– one can assert, with 99% probability, that the flame retardant efficiency depends on the concentration of the active flame retardant reagent, on the cure temperature and on the way the neutralization and final washing-out are accomplished;

– as a result of employing the analysis of variances, we can affirm that the most significant effect among the three studied factors is that of the Pekoflam DPN 1 concentration which determines the appearance of some positive influences upon the 100÷400 g/L concentration as well as negative effects upon concentrations higher than 400 g/L Pekoflam DPN 1;

– in what the cure temperature is concerned, only the 160°C temperature determines influences upon the flame retardant efficiency expressed in the length of the non-carbonization area and in the rate of spread of flame, respectively.

References

1.GRINDEA, M., GRIGORIU A., HANGANU. A., PUSCAS, E.L.,Tehnologia Chimicã Textilã, Editura Tehnicã, Bucuresti, 1981, p. 351

2.EINSELE, W., Wirkungsweise und synergetiscke Effekte bei, Flommschutzmittelen f. Chemiesasern, Mell. Textilber. 7, nr.11, 1976, p. 621

3.ALNISHAENSKIN, R., Possibilities d'appret ignifuge sur textile. Les cahiers Ciba, nr. 4, 1968, p. 35

4.GRINDEA, M., Metode de protejare a materialelor textile împotriva degradării, Bucuresti , IDT, 1966, p. 64

5.*** Columbia Encyclopedia Sixth Edition, 2004

6.HORROCKS,A.R., PRICE, D.- Woodhead Publishing Limited, Cambridge CB1 6AH, England, February, 2001

7.BAJAJ, P., Textile Research Journal, **54**, nr. 9, 1984, p. 619

8.LE BRAS,M., BOURBIGOT,S., CAMINO, G. - Woodhead Publishing Limited, Cambridge CB1 6AH, England, January, 1998

9.BOYER,N.E,VAJDA, A.E-Polymer Engineering and science, **4**, nr. 1, 2004, p. 45

10.QUINTIERE, J., World book online reference center, 2004

11.TUCU, D., ROTARESCU, V., BORDEASU, I., BAYER, M., HADAR**, A.,** Mat. Plast., **43**, nr. 4, 2006, p.308

12.POPESCU, D., HADAR, A., COTET, C., Mat. Plast., **43**, nr. 2, 2006, p. 175

13.AMZA, GH., MARINESCU, M., MORARU, A., C., NEGUT, N., STOICA, G., Mat. Plast., **45** nr. 1, 2008, p.61

STANCIU, C., CIUREA, A., Mat. Plast., **45**, nr. 3, 2008, p.232

Manuscript received: 8.12.2008