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# DYEING OF PA6.6 FIBERS
## Effect of solvent and temperature on thermal properties

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## Abstract

Dyeing fibers at low temperatures has many advantages such as savings in energy and avoiding alterations to the physical properties of the fibers being dyed or other fibers also present in blends. The problem of low temperature dyeing in synthetic fibers is that it difficults the dye diffusion into the fiber. In the case of polyamide 6.6 microfibers, by using benzyl alcohol as an auxiliary dyeing, it was shown that good diffusion was obtained for the dye exhaustion with metal complex dyes at temperatures more than 30ºC below the normal dyeing temperature for the dye exhaustion with metal complex dyes. Using thermal analysis methods these results were shown to be caused by the lowering of the $T_g$ of the fiber when in the presence of benzyl alcohol.

**Keywords:** benzyl alcohol, dyeing, low temperature, microfibers, polyamide

## Introduction

The conventional dyeing of synthetic fibers in the textile industry is usually performed at high temperatures although it is possible to dye fibers at low temperatures. Dyeing of fibers at low temperature does have some advantages from the industrial point of view, namely energy saving, environmental control and fiber protection during the dyeing.

The conventional process of exhaustion dyeing of the microfibers of PA6.6 takes place at temperatures between 98 to 115ºC, in spite of it being possible to dye at lower temperatures. For this latter process, dyes with low molecular mass are used, as is the case of some acid dyes. However, when dyeing with large molecules, as metal complex dyes, defective dyeing can occur due to lower diffusion and migration properties. Dyeing at low temperatures without affecting dyeing diffusion and levelness has been shown to be possible with the aid of solvents. Polyester has been dyed with

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methylene chloride at 40ºC and wool has been dyed at lower temperatures with *n*-butanol and benzyl alcohol [1].

In this work, we studied the use of benzyl alcohol for lowering the dyeing temperature of PA fibers. The plasticizing action of benzyl alcohol was also confirmed for PAN fibers, where it was found that the extent of plasticization ($T_g$ reduction) increases with increasing the concentration of benzyl alcohol in the fiber [2]. The effect of benzyl alcohol in the dyeing of polyamide fibers is analyzed since this product is referred in the literature as a solvent of PA at its boiling temperature, and also a product that causes the de-aggregation of acid dyes in the dyeing of PA fibers [3]. To this effect, we carried out exhaustion dyeings with metal complex dyes for evaluating the minimum temperature of dyeing with benzyl alcohol and its effect on the exhaustion and diffusion of the dyes.

Thermal analysis techniques were used to understand the influence of dyeing, with and without benzyl alcohol, on properties and thermal behavior of PA6.6 microfibers.

## Experimental

### *Materials*

The material used in this work was interlock knitted fabric made with textured yarn of PA6.6 microfibers (Meryl). For a filament to be considered as a PA6.6 microfiber, it should have a linear density lower than 1.2 dTex (0.12 g per km). For further improvement of the mechanical properties, the as-spun filament microfibers are, after an initial filament compaction in a single cable, cold-drawn at room temperature, with a draw ratio of 5. After additional processing, two cables, each with 68 filaments of PA6.6 microfibers, are twisted to form a yarn with a linear density of 2×78 dTex. The microfiber has a circular cross-section, tenacity equal to 36.5 cN/tex and elastic recovery of 38.7%.

The microfibers were prepared previously for dyeing, for extraction of grease and oils, by washing with a surfactant at 80ºC for twenty minutes. Undyed and dyed samples of these microfibers were used for thermal analysis studies.

### *Dyes, auxiliary products and dyeing procedure*

The dyes used were the following metal complex dyes, commercial grade (Dystar): C.I. Acid Yellow 232, C.I. Acid Red 414, C.I. Acid Blue 335 and C.I. Acid Black 220. As mentioned previously, the dyeing with large molecules is more difficult due to their lower diffusion. However, when successful, it results in improved dyeing characteristics of the final fabrics.

Leveling agent Levegal FTS (Dystar) was used in all dyeings and benzyl alcohol (95.5% pure) was used when dyeing was carried out at lower temperatures than the standard dyeing temperature.

Dyeing was performed in an Ahiba Turbo Color dyeing machine with a liquor ratio of 1:50 and pH of 4.5. The absorption measurements for the calculation of dyebath exhaustion were obtained in a Unicam uv/vis UV2 reflection spectrophotometer. Analysis of exhaustion results of several dyeings allowed us to conclude that the lowest dyeing temperature for a complete dyeing consumption was 40ºC. Based on these results, the lowest temperature chosen for dyeing was 50ºC, to ensure the most efficient dye diffusion and a safety margin of 10ºC. Dyeing was then started at a temperature of 20ºC and the temperature was raised at a rate of 1ºC min$^{-1}$ up to the final dyeing temperature, 50ºC with benzyl alcohol (98ºC in the case of the standard dyeing), and kept at this temperature for 60 min.

### *Thermal analysis experiments*

These experiments were performed with a Perkin Elmer DSC7. The instrument was calibrated with two metal standards (indium and lead) at the scanning rate used in the experiments (10ºC min$^{-1}$). Samples of dyed and undyed PA6.6 microfibers, with an approximate mass of 20 mg, were crimped in 50 μL aluminium pans. A base line, used in all experiments, was drawn, with empty pans in both ovens, covering the working temperature range. The high temperature scans were performed with the bock cooled by water at a temperature of 5ºC and for the lower temperatures scans an intercooler was used. The purge gas used was nitrogen with the flow rate recommended by the manufacturer for experiments at low and high temperature.

## Results

### *Dyeing results*

To find out which was the minimum concentration of benzyl alcohol, several dyeing experiments were carried out at different concentrations of benzyl alcohol, with the metal-complex dye C.I. Acid Black 220, at 50ºC, Fig. 1.

The exhaustion curves obtained when dyeing at the standard temperature of 98 and at 50ºC are shown in Figs 2a to 2d for four dyes – Acid Red 414, Acid Yellow 232, Acid Blue 335 and Acid Black 220, respectively.

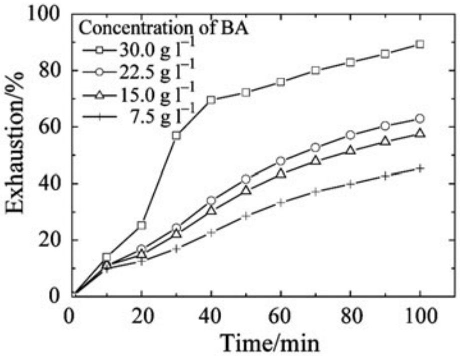

**Fig. 1** Exhaustion curves for C.I. Acid Black 220 at different benzyl alcohol concentrations

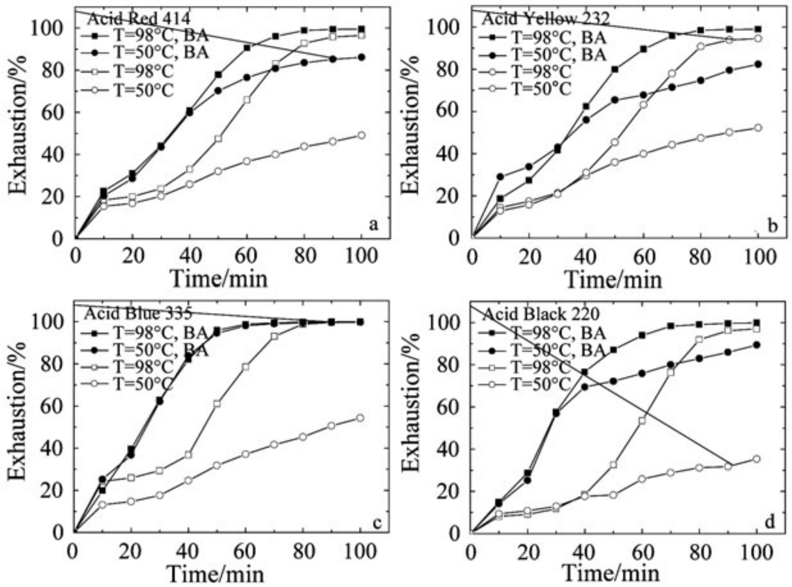

**Fig. 2** Exhaustion curves for metal complex dyes in the presence and in the absence of benzyl alcohol

As can be seen from the graphs in Fig. 2, all dyes had a much higher exhaustion in the presence of benzyl alcohol at 50ºC than in its absence, reaching the same final exhaustion as the classical dyeing at 98ºC (without benzyl alcohol). When dyeing at 98ºC, the recommended temperature, the exhaustion curve's profile is more steep from the beginning of the dyeing when using benzyl alcohol, than in its absence.

Since exhaustion is the measure of the migration of dye from the dyebath onto the fiber, it is not sufficient to give us the result in terms of diffusion into the fiber, which is an essential factor for a good washfastness. So, for evaluating the diffusion into the fibers, samples of the PA yarn were taken throughout the dyeing and the % reflectance of the samples was measured (relative to the sample of maximum reflectance taken at the end of dyeing), for the dye C.I. Yellow 232.

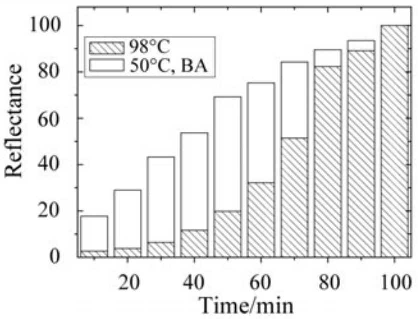

**Fig. 3** Reflectance of PA samples dyed with C.I. Yellow 232 in the presence and in the absence of benzyl alcohol

From the graph in Fig. 3 it can be seen that when dyeing at 50ºC in the presence of benzyl alcohol the same final reflectance value is obtained as with dyeing without benzyl alcohol at the recommended temperature of 98ºC, showing that diffusion of the dye into the fiber is the same in both cases. The graph also shows that diffusion during dyeing is a more rapid process when dyeing in the presence of benzyl alcohol.

### *Thermal analysis results*

Based on the exhaustion results of the dyes in both procedures, the dyeing results with benzyl alcohol should be related to the lowering of the glass transition temperature of the mixture (PA6.6+benzyl alcohol+$H_2O$).

The analysis of this change, using standard thermal analysis techniques, is difficult and not possible using standard means of evaluation. An indirect evaluation of the above effect is done in this work. Also, the effect of the two dyeing processes on the glass transition temperatures of the dried fibers is evaluated.

For this purpose, and for comparison with the results obtained further on, a standard DSC curve was obtained on a PA6.6 knitted fabric sample which was treated at 80ºC with a surfactant for 20 min and dried at 140ºC in a drying machine (stenter) at 50 m min$^{-1}$. Its mass was 22.63 mg and Fig. 4 shows the resulting scan at 10ºC min$^{-1}$. The figure shows an endothermic peak – peak A – with an onset at $T_1$=154ºC, which is due to the melting of the crystalline lamellae that were recrystallized at the drying temperature (140ºC). The melting of PA6.6 occurs at $T_2$=257ºC and the heat of fusion is 87 J g$^{-1}$.

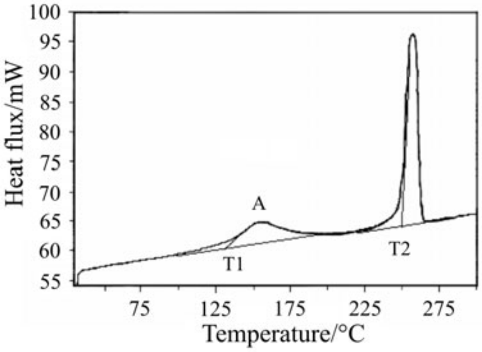

**Fig. 4** DSC curve of a dried standard sample of PA6.6. Sample mass 22.63 mg. Heating rate 10ºC min$^{-1}$

The effect of the dye and the different dyeing treatments on the crystalline portion of the polymer was analyzed through a set of experiments described below. These experiments will allow us to draw some conclusions on the final effect that the dye may have on the crystalline portion of the fiber. First, a sample of PA6.6 was immersed in the circulating dyebath (water, buffer pH, dyes, leveling auxiliary agent according to the previously defined formulation [4]) usually used for dyeing treatments

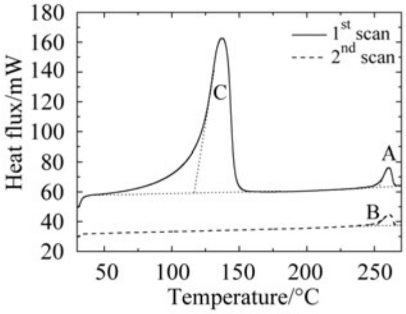

**Fig. 5** DSC curve of a PA6.6 sample immersed in the bath used to perform the dyeing at low temperature. The first scan (solid line) is performed on a wet sample. Peak C is the evaporation of water and peak A is the melting of PA6.6. In the second run (dashed line) only the melting of PA6.6 is observed (peak B)

with benzyl alcohol. The result obtained is shown by the first scan of Fig. 5 and the peak (C), corresponding to the evaporation of water, masks any transition that might appear in the temperature region from 50 to 150ºC. In the second run only the melting of PA6.6 is observed. This last run was performed after a fast cooling to the room temperature of the sample melted in the first run and also with a heating rate of 10ºC min$^{-1}$. The two peaks A and B occur at 260.66 and 260.96ºC, and their enthalpy of fusion is 60 and 49 J g$^{-1}$. These enthalpies were measured by subtracting from the initial sample mass (16.05 mg) the mass of water, estimated from the area of peak C and the heat of fusion of pure water (2279 J g$^{-1}$), as 6.59 mg. The enthalpies measured for the two peaks are not comparable since the lower value obtained for this second scan is probably originated by the different thermal treatment of the sample prior to the second scan. The onset temperature of peak A is 118.20ºC and it is assigned to the evaporation of water in the mixture, which is extended to temperatures around 150ºC. The results of the experiments shown in Fig. 5 shows that, for wet samples, due to the presence of water, it is not possible to analyze the combined effect of water and the dyeing agent on the lowering of the glass transition temperature of PA6.6.

A series of scans on dried samples were then performed. For this purpose, a set of four samples obtained from the conventional and benzyl alcohol dyeings, at low and high temperatures, were selected. The DSC curves are shown in Fig. 6. A sample mass of approximately 23 mg was used for all samples. The heat of fusion and the peak temperature of PA6.6 are similar for all runs, approximately 87 J g$^{-1}$ and around 260ºC, respectively. These values are similar to those obtained for the standard sample of Fig. 4, indicating that no irreversible changes took place during the dyeing and suggesting that, contrary to results obtained for other systems [5], the crystalline regions were unaffected by this process. The peaks A and B are the results of the thermal treatment at which the sample is submitted during the dyeing. Those peaks will be analyzed further on below.

In the DSC curves of Fig. 6 it is not possible to detect the glass transition temperature of PA6.6. For this purpose, the DSC block was cooled at a lower temperature and temperature runs were performed from –40 up to 300ºC at scanning rate of 10ºC min$^{-1}$.

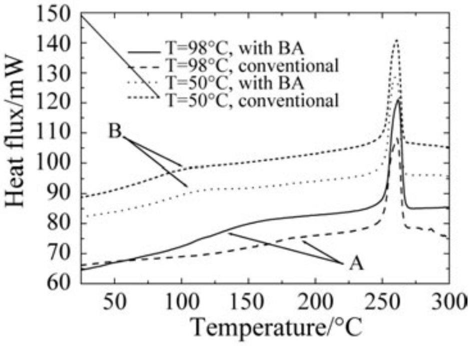

**Fig. 6** DSC curves at 10ºC min$^{-1}$ performed on dried PA6.6 samples after dyeing with benzyl alcohol at 98ºC (solid line) and conventional dyeing at the same temperature (dashed line). Dotted lines stand for the low temperature dyeings with and without benzyl alcohol. Peaks A and B are the results of the sample thermal treatment during dyeings at high and low temperatures, respectively

Figure 7 shows the results for the samples dyed at high temperature. The glass transition temperatures for the sample dyed and undeyed were 32.07 and 30.25ºC, respectively. A precise measurement of this transition temperature is difficult, as may be noted from the run performed over the sample dyed at 98ºC with benzyl alcohol. This difficulty arises from the masking effect of the peak A shown in Fig. 6. Similarly, peak B shown in the same figure masks completely the glass transition temperature of the samples dyed at lower temperature (50ºC), rendering it impossible the detection of this transition in these samples. DMA experiments performed over the undyed PA6.6 sample have confirmed the DSC measurements on the glass transition temperature of Fig. 7 [4].

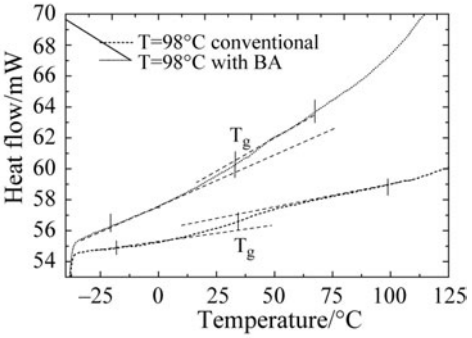

**Fig. 7** Measurement of the glass transition temperature of two samples dyed at high temperature, with and without benzyl alcohol

In order to certify the origin of peaks A and B of Fig. 6, the samples of the standard, undyed, material were placed in the DSC cell, and run with similar programs as in the high and low temperature dyeings. These temperature programs were described in the experimental section of this work. Figure 8 shows the results obtained for scans at 10ºC min$^{-1}$ performed over thermally treated samples.

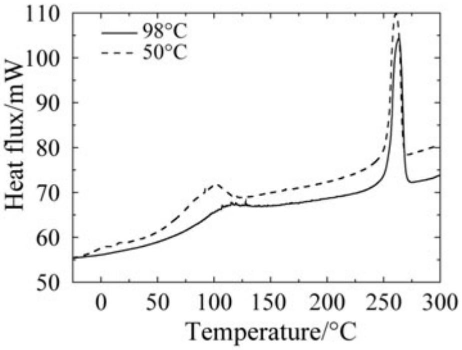

**Fig. 8** DSC curves performed over a standard undyed sample recorded at 10ºC min$^{-1}$ using the same temperature program as in the low and high temperature dyeings

The lower temperature enthalpic peaks of Fig. 8 are the result of the annealing treatment carried out with the purpose of replicating in the DSC oven the thermal treatment at which the samples were submitted during the dyeing process. These enthalpic peaks are originated by the selective melting of the new lamellae created during the annealing stage, or the thickening of the existing lamellae, by the incorporation of lower molecular mass material. Since the temperatures used for the annealing treatments (or the high and low temperature dyeings) are higher than the polymer glass transition temperature, the formation of the new structures leading to the enthalpic peaks of Fig. 8 is controlled mainly by the molecular diffusion of the polymer segments, which is possible at any temperature above the glass transition temperature.

## Discussion

An explanation of the results obtained for the dyeing of the PA6.6 fibers with benzyl alcohol, in comparison with those obtained with conventional dyeing, would require a set of thermal analysis experiments with the fibers immersed into the dyeing baths in a temperature range between – 100 and 50ºC. Those experiments should be able to confirm the lowering of the glass transition temperature of PA6.6 due to the absorption of water (in the conventional dyeing) and due to the mixed absorption of water and benzyl alcohol (in the low temperature dyeing).

The DSC experiments clearly confirm that the glass transition temperature of dried PA6.6 was not changed by the dye (Fig. 7). The small variations observed are acceptable within the experimental errors. Also, the heat of fusion of the dyed and undyed samples is similar ($\Delta h \approx 87$ J g$^{-1}$), as is confirmed from the results of Figs 4 and 6, indicating that the crystalline regions are unaffected by the dyeing process. The dyes used are large molecule metal complex dyes, and there incorporation in the crystalline regions of the polymer should have affected the melting process. Since no major changes on the melting peaks were observed, we assume that the diffusion of the dye was made mainly into the amorphous interlamellar and interspherulitic regions. Since the dye was exhausted in both treatments, at high and low temperatures, its diffusion was effective in both processes (Figs 2a to 2d).

The incorporation of the large metal complex dyes into the polymer matrix requires a free volume, which should be supplied by the amorphous component. Since the low and high temperature dyeings were carried out with the same metal complex dyes, and both had the same efficiency, the free volume for the migration of the dyes should be similar in both dyeing processes. With the above assumption, we may estimate the lowering of the glass transition temperature of the PA6.6 fibers, with respect to the dried material, in both treatments.

As referred previously, the conventional dyeing process is performed in the presence of water. It is known that the water acts as a plasticizer for PA6.6, thereby decreasing its glass transition temperature [6]. Studies on the effect of water on $T_g$ and Young modulus of PA6 have shown that $T_g$ decreases up to a finite value with increasing water content. For acting as a plasticizer, water must be adsorbed by the polymer, disturbing its regular structure and reducing the magnitude of the interchain bonding. The mechanism purposed by Reimschussel for the plasticizing action of water, is that the water is reversibly bound (via hydrogen bonding) to appropriate ($-NH_2$) groups within the polymer. The limiting value of $T_g$ was approached when the water content of the polymer approached that required for complete interaction with all accessible amine groups [7], the same mechanism being also applicable to PA6.6.

Concerning the $T_g$ values found in the literature for PA6 and PA6.6 a large discrepancy may be found [8], not only because of the probable water content existing in these materials, acting as a plasticizer and thereby decreasing the glass transition temperature, but also because of the kinetic character of this transition, $T_g$ being dependent on the thermal history of the polymer and on the scanning rate used for its measurement. Therefore, we will use as a reference for further discussion related to the glass transition temperature of PA6.6 the values found in reference thermal analysis literature [9] and also the values evaluated in this work, under appropriated controlled conditions.

For the estimation of the lowering of the glass transition temperature of PA6.6 in the presence of water some additional comments must be made on the validity of the approach that will be used. The approach is based on the application of the Fox equation. Some authors [8] based on dilatometric measurements of the glass transition of PA6 with different water contents questioned the validity of this equation. They suggested that the water does not behave as a simple plasticizer for PA6. Since a more reliable quantitative description of the change of the glass transition with water content is unknown by the authors, and since our purpose is to explain the accelerated dyeing action of the mixture benzyl alcohol and water, we assume the validity of the Fox equation for the system PA6.6+water+benzyl alcohol.

According to this equation, since the absorption of water by PA6.6 during the dyeing is approximately 8.75% [10] and the glass transition temperature of water is 135 K [11, 12], then the glass transition temperature of the mixture PA6.6 and water (used for dyeing at high temperature) can be calculated as follows:

$$\frac{1}{T_{\mathrm{g,mix}}}=\frac{w_{\mathrm{H_2O}}}{T_{\mathrm{g,H_2O}}}+\frac{w_{\mathrm{PA6.6}}}{T_{\mathrm{g,PA6.6}}} \tag{1}$$

With $T_{g,PA6.6}$=30ºC, as evaluated from our DSC experiments, the glass transition temperature of the mixture is $T_{g,H_2O+PA6.6}$=273 K=0ºC, in accordance with the value obtained in [8] and [13] for PA6 and PA6.6 for similar water content. This means that during the conventional dyeing process, which is performed at 98ºC, the glass transition temperature of the mixture is 30ºC lower than the glass transition temperature of the dried sample.

An approximate value for the glass transition temperature of the mixture with benzyl alcohol may now be estimated in a simple way. Assuming constant water content during the dyeing, the free volume fraction of the mixture (A) used in the conventional dyeing at the temperature at which the dyeing is performed ($T_A$=98ºC) is

$$f_A(T=T_A)=f_{g,A}+\alpha_{f,A}(T_A-T_{g,A}) \tag{2}$$

where $f_{g,A}$ is the fractional free volume at the glass transition temperature, $\alpha_{f,A}$ is the linear expansion coefficient of the free volume and $T_{g,A}$ is the glass transition temperature of the mixture used during the dyeing at high temperature ($T_{g,A}=T_{g,H_2O+PA6.6}$=0ºC).

In a similar way, for the mixture (B) with benzyl alcohol, we have for the fractional free volume at the temperature $T_B$=50ºC,

$$f_B(T=T_B)=f_{g,B}+\alpha_{f,B}(T_B-T_{g,B}) \tag{3}$$

where $T_{g,B}$ is the glass transition temperature of the new mixture, the other terms having a similar meaning as in Eq. (2).

Since the dyeing was efficient for both processes, the free volume fraction at the two temperatures may be assumed to have the same value, $f_A(T_A$=98ºC$)=f_B(T_B$=50ºC$)$. Also the fraction of free volume at the glass transition temperature should be the same for both mixtures ($f_{g,A}=f_{g,B}$) as well as the coefficients of the thermal expansion of the free volume ($\alpha_{f,A}=\alpha_{f,B}$), since both are universal values.

Then, equating the Eqs (2) and (3) we have $T_A-T_{g,A}=T_B-T_{g,B}$, and $T_{g,B}$=–48ºC, which is a lowering of 78ºC with respect the glass transition temperature of the dried PA6.6 and 48ºC with respect to the glass transition temperature of mixture used in the conventional dyeing process.

One of the basic assumptions that led to this evaluation was that the free volumes $f_A$ and $f_B$ were the same at 98 and 50ºC for high and low temperature dyeing bath, respectively. Let's assume for example that $f_B$ is larger than $f_A$ by a constant $c$. The opposite may also be assumed, since the purpose here is the estimation of the error in the evaluation of the lowering for the glass transition temperature by neglecting the eventual differences between $f_A$ and $f_B$. For these situations we should have then $T_B-T_{g,B}=T_A-T_{g,A}\pm c/\alpha$. Since $\alpha=4.8\cdot10^{-4}$ and the expected value for $c$ should be of the order of $10^{-3}$, the expected variation in the prediction of the glass transition temperature of the mixture B is 2ºC.

## Conclusions

The dyeing of PA6.6 microfibers can be carried out efficiently at high and low temperatures. This last process requires the use of benzyl alcohol as an auxiliary for the dyeing process and its incorporation in the dyeing bath results in the lowering of the glass transition temperature of the polymer, which is caused by the plasticizing effect of the mixture water and benzyl alcohol. The lowering of the glass transition temperature was quantified by assuming constant free volumes for the polymer samples at the two dyeing temperatures. It was predicted a decease of 30 and 78ºC for the glass transition temperature in the high and low temperature dyeing baths, respectively. When the free volumes at the two temperatures are different, the error associated to those predictions is estimated to be 2ºC.

The results obtained indicate also the crystalline regions were unaffected by the dyeing process and that the thermal treatments of the dyeing processes results in detectable annealing peaks that occur at temperatures near to those of the thermal treatments.

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