The Grafting of a Nylon Fiber Surface by a Mixture of Two Acrylic Monomers and the Evaluation of Optimum Values by using a Traditional Design of Experiment Software

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1. Introduction
The biofouling is any accumulation and growth of living matters on the manmade material surfaces. The biofilm formation has harmful effects on the vessel surfaces, navy piers and sea water submerged fish cages and constructions. It restricts the vessel movement resulting in 40% extra fuel consumption. Several anti-biofouling methods proposed. In this study a dual mix of 2-Hydroxy ethyl methacrylate (HEMA) and methyl acrylate (MA) was grafted on the fiber surface. Subsequently, degree of grafting and homo polymer % of the aforementioned monomers at different operative parameters including reaction temperatures, reaction times, pre-irradiation time and also initiator concentration were measured and the results were compared and discussed with those calculated values by a traditional design of experiment software (Design expert®). Also, two equations were proposed by the software for calculation of the aforementioned parameters with studied operative parameters.

2. Experimental
2.1. Materials
Polyamide fiber, PA6 with 210 Denier (1 Denier = 1 g/9000m), 34 filaments, entirely drawn yarn (FDY), methyl acrylate (MA) and 2-hydroxethyl methacrylate (HEMA), IRAMID-CD (non-ionic detergent, Toluene-4-sulfonic acid monohydrate (PTSA, 90%, inhibitor for homo-polymerization), dichloromethane (99%), methanol (99%), sodium carbonate and benzophenone (BP, 99%, photo-initiator).

2.2. Method
The 10 g of cut 10 cm fiber samples was weighed and put inside a baker containing 500 ml distilled water. I g IRAMID-CD, I g sodium carbonate and was heated for 300 min at 70°C. In next stage, the fibers removed from solution and after washing with distilled water and subsequent drying at 50°C for 24 h, they used for monomer grafting. For monomer grafting, a solution containing 32cc dichloromethane, 8cc methanol and different amounts of BP was prepared and during stirring, 1.84 g fiber was added to the solution. The stirring continued up to 24 h. Subsequently, the fibers were removed and put under UV irradiation for selected irradiation times. The irradiated fibers were put inside a three-span flask containing 50 cc de-ionized water, 0.243 g PTSA and a dual monomer mix (1 cc HEMA-2cc MA) for different reaction time and temperatures. After finishing the grafting reactions, the treated fibers were washed by hot de-ionized water to remove unreacted materials and dried under vacuum.

3. Results and Discussion
The optimum degree of grafting and homo polymer % and also the evaluation of the interaction between studied parameters (reaction time and temperature, pre-irradiation time and initiator concentration) was accomplished by the software using four variables and two surface responses with central point design method. Table 1 represents the studied parameters limits used for surface response method. Figures 1 and 2 show normal probability versus degree of grafting and homo polymer % residuals, respectively. As observed, the points are more or less along a line and follow a normal distribution.

With consideration of the above founds, the following equations were proposed by the software for prediction of degree of grafting and homo polymer %:

Degree of grafting (%) = +58.27481-2.63825*A+29.81527*B+0.15126*C+1.70849*D-0.11965AB-0.24102BC-1.23401BD+0.13378CD+0.019758A²-1.41293B² (1)

Degree of homo and co-polymer (%) = +48.94532-0.041657*A+8.99374*B+0.12089*C-3.16614*D+0.12208*AB-3.48604E-003*AC+4.97687E-003*AD-0.10497BC+0.80207*BD+0.066134*CD (2)

Where A, B, C and D are reaction temperature (°C), reaction time (h), pre-irradiation time (min) and initiator concentration (wt%), respectively.

<table>
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4. Conclusion
The Design expert® software is a suitable and powerful tool for the analysis and evaluation the optimum grafting % values for a mix of studied monomers, MA and
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HEMA. Using the introduced optimum parameters namely, reaction temperature (75 °C), reaction time (1 h), pre-irradiation time (40 min) and initiator concentration (9 wt%), the predicted values for grafting and homo-polymer %’s by mathematical model were 38.59 and 43.42%, respectively. They were in conformity with real values of 37.89 and 42.98%.

Figure 1. Normal probability versus degree of grafting % residuals

Figure 2. Normal probability versus homo-polymer % residuals