

KINETICS OF GRAFTING AND DYEING ACRYLIC ACID-GRAFTED POLY (ETHYLENE TEREPHTHALATE) FIBERS

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ABSTRACT

The kinetic parameters for grafting and dyeing acrylic acid-grafted Poly (ethylene terephthalate) PET fabric has been studied. Optimum grafting and dyeing conditions have been evaluated. The effect of acrylic acid (AA) and Sandocryl Blue (SB) dye concentrations on the yield-time relationship was investigated at different test temperatures. The reaction order and rate constant for radiation grafting and dyeing PET fabric were calculated from logarithmic plots of grafting and dyeing rates versus AA and SB concentrations. The order of the grafting process increases linearly with the increase in radiation temperature. It increases at a rate of $0.01/^{\circ}\text{C}$ with a value of 1.32 at zero $^{\circ}\text{C}$. The dyeing process follows 0.5 order reaction and is temperature independent. The reaction rate constant (k) is found to increase exponentially with temperature according to Arrhenius relationship. The preexponential rate constant (A) for dyeing is 1.61×10^4 times higher than that of grafting. The apparent activation energy (Q) for grafting and dyeing processes are 22.53 and 12.73 kJ/mole respectively.

KEYWORDS: Kinetics, radiation grafting, dyeing, rate, order, activation energy.

1. INTRODUCTION

The graft copolymerization of acrylic acid (AA) and methacrylic acid (MAA) with artificial and synthetic fibers is known to modify their properties⁽¹⁻⁶⁾ especially their dyeability towards different types of dyes. Poly(ethylene terephthalate) fibers are difficult to dye because of their high fiber crystallinity, marked hydrophobic properties and absence of chemically reactive groups. Attempts to improve the dyeability of PET fiber towards disperse dyes was made to overcome the low dyeing rate. This was achieved by building up dye molecules inside the polyester, opening the fiber structure

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to bring down the glass transition temperature or heating the dye in dry state together with the fiber near the softening temperature.

Several investigations, using high rate radiation grafting techniques (electron beam accelerators), have been carried out to graft and dye PET fiber with disperse dyes [7-11]. It was shown that considerable improvement in the dyeability of PET fiber is possible through grafting with AA and AN. About 50% improvement with disperse dye was observed in case of polyester fiber containing 22.4% graft [7].

In a previous investigation we have shown that radiation grafting of PET with MAA improved considerably the dyeability of the fabric towards basic dyes [11]. The kinetic of the dyeing process was also investigated [12, 13]. The aim of this work is to report a comparative study of the kinetic parameters of radiation grafting AA onto PET with those obtained from dyeing the grafted fibers. Kinetic parameters for both processes were evaluated.

2. EXPERIMENTAL

2.1 Materials and Methods

2.1.1 Materials

Thermally stabilized, heat treated at 220°C for 1.5 min, low density polyester (PET) fabric, product of Hankook Synthetic Inc., Korea, is mill-scoured in a solution containing 0.001 g/l Data scour WS-100 and sodium carbonate (0.5 g/l) at boil for 1h. The fabric was thoroughly washed with hot water, dried at ambient temperature and then used for grafting. Acrylic acid (AA) monomer and other chemical reagents were used as received. Chloroform, methanol, acetic acid and Sandozin NIT liquid were used. Sandocryl Blue (SB), a basic dye, produced by Sandoz, was used. The structure of the dye is given elsewhere [12].

2.2 Methods

2.2.1 Radiation grafting

Grafting was carried out by the direct irradiation method in a ⁶⁰Co gamma source of 1.98 Gy/s dose rate, for different doses and AA concentrations to achieve a

wide range of graft yield. Dry weighed PET samples were impregnated in chloroform, as a swelling agent, for overnight before the introduction into wide mouth tubes provided with ground joint stoppers containing the solvent, the monomer and the inhibitor. About 0.7 g sample was then added to the grafting solution and de-aerated with bubbling nitrogen for 5 min. The graft yield or degree of grafting is calculated as percent increase in weight [6].

Low test temperatures are reached by placing the tubes with the samples and grafting solution in a container filled with crushed ice/water mixture. The container is then left to reach equilibrium temperature before the introduction in the gamma cell. Measurement of temperature inside and outside the grafting solution was made at irradiation intervals of 15 min. The temperature inside the tube is ± 2 K of that before and after irradiation.

2.2.2 Viscosity measurements

The apparent viscosity of the solutions is measured by a cone-plate type digital rheometer, Brookfield Engineering Laboratories, Inc. The coefficient of viscosity (η) is obtained from the slope of the shear stress-shear rate linear relationship. Its unit is Poise (P) or cent Poise (cP).

2.2.3 Dyeing procedure and colour strength measurements

1-% dye stock solution was prepared by pasting the dye in acetic acid before adding the required distilled water. Aqueous dye solutions containing 2% of weight of fabric (owf) dye were prepared from the dyestuff at a fabric-to-liquor ratio 1:50. The concentration of the dyeing solution was adjusted to 1.1×10^{-3} mol/l. The pH of the dye bath was adjusted and the dyeing process was carried out in the presence of 10 g/l of dyeing solution sodium sulfate and few drops of 0.1 g/l Sandozin NIT liquid as a wetting agent. The temperature of the dye bath was then raised to 85°C and kept constant for 45 min. After dyeing, the samples were rinsed in hot water containing nonionic detergent, followed by tap water rinse and allowed to dry. This procedure was applied for dyeing samples at different pH and graft yields.

A computerized micro colorimeter unit made by Dr. Lange [14] (Germany) was used for colour measurements. The L^* , a^* and b^* system used is based on the CIE-colour Triangle (Commission International de l'Eclairage Units X, Y and Z). In this system the L^* value represents the dark-white axis, a^* represents the green-red axis and b^* represents the blue-yellow axis. The L^* , a^* and b^* values of grafted fabrics before dye sorption were measured and taken as a reference. The colour difference (CD) measured by (ΔE^*) , intensity of the grafted samples after dyeing, was determined as follows:

$$E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Kinetics of Grafting.

3.1.1 Optimum grafting conditions.

PET fiber is of hydrophobic nature. It is difficult to achieve reasonable degree of grafting with vinyl monomers without using proper solvent and swelling agent. Different solvents and swelling agents were used and the highest graft yield was achieved at overnight impregnation of samples in chloroform and using methanol/water mixture as a solvent.

The effect of methanol-to-water ratio on the grafting of AA onto PET fabric is shown in Fig. 1. The degree of grafting increases from zero to 13% maximum at 50:50 by weight methanol-to-water ratio. It then decreases to 6.8% for 100% methanol. This indicates that the best solvent ratio for the grafting process is 1:1.

In previous investigations^(4,5) we have shown the important role of the fabric-to-liquor ratio (LR) in the grafting process. Figure 2 shows that the maximum graft yield occurs at LR of 1:40, by weight. During grafting AA onto PET fabric a high degree of homopolymerization is observed, especially for high monomer concentrations. Viscosity measurements of grafting solutions containing 22.5 wt% AA concentrations, 1-2 % ovm Mohr's salt and irradiated to different doses showed considerably high increase in the coefficient of viscosity η (Table 1). Although the grafting solution

contains inhibitor to depress the homopolymerization process the viscosity increased by 1488% as the dose increased to 15 kGy. Fig. 3 shows the dependence of graft yield on inhibitor concentration. Maximum graft yield is obtained with 1-2% ovm Mohr's salt.

Fig. 1. Effect of methanol-to-water content on the graft yield.
Conditions: 10% owf AA; 1:40 LR; 20 kGy, dose.

Table 1. Dependence of coefficient of viscosity on radiation dose at 4°C.

Dose, kGy	0.0	3.1	10.1	15.0
η , cP	1.82	5.50	6.60	28.90

Fig. 2. Dependence of graft yield on fabric-to-liquor ratio.

Fig. 3. Dependence of graft yield on inhibitor concentration;
10% AA; 1:40 LR; 20 kGy, dose; 30°C.

3.2 Effect of AA Concentration on the Grafting Rate

The dependence of graft yield on irradiation time at different AA concentrations and different irradiation temperatures is shown in Figs. 4, 5 and 6. In general, the graft yield increases with the increase in irradiation time and AA concentration. It is clear that induction period (IP) appears before the start of the grafting process. The IP decreases with the increase in AA concentration and irradiation temperature. Details of the factors affecting the IP are given in separate investigations [5, 6].

The initial rate of grafting (R_G), the slope of the graft yield-irradiation time relationship, is calculated at different AA concentrations and irradiation temperatures. Table 2 shows the value of R_G at different AA concentrations and temperatures. It is obvious that the R_G increases with the increase in AA concentration and irradiation temperature.

Table 2. Dependence of rate of grafting on AA concentration and irradiation temperature.

AA concentration, wt%	7.5	15.0	22.5	30.0
$(R_G)_{277\text{ K}}, \%h^{-1}$	0.59	1.40	2.60	3.78
$(R_G)_{296\text{ K}}, \%h^{-1}$	---	1.60	2.82	4.51
$(R_G)_{303\text{ K}}, \%h^{-1}$	0.71	1.78	3.98	7.08

Fig. 4. Effect of AA concentration on the dependence of graft yield on irradiation time at 303 K

Fig. 5. Effect of AA concentration on the dependence of graft yield on irradiation time at 296 K

Fig. 6. Effect of AA concentration on the dependence of graft yield on irradiation time at 277 K

3.3 Order Of The Grafting Process.

It is known that the rate of grafting is related to the monomer concentration according to the equation:

$$R_G = k [C]^n \quad (2)$$

Where R_G , k , C and n are the rate of grafting, the rate constant, the AA concentration and reaction order respectively. Taking the logarithm of both sides eqn.2 becomes:

$$\log R_G = \log k_G + n \log [C] \quad (3)$$

The plot of $\log R_G$ versus $\log [C]$ gives a straight line the slope of which is the order n and the intercept is $\log k_G$. Fig. 7 shows logarithmic plots of R_G versus $[C]$ at different irradiation temperatures. The values of R_G and $[C]$ are plotted as fraction per hour and

fraction respectively. The results displayed on the computer's chart give the values of n and $\log k$. Table 3 shows the values of n , $\log k_G$ and k_G at the corresponding irradiation temperature. It is shown that n and k increases with temperature. Fig. 8 shows linear dependence of n on temperature with a slope indicating that n increases at a value of 0.01 per increase in temperature by one °C. The intercept gives n of 1.32 at zero °C.

Fig. 7. Logarithmic plots of rate of grafting versus AA concentration.

Table 3. Values of n , $\log k_G$ and k_G at different irradiation temperatures.

Temperature, °C	4	23	30
Order (n)	1.374	1.488	1.655
$\log k_G$	-0.6977	-0.434	-0.320
k_G, h^{-1}	0.201	0.367	0.479

Fig. 8. Dependence of the order of the grafting process on irradiation temperature.

The variation of n with irradiation temperature implies the complexity of the grafting process. Not only the rate of production of free radical increases but also the rates of its recombination and degradation of the grafted fabrics are affected by irradiation temperature. Moreover, the homopolymerization process as well as the viscosity of the grafting solution is affected by irradiation temperature. Consequently, it is expected that the monomer diffusion increase with the increase in temperature. This results in accelerated grafting and termination processes. The molecular weight of the grafted segments is expected to decrease with increase in temperature.

3.4 Activation Energy of Grafting.

The effect of irradiation temperature on the rate constant k_G of the grafting process is shown in Table 3. It is shown that k_G increases with the increase in temperature. Applying Arrhenius equation

$$k = A e^{-Q/RT} \quad (4)$$

and taking the natural logarithm of both sides, then

$$\ln k = \ln A - Q/RT \quad (5)$$

Where k , A , Q , R and T are the rate constant, the pre-exponential rate constant, the overall activation energy of grafting, the universal gas constant ($\text{Jmole}^{-1}\text{K}^{-1}$) and the absolute temperature respectively. The plot of $\ln k_G$ versus $1/T$ gives a straight line with slope Q/R and intercept $\ln A$. Fig. 9 shows Arrhenius plot of $\ln k_G$ versus $1000/T$ as given in Table 3. The relationship displayed on the chart is as follows:

$$\ln k = -2.722 (1000/T) + 8.215$$

From the value of the slope, $Q/R = 2.722$, an overall activation energy of 5.4 kcal/mole (22.53 kJ/mole) is calculated. The preexponential rate constant A is calculated from $\ln A$ of 8.215. The corresponding value of A is 3696.0 h^{-1} (1.03 s^{-1}). Consequently, Eqn. (4) becomes:

$$k_G = 1.03 e^{-22530/RT}, \text{ s}^{-1}$$

Fig. 9. Arrhenius plot of the natural logarithm of the grafting rate constant in k_G versus $1000/T$

The overall activation energy for grafting AA onto PET fabric falls within the acceptable range for the grafting process. The highest value for Q is 8.0 kcal/mole (33.44 kJ/mole) as reported by Chapiro [1]. Kaji et al. [15] and Shimano et al. [16] carried out radiation-induced graft copolymerization of PET using methacrylic (MAA) acid and AA in the presence of ethylene dichloride. The reported activation energy for AA was 8.0 kcal/mole in the range of 18-40°C and 8.77 kcal/mole for MAA in the range of 15-20°C. Rao and Rao [17] reported a value of 10.7 kcal/mole for Q of grafting by the catalytic method. It is clear that the value of Q of this work is lower than that reported by other investigators. This can be probably attributed to differences in the optimum grafting conditions used in the different investigations.

4. KINETICS OF DYEING AA-GRAFTED PET FIBERS

4.1 Optimum Dyeing Conditions

The effect of pH of SB dye solutions on the colour difference (CD) of grafted PET fabric is shown in Fig. 10. The results indicate that maximum CD is obtained at pH 5.0. The affinity of the grafted fabric (7.1% GY) towards SB dye increases from CD of 56 to 66 as the pH increases from 1.7 to 11.5. Further increase in pH to 11.5 decreased the CD to 61. Consequently, all dyeing experiments are carried out at pH 5.0. The effect of degree of grafting on the colour difference of PET fabric dyed in aqueous solutions containing 2% owf dye at a fabric-to-liquor ratio 1:50 is shown in Fig. 11. The concentration of the dye solution is 1.1×10^{-3} mole/l. The acidity of the dye

bath is adjusted to pH 5.0. It is observed from Fig. 11 that the CD of dyed fabric increases as the degree of grafting increases till reaching its maximum of 75 at about 10% GY and thereafter it levels off up to 24% GY. It is clear from the results that the initial value of CD increases almost linearly with the increase in graft yield up to 5%. This necessitates the dyeing of samples with graft yield around 5%. The improvement in the dyeability of PET fabric due to AA grafting is attributed to the introduction of carboxylic groups in the matrix of the fiber. Details of this effect are given in our previous investigations [6, 12].

Fig. 10. Effect of pH of dye solution on the colour difference at a constant graft yield of 7.1%.

Fig. 11. Effect of graft yield on the colour difference of samples dyed in solution adjusted to pH 5

4.2 Effect of Dye Concentration on the Colour Difference

The effect of SB dye concentration C_0 on the colour difference of samples grafted at graft yields ranging from 1.4% to 11.8% is shown in Fig. 12. The CD increases suddenly with slight increase in C_0 followed by a tendency to level off on further increase in dye concentration. The initial increase in CD with the increase in C_0 is graft yield dependent. As the GY increases the critical concentration, after which the CD shows tendency to level off, increases. Consequently, almost all the dyeing experiments are carried out at dye concentrations less than the critical concentration. Dye concentrations ranging from 10^{-6} to 2.5×10^{-4} mole/l are used in the following experiments.

Fig. 12. Effect of SB dye concentration on the colour difference of PET fabric grafted to different yields

4.3 Effect of Dye Concentration on Dyeing Rate

In the kinetics study, the colour difference of the dyed PET samples is measured by the CD value per unit graft yield to avoid the contribution of the degree of grafting in CD measurements as shown in Fig. 11. Preliminary experiments were carried out to study the dependence of CD on the dyeing time (t). Dyeing intervals ranging from 1 min to 10 min were tried and the corresponding CD values per GY

were measured. All samples gave almost the same CD value. Consequently, the intervals in the order of 10 s to 20 s were used to measure the dyeing time. In each experiment the grafted and ungrafted samples were dyed together in the same dye bath and the net increase in CD/GY was calculated.

The dependence of CD/GY of grafted PET fabric on the dyeing time for dye concentrations of 10^{-6} , 5×10^{-6} , 1.0×10^{-5} and 2.5×10^{-5} mole/l is shown in Fig. 13. The dye solutions were adjusted to pH 5.0 and dyed at 278, 292 and 308 K. The general feature of the curves is the same. The CD/GY increases with the increase in dye concentration C_o and dyeing temperature T . The CD/GY increases linearly with the increase in dyeing time t up to about 10 s then followed by slower increase with tendency to level off. The time at which the slope changes is dependent on C_o and T . The initial rate of dyeing (R_d) is calculated from the slope of the linear part of the (CD/GY)- t relationship. Table 4 shows the dependence of R_d on C_o and T . It is observed that as C_o increases R_d also increases.

Table 4 Dependence of initial dyeing rate (R_d , CD/GY s^{-1}) on dye concentration (C_o) and dyeing temperature (T) for SB dye solutions adjusted to pH 5.0

C_o , moles/L	10^{-6}	5×10^{-6}	1.0×10^{-5}	2.5×10^{-5}
R_d (s^{-1}) at 278 K	0.050	0.083	0.210	0.251
R_d (s^{-1}) at 292 K	0.110	0.252	0.468	0.499
R_d (s^{-1}) at 308 K	0.199	0.399	0.741	0.794
R_d (s^{-1}) at 328 K	0.224	0.562	0.794	1.250

It is of interest to compare the CD/GY values obtained from their dependence on dyeing time at different dyeing conditions, as given in Fig. 13, with those obtained from the initial slope of CD versus GY presented in Fig. 11. The values compared are those obtained for samples dyed at different temperatures for 6 min in a dye solution of 2.5×10^{-5} mole/l and samples dyed for 45 min at 85°C in a dye bath of 1.1×10^{-3} mole/l (2% owf dye at 1:50 fabric-to-liquor ratio). The CD/GY values of Fig. 13 are 4.67, 7.0 and 9.9 respectively for samples heated at 5, 19, and 35°C for 6 min. The

corresponding CD/GY value of Fig. 11 is 10. This indicates that 50-99% of the colour strength is obtained at such low dyeing temperature, low dye concentration and extremely short dyeing time.

Fig. 13. The dependence of colour difference/graft yield on dyeing time for dye concentrations of 10^{-6} , 5×10^{-6} , 1.5×10^{-5} and 2.5×10^{-5} mole/l for curves 1,2,3 and 4, respectively at 278, 292 and 308K.

4.4 Order of the Dyeing Process

The reaction order of the dyeing process is calculated from the values of R_d and C_o at different dyeing temperatures (Table 5). Fig. 14 shows logarithmic plots of R_d versus C_o at the corresponding temperatures. The relationship is linear and its slope (n) is the reaction order. The value of n is constant and is independent of T with an average value of 0.5. Therefore, the R_d dependence on C_o can be written as follows:

$$R_d = k_d C_o^{0.5}$$

Where k_d is the rate constant of the dyeing process. The intercept of the linear relationship of the logarithmic plots of R_d versus C_o (Fig. 14) gives the value of $\log k_d$. The obtained values of k_d are 59.4, 93.3, 168.8 and 457.3 (CD/GY) s^{-1} for the temperatures 278, 292, 308 and 328 K, respectively.

Fig. 14. Logarithmic plots of dyeing rate versus SB dye concentration at different dyeing temperatures.

4.5 Activation Energy of Dyeing

The dependence of k_d on T indicates that k_d increases with the increase in T . The dependence of k_d on T is presented by the Arrhenius type plot of the natural logarithm of k_d versus T as shown in Fig. 15. The relationship is linear and the slope gives the value of Q/R , where Q is the activation energy of the dyeing process and R is the universal gas constant. Activation energy of 12.7 kJ/mole is calculated for the SB dye. The intercept of the straight line relationship gives the value of 9.72 for $\ln A$, where A is the preexponential rate constant. The value of 1.66×10^4 (CD/GY) s^{-1} is calculated for A . The general equation relating the rate constant k_d to T is given as follows:

$$k_d, (\text{CD/GY}) = 1.66 \times 10^4 e^{-12730/RT}, \text{ s}^{-1}$$

The calculated value of the activation energy for SB dye (12.73 kJ/mole) is high enough to explain the reaction between grafted PET fabric and the basic dye. This reaction takes place at an extremely high rate and requires very small activation energy. This suggests that the calculated rates and activation energy are those for the

diffusion of the dye molecules through grafted and dyed PET fabric to reach grafted areas in the bulk of the fiber matrix. This activation energy is similar to that calculated, in our previous investigation for cotton fabric⁽¹¹⁾, during dyeing AA-grafted cotton fabric with SB dye (11.2 kJ/mole). The similarity in the value of Q indicates that the activation energy for dyeing SB dye is independent of the type of grafted fiber but is dependent only on the diffusion of the dye, in its aqueous solution, through the grafted fabric till reacting with the introduced active sites.

It is of interest to compare the kinetic parameters of grafting and dyeing processes. The grafting process follows 1.32 order kinetics at zero °C and is temperature dependent while that for the dyeing process is independent of dyeing temperature and has a value of 0.5. The dyeing rate constant increases with temperature increase at a rate faster than that of grafting. Consequently, the activation energy for the dyeing process is smaller than that of grafting as given above. The comparison between grafting and dyeing kinetics gives a general idea about the different mechanisms involved in both processes.

Fig. 15. Arrhenius plot of the natural logarithm of dyeing rate constant versus inverse of absolute dyeing temperature.

5. CONCLUSION

Optimum conditions for grafting AA onto PET fiber is achieved via pre-swelling the samples by overnight impregnation in chloroform followed by irradiation in AA solution containing: 1:1 methanol-to-water, solvent; 1-2% ovm Mohr's salt, inhibitor; 1:40 fabric-to-liquor ratio.

The initial rate of grafting R_G increases with the increase in monomer concentration and irradiation temperature.

The order of the grafting process increases linearly from 1.37 to 1.66 with the increase in irradiation temperature from 4 to 30°C. It increases at a rate of 0.01/°C.

The grafting rate constant k_G increases exponentially with the increase in irradiation temperature. The activation energy of grafting Q , the preexponential rate constant A and the absolute temperature T are related to k_G according to the equation:

$$k_G = 1.03 e^{-22530/RT}, \quad s^{-1}$$

The grafting kinetics play an important role in saving the monomer, the solvent and predicts the grafting rate as well as giving information about the rate controlling process.

Optimum conditions for dyeing AA-grafted PET fabric with SB, a basic dye, is achieved in acidic aqueous solution of pH 5.0. The colour difference CD increases with increase in graft yield GY and dye concentration C_o . Initial fast and linear increase in CD with the increase in GY and C_o is observed. The CD tends to level off at further increase in GY and C_o . Dye concentration ranging from $10^{-6} - 2.5 \times 10^{-5}$ mole/l is used in the kinetic study of grafted PET fabric.

The initial rate of dyeing R_d increases with the increase in C_o and dyeing temperature T . The order of the dyeing process is constant and is independent of T . The dyeing rate R_d , the rate constant k_d , the dye concentration C_o and the reaction order follows the relationship:

$$R_d = k_d C_o^{0.5}$$

The dyeing rate constant increases exponentially with the absolute temperature T . It is related to the activation energy, the pre-exponential rate constant and absolute temperature according to the equation:

$$k_d, (CD/GY) = 1.66 \times 10^4 e^{-12730/RT}, \quad s^{-1}$$

The dyeing process is diffusion controlled and the activation energy is independent of the type of grafted fiber.

The kinetic study of dyeing AA-grafted PET fabric indicated that 99% of the CD of samples dyed in a solution of 1.1×10^{-3} mole/l at 85°C for 45 min is obtained

when the samples are dyed at 35°C for 6 min in aqueous dye solution of 2.5×10^{-5} mole/l. Such low dyeing temperature and dye concentration at the considerably short dyeing time emphasizes the importance of studying the dyeing kinetics in saving the energy and time required for the dyeing process.

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كيناتيكية التطعيم وصباغة ألياف البولي ايثيلين ترفيثاليت المطعم بحامض الأكريليك

يقدم البحث دراسة للعوامل الكيناتيكية لعملية التطعيم وصباغة البولي ايثيلين ترفيثاليت (البولي أيستر) المطعم بحامض الأكريليك، حيث تم تحديد الظروف المثلى لكل من عمليتي التطعيم والصباغة، ودراسة تأثير كل من درجتي تركيز المونومر والصبغة على العلاقة بين مقداري التطعيم والصباغة على القماش وزمنى التشيع والصباغة وذلك عند درجات حرارة مختلفة وحساب رتبتي التطعيم والصباغة من العلاقة بين لوغاريتم معدليهما ولوغاريتم درجة تركيز كل من المونومر والصبغة، ولقد وجد أن رتبة التطعيم تزداد خطيا بزيادة درجة الحرارة بمعدل 0,01 لكل درجة حرارة مئوية، أما رتبة الصباغة فلا تعتمد قيمتها على درجة الحرارة وتساوى 0,5، كما تم حساب كل من معدل ثابت التفاعل k ، و ثابت ما قبل الجزء الأسى A ، وطاقة التنشيط لكل من عمليتي التطعيم والصباغة، ووجد أن كلا من العمليتين يتبع معادلة أرهنييس و أن قيمة A للصباغة أكبر من التطعيم بمقدار $1,6 \times 10^7$ مرة وأن قيمة طاقة التنشيط لكل من التطعيم والصباغة تساوى 22,5 و 12,7 كيلو جول/مول على التوالي.