

MLV Liposomes in Dyeing of Wool with Madder

M. Montazer(a), F. Taghavi(b), T. Toliyat(c), S. Fallahpour(d)

(a)Textile Department, Amirkabir University, Hafez Avenue, Tehran, Iran

(b)Textile Chemistry, Tehran South Branch, Azad University

(c)Faculty of Pharmacy, Tehran University of Medical Science

(d)Department of Statistics, Allameh-Tabatabai University, Tehran, Iran

Abstract

The multi-lamellar liposomes (MLV) from Soya lecithin with 75% phosphatidylcholine were prepared and the behavior of liposomes in dye-bath at different temperatures, time and concentrations were examined. The results showed that liposomes with concentration of below 3% o.w.f. (on weigh of fabric) in the dye-bath increases the K/S for the samples dyed at 85°C or below for 60 min. Dyeing of wool at higher temperature and longer time with higher concentration of liposomes reduces the colour strength. This can be explained by the changes in the formation of the liposomes with increasing of temperature. Liposomes above 50°C converted to the large particles of phospholipids at 60°C to 75°C. However the large particles of phospholipids transfer to smaller particles above 75°C. The changes of the particles size of liposome leads to produce a uniform layer of phospholipid on the wool fabric surface above 85°C and decreasing the colour strength. It can be concluded that using of 2% o.w.f of liposomes in dyeing of wool with madder at 85°C for 60 min leads to improve K/S. The results also indicated that wash, light, wet and dry rub fastness properties of samples dyed with madder including liposomes has not been changed significantly.

Keywords: Liposomes, Wool dyeing, Colour strength (K/S), Fastness.

Introduction

Low temperature of wool dyeing has benefits such as lower energy conservation and wool fibers protection by either decreasing the temperature or shortening the processing time at high temperature during dyeing [1]. The wool fabric dye at low temperature has both more natural feeling and improved durability by using some of the known synthetic auxiliaries in dye-bath during low-temperature dyeing [1].

Liposomes are spherical synthetic layers of phospholipids, which has been formed like closed vesicles with an aqueous core and ranging from 10 nm to 10 µm in diameter [2, 3]. Liposomes compose of lipid vesicle bi-layers enclosing a volume. These structures have hydrophobic and hydrophilic parts. The hydrophilic part is composed of phosphate and choline groups, and the hydrophobic part is made up of hydrocarbon chains [4]. Phosphatidylcholine is the most widely used in biological lipid for producing liposomes [1].

Wool dyeing and wool blends with liposomes have demonstrated that improve quality, energy conservation, and lower environmental impacts.

Recently, commercial liposomes were incorporated into textile auxiliaries, mainly for wool dyeing [5, 6, 7]. This is a clean technology that has already been adapted by some textile industries. These are additional benefit for material weight yield during subsequent spinning. These improved smoothness and wash fastness properties of dyed samples with liposomes have also improved.

We try to prepare and produce multi-lamellar liposomes (MLV) from Soya lecithin with 75% phosphatidylcholine and study the influence of liposomes in dye-bath at different temperature, time and concentration during wool dyeing with

mechanical properties of the dyed textiles, and a clear reduction in the contamination load of the dye-baths [8].

Use of liposomes as an auxiliary in wool dyeing can be related to the bi-layers structure of lipids from the cell membrane complex of wool that is similar to the liposomes and the action of this morphological fraction of the fiber in wool processing [4]. A wool fiber include of cuticle and cortical cells held together by the cell membrane complex (CMC) and forms the continuous phase in the keratin [9]. This phase contains a small amount of lipid material. Diffusion properties of wool fibers are influenced by the lipid structure of the intercellular spaces that could act as "solvents" for hydrophobic chemical. The dyes diffuse with ease into swollen regions such as the CMC (intercellular diffusion) rather than through the cuticle cells (trans-cellular diffusion) [10].

Last few years, several papers have related the potential application of liposomes in wool dyeing. Meza et al has investigated of liposomes as doer in wool dyeing with acid [11, 12], disperse [13, 14] and metal complex dyes [15]. Also they have worked on the effects of commercially available liposomes as a simple additive [1, 15, 16]. Recently they use an optimized mixture of commercial liposomes and cationic surfactant to improve leveling property [16]. In the previous paper, the influence of temperature on stability of multi-lamellar liposomes in wool dyeing was studied and it was found that the presence of 1% o.w.f of liposomes at 85°C could improve the dye exhaustion of Irgalan Blue FBL on wool fabric. It has also reported that the madder as a most famous natural dye. The dyeing temperature and time was optimized with optimum concentration of liposomes, and the morphology of the liposomes dyed samples has investigated by SEM. The wash, light, wet and dry rub fastness properties of samples have also reported. The optimum conditions of dyeing were also obtained by application of BBD

(Box Behnken Design) as an experimental plan software.

Materials and Methods

The wool fabric with plain woven structure from 48/2 Nm yarns was supplied by Iran Merino. The fabric was scoured with 1% anionic detergent VEROLAN-NBO (supplied by Rodulf) at 70°C for 45 min and then washed with tap water and dried at room temperature. Industrial grade of aluminium sulphate used for mordanting of wool samples. Soya lecithin (containing 75% phosphatidylcholin) with phase transition temperature (T_c) of -18°C was gifted by Lipoid (Germany). The chemical structure of the phosphatidylcholin illustrated in Fig. 1.

Madder was prepared from Yazd providence of Iran. The chemical structure of important dyes in madder was illustrated in Fig. 2.

The reflectance spectra of the dyed samples were recorded on an ACS Spectra Sensor II integrated with an IBM-PC. The wash –fastness of the liposomes treated madder-dyed fabric were measured according to ISO 150-C01. For light-fastness measurements, the samples were exposed to the daylight for 7 dyes according to the daylight ISO 105-B01 and changes in the colour (fading) were assessed by the blue scale. Also the dry and wet rub fastness of the samples evaluated according to ISO 105-X12. Picture of the samples were taken with Philips XL30 scanning electron microscope (SEM) with 4000X.

Liposomes Preparation

MLV Liposomes were prepared following the thin film hydration method. A lipid film was formed by removing the organic solvent with rotary evaporation (with temperature of bath being 35°-40°C and 30 rpm) from a chloroform solution containing Soya lecithin. Aqueous phase containing distilled water added to the lipid film. The solution was shaken by hand to deliver the lipid from the walls of flask and disperse large lipid aggregates; glass beads were added to facilitate dispersions. The milky suspension was agitated at 40°C to obtain a complete emulsion. This means that the lipid extensively hydrated and MLV liposomes formed [1]. The aggregation states of the vesicles were estimated as a measure of the physical stability of the liposomes suspensions. This was done by monitoring the variations of vesicle size in different temperature (40°C, 50°C, 60°C, 75°C, 85°C and 95°C). An optical microscope used showing the changes of liposomes in lipid phase as function of temperature.

Preparation for Dyeing

Before dyeing, the wool samples should be cleaned to prepare the samples free from the impurities. Therefore the samples scoured in first step and then dyed latter. Also the dyestuff should be ready for process too. We can extract dyestuff from the natural collected madder.

Scouring

The samples were scoured in a bath containing 1 gr/l anionic detergent, 1 cc/l ammonia (pH=8.5) in 70°C for 45 min with Liquor to Good Ratio of 40:1. The samples were then rinsed with warm water (60°C) and tap water and then dried at room temperature.

Dyestuff Extraction

For extraction of Dyestuff, the madder were steeped in water solution for 24 hours and then heated at 70°C for 20 min, the solution was then passed through the filter. The filtered solution

was transferred to a glassing flask. The solution of dye was concentrated by removing the water with rotary evaporation.

Mordanting

The scoured samples (L:G=40:1) were steeped in the mordant bath prepared with 20% o.w.f (on weight of fabric) of aluminium sulphate with pH=4.5-5.8 (adjusted by acetic acid).

Mordanting of sample was started at room temperature and the temperature was raised for 2°C/min to boil and heated for 60 min. The samples were rinsed with tap water and dried at room temperature.

Dyeing

The mordanted wool samples were steeped in the dye bath with Liquor to Good ratio (L:G) of 40:1 that prepared by 2% o.w.f (on weight of fabric) of extracted dye at pH 4.5-5.5 (acetic acid) with different concentrations of freshly prepared MLV liposomes (0%, 1%, 2%, 3%o.w.f.).

Dyeing was started at room temperature and then raised 2°C/min to the final desired temperature including 75°C, 85°C and 95°C. The dyeing was carried out with liposomes and without liposomes in various times of 30, 45 and 60 minutes. The samples were rinsed with tap water and dried at room temperature. The amount of reflectance was selected at the maximum wavelength and the K/S value was calculated according to the Kubelka-Munk equation:

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad \text{Kubelka-Munk equation}$$

Experimental design

The Box-Behnken Design (BBD) used for experimental plan with three variables which is shown in Table 1. Three variables including liposomes amount, time and temperature were studied.

The ranges of these variables are shown in Table 1. Also the influence of the variable on the results Y (colour strength (K/S)) is adjusted using the following second order polynomial function:

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum c_i X_i^2 \quad i \geq j \quad i, j = 1, 2, 3$$

In this equation, b_0 is an independent term according to the mean value of the experimental plan, b_i are regression coefficients that explain the influence of the variables in their linear form, b_{ij} are regression coefficients of the interaction terms between variables and c_i are the coefficients of quadratic form of variables.

Details of Box-Behnken Design for dyeing of wool with madder are demonstrated in Table 2.

Equation regression coefficients b_i , b_{ij} , c_i and the determination coefficient R^2 are shown in Table 3.

Table 1 Ranges of variables

Variable	Lower Limit	Upper Limit
Temperature (°C)	75	95
Time (min)	30	60
Liposome (%)	0	3

Table 2 Box-Behnken Design (BBD) for dyeing of wool with madder

Run Number	A: Temperature (°C)	B: Time (min)	C: Concentration (mg/ml)	Y: Colour (K/S)
1	75.00	30.00	2.00	8.79
2	75.00	45.00	3.00	13.54
3	75.00	45.00	1.00	11.57
4	75.00	60.00	2.00	16.32
5	82.5	30.00	1.00	16.13
6	82.5	30.00	3.00	16.11
7	82.5	45.00	2.00	20.94
8	82.5	45.00	2.00	20.6
9	82.5	45.00	2.00	20.7
10	82.5	45.00	2.00	20.84
11	82.5	45.00	2.00	20.79
12	82.5	60.00	3.00	20.19
13	82.5	60.00	1.00	19.4
14	90.00	30.00	2.00	23.43
15	90.00	45.00	1.00	23.95
16	90.00	45.00	3.00	22.78
17	90.00	60.00	2.00	23.3

Table 3 Regression coefficients and determination coefficient R^2

Coefficients	Colour strength(K/S)
b_0	-312.1612
b_1	5.816
b_2	2.064
b_3	13.864
c_1	-0.0294
c_2	-0.0062
c_3	-1.409
b_{12}	-0.017
b_{13}	-0.1046
b_{23}	+0.0134
R^2	0.99

Therefore, the final model is:

$$K/S = -312.1612 + 5.816 * A + 2.064 * B + 13.864 * C - 0.0294 * A^2 - 0.0062 * B^2 - 1.409 * C^2 - 0.017 * A * B - 0.1046 * A * C + 0.0134 * B * C$$

In this equation, A is temperature (°C), B is time (min) and C is concentration (mg/ml).

Results and Discussions

Stability of Liposomes

To determine the stability of prepared liposomes, variety of liposomes size due to aggregation or solubilization was monitored by measuring the variations in mean vesicle size distribution during preparation of liposomes.

The results of micrograph for 20 mg/ml liposomes showed that, preparation of liposomes at 50°C can be done without any changes in the particles size of liposomes distribution due to the aggregation (Fig 1a).

Increasing of temperature above 50°C converted the liposomes in to large particles of phospholipids at 60°C to 75°C (Fig 1b and 1c) and above 75°C the large particle of phospholipids transfer to smaller particles (Fig 1d and 1e). These changes of the particles size of liposome leads to producing of a uniform layer of phospholipid on the wool fabric surface above 85°C. This also leads to a decrease in the amount of K/S. From these results, it can be concluded that the most ability of liposomes as doer for dyeing can be obtained at the 40°C-80°C.

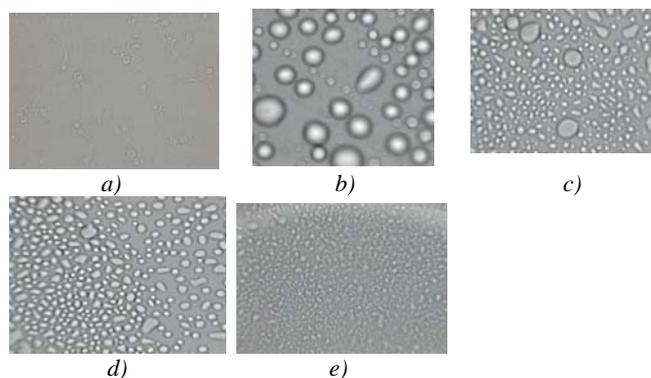


Fig. 1. Liposomes solution with 20 mg/ml concentration at a) 50 °C, b) 60 °C, c) 75°C, d) 85 °C, and e) 95 °C (X100)

Dyeing Profiles

The color strengths (K/S) were measured by the spectrophotometer (Texflash from Data colour). The reflection of the samples was measured at 400-700 nm wavelengths. All of the madder dyed samples indicated the low value of reflectance at 485nm (λ_{max}).

The K/S values were obtained on the samples applied with liposomes concentration from 0% to 3% o.w.f and madder dye on the aluminum mordanted wool at three different temperatures (75°C, 85°C, 95°C) and time (30 min, 45 min, 60 min). It can be observed from Table 4 and 5 that any increase in the time of dyeing and concentration of liposomes caused an increase in the values of K/S. The results indicate that the temperature is more effective than both time of dyeing and liposome concentration at 75°C and 85°C. The values of (K/S) continue to increase at 85°C for 60 min with 2% o.w.f liposomes concentration. It seems that liposomes apply as doer for dye at these conditions.

Increasing of temperature to 95°C, with different time and liposomes concentrations decreases the value of K/S (Table 6). This could be related to the liposomes stability. The liposome at 95°C converted to the smaller particles of phospholipids. These changes of the particle size of phospholipid leads to coating of wool surface with a layer of phospholipid above 85°C which leads to decrease the value of K/S. The results also indicated that the samples dyed without liposomes have a higher value of K/S comparing with the sample dyed with liposomes above 85°C. According to Table 5, it may conclude the same results as colour strength results. It means that higher reflectance leads to lower absorption and lower colour strength. It can be concluded that utilization of 2% o.w.f liposomes in dye-bath at 85°C for 60 min, clearly reduce the temperature of dyeing temperature about 10°C compared with a conventional dyeing process. These results are in accord with the result obtained by Maza et al for the dyeing of wool with metal complex dyes.

In order to study the effect of liposomes on the dyed wool samples, wash, light, wet and dry rub fastness were tested and the results listed in Tables 7, 8 and 9.

Table 4. K/S values of the dyed samples with different liposomes concentration and time and at 75°C.

Liposomes concentration	Time(min)		
	30	45	60
0%	7.89	9.28	10.70
1%	8.31	9.55	10.53
2%	8.20	11.71	17.25
3%	9.27	12.63	17.81

Table 5. K/S values of the dyed samples with different and liposomes concentration and time at 85°C.

Liposomes concentration	Time(min)		
	30	45	60
0%	17.87	18.62	23.11
1%	17.89	19.92	24.66
2%	17.80	20.94	25.82
3%	20.72	20.97	24.45

Table 6. K/S values of the dyed samples with different liposomes concentration and time at 95°C.

Liposomes concentration	Time(min)		
	30	45	60
0%	22.93	25.76	25.96
1%	21.54	25.05	21.59
2%	21.07	22.56	19.74
3%	20.95	2.38	19.03

Table .7. Wash fastness of dyed samples

Sample	Wash fastness	Staining on wool	Staining on cotton
Dyed without liposome at 95°C for 60 min	4-5	5	5
Dyed with liposome at 85°C for 60min	4	5	5

Table 8. Dry and wet rub fastness of the dyed samples

Sample	Dry rub fastness	Wet rub fastness
Dyed without liposome at 95°C for 60 min	3-4	4-5
Dyed with liposome at 85°C for 60min	3-4	4-5

Table .9. Light fastness of the dyed samples

Sample	Light fastness
Dyed without liposome at 95°C for 60 min	4-5
Dyed with liposome at 85°C for 60min	4-5

Statistical analysis

The Analysis of variance (ANOVA) is given in Table 10. It can be concluded that all of the terms in this model are significant. Also the lack of fit test with the p-value of 0.95 shows the model is significant and it is fitted well.

According to the ANOVA results, the fitted model is:

$$K/S = -312.1612 + 5.816 * A + 2.064 * B + 13.864 * C - 0.0294 * A^2 - 0.0062 * B^2 - 1.409 * C^2 - 0.017 * A * B - 0.1046 * A * C + 0.0134 * B * C$$

The Fig 2 also shows the response surface of the model. By using Design Of Expert software the optimum design point with desirability of 96.7 % is about temperature of 85°C, time of 60 min and liposome concentration of about 2% .

Table 10 ANOVA for Response Surface Quadratic Model

Source	Sum of Squares	DF	Mean Square	F Value	Prob>F
Model	306.51	9	34.06	3485.91	<0.0001
A	233.77	1	233.77	23927.38	<0.0001
B	27.16	1	27.16	2779.83	<0.0001
C	0.31	1	0.31	31.34	0.0008
A ²	8.31	1	8.31	850.15	<0.0001
B ²	8.35	1	8.35	854.69	<0.0001
C ²	8.37	1	8.37	856.21	<0.0001
AB	14.69	1	14.69	1503.41	<0.0001
AC	2.46	1	2.46	252.30	<0.0001
BC	0.16	1	0.16	16.58	0.0047
Residual	0.068	7	9.770E-003		
Lack of Fit	4.688E-004	3	1.563E-004	9.202E-003	0.95
Pure Error	0.068	4	0.017		
Cor Total	306.58	16			

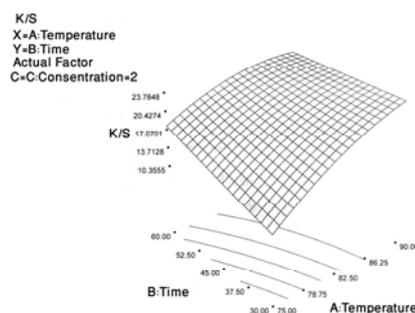


Fig. 2. Design of Expert Plot

SEM

SEM was utilized in considering of liposome effect and mordant on the wool fabric surfaces. The results in Fig.3 show a normal morphological form for the row wool and scales clearly has been seen (3a). For the mordanted wool some particles of mordant has been observed on the fiber surface (3b). The wool sample treated with 2% o.w.f of liposomes indicated an aggregation of phospholipids on the edge of scales (3c). The surfaces of the wool sample dyed with optimum conditions (85°C, 60min and 2% o.w.f Liposomes) indicated again some particles on the surface. These could be presumably produced by the mordant and liposomes which are scattering on the fiber surface randomly. The picture of the sample dyed without liposome indicated the same particles on the fiber surface but the coating on the sample dyed with liposomes is more than without liposomes. Also the liposomes remaining on the edge of the scale of the fiber dyed with liposome has been clearly observed.

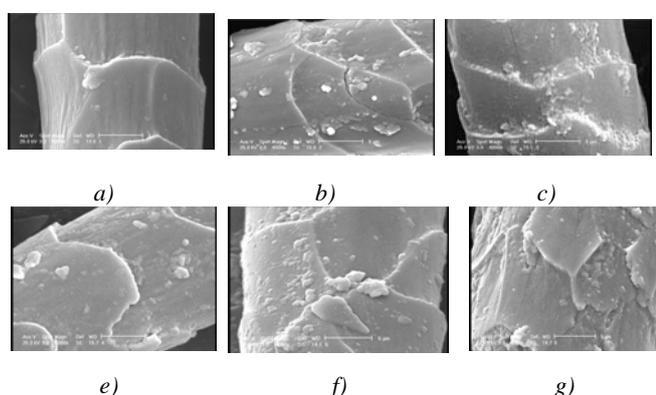


Fig. 3. SEM's of a) raw wool, b) Aluminum mordanted, c) treated with 2% liposome, d) Al. mordanted dyed with madder for 60 min at 95°C, e) Al. mordanted dyed with madder and 2% liposome for 60 min at 85°C for 60 min, f) same as e with 4% liposome (4000X).

Water drop absorption test

The results indicated that the time required for row wool sample was 294"(average of 20 tests), for mordanted and dyed wool 486"(average of 20 testes) and for liposome dyed 540"(average of 20 tests)(Table 11).

Table 11. The mean values of water drop absorption time on the different wool fabric samples

Sample	Dry rub fastness	Wet rub fastness
Dyed without liposome at 95°C for 60 min	3-4	4-5
Dyed with liposome at 85°C for 60min	3-4	4-5

These results show that mordanting and dyeing process on wool reduce the water absorption and make the fiber wool more hydrophobic. Also the liposomes dyeing made the fiber hydrophobic. This is because of the coating of the fibers surface by the phospholipids of the collapsed liposomes.

Conclusions

Liposomes are environmental friendly compounds that can be used in dyeing of wool. Applications of liposomes as assistant or carrier in dyeing of wool by some of the synthetic dyes have already been reported. However, the dyeing of wool dye with natural dyes is an interesting and new subject. Liposomes in dyeing of wool with madder show a clear reduction in dyeing temperature. The mechanism action of liposomes in wool dyeing with madder is similar to the dyeing of wool with synthetic dyes and it has the same influence on the dyeing process. It can be hypothesized that the liposomes apply as a carrier of dye and absorbed by the wool fiber and the interaction between the lipid concentration of liposomes and cell membrane complex of wool (CMC) take place. This leads to accelerate dye diffusion and dye uptake at 85°C. However above this temperature the liposomes collapsed and covered the wool fibers. Thus acting as a barrier for dye uptake and resulting reduced K/S. Statistical analysis by DOE indicated that application of 2% liposome at 85°C for 60 min on wool dyeing with madder produces an optimum design point with desirability of 96.70%.

References

- [1] Montazer, M., Validi, M.,Toliat, T., Influence of Temperature on Stability of Multilamellar Liposomes in Wool Dyeing. *Journal of Liposomes Research* 16:81-89 (2006).
- [2] Fegner, P.L., Nonviral strategies for gene therapy. *Special Report, Making Gene Therapy Work*, Scientific American, (1997)
- [3] Lasic, D.D., Papahadjopoulos, D., Liposomes revised, (Review). *Science* 267:1275-6, (1995).
- [4] Marti, M., Coderch, L., de la Maza, A., Manich, A., Parra, J.L., Phosphatidylcholine Liposomes as Vehicles for Disperse Dyes for Dyeing Polyester/Wool Blends. *Textile Research Journal* 68(3), 209-218, (1998).
- [5] Coderch, L., Manich, A.M., Martf, M., de la Maza, A., Parra, J.L., and Serra, S. Coplementary Study of Optimizing a wool Dyeing Process with Commercially Available Liposomes. *Textile Research Journal* 69,789-790. (1999).
- [6] de la Maza, A., Coderch, L., Manich, A.M., Martf, M., Parra, J.L., and Serra, S., Optimizing a Wool Dyeing Process with an Azoic 1 :2 Metal Complex Dye Using Commercially Available Liposomes. *Textile Research Journal* 68(9), 635-642., (1998).
- [7] Marti, M., Coderch, L., de la Maza, A., Manich, A., Parra, J.L., Industrial Use of Liposomes in wool dyeing, in "Proc.IWTO Florence Meeting", rep. no.CTF4. (1999).
- [8] Leeder, J. D., The Cell Membrane Complex and its Influence on the Properties of the Wool Fiber, *Wool Science Rev.*, 63, 3., (1986).
- [9] Coderch, L EL Complejo Membranoso CEular de la Fibra de Lana, Invest. In form *Textile Tensiact*.33(1/2),43-51.,(1990).
- [10] de la Maza, A.,Parra, J.L., Large Unilamellar Vesicle Liposome for Wool Dyeing : Stability of dye-liposomes system and their application on untreated wool, *Textile Research Journal*, 62(7):406-413., (1992).
- [11] de la Maza, A.,Parra, J.L.,Manich, A.M, Lipid bilayers including cholesterol as vehicles for acid dyes in wool dyeing. *Textile Research Journal* 63(11):643-649, (1993).

- [12] de la Maza, A., Manich, A.M., Multilamellar Liposomes including cholesterol as azobenzene disperse dyes in wool dyeing. *Textile Research Journal* 65(3):163-170, (1995).
- [13] de la Maza, A., Parra, J.L. Phosphatidylcholine/cholesterol liposomes as vehicles for anthraquinone disperse dyes in wool dyeing. *Journal of Society of Dyers and Colourists* 111:30-35., (1995).
- [14] de la Maza, A., Coderch, L. Multilamellar Liposomes including cholesterol as carriers of 1:2 metal complex dye in wool dyeing. *Textile Research Journal* 67(5):325-333, (1997).
- [15] Marti, M., Coderch, A. Phosphatidylcholine liposomes as vehicles for disperse dyes for dyeing polyester/wool blend. *Textile Research Journal* 68(3):209-218. (1998).
- [16] Marti, M., Serra, S. New liposomes formulation to favor wool dye migration. *International Textile Bulletin* 2:60-63. (2003).