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KINETICS OF RADIATION GRAFTING OF GLYCIDYL METHACRYLATE AND VINYLBENZYL CHLORIDE ONTO POLYMER FIBERS

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Abstract

The kinetic of grafting of glycidyl methacrylate (GMA) and vinylbenzyl chloride (VBC) monomers onto nylon-6 fibres using an electron beam was investigated in conjunction with reaction parameters namely, monomer concentration, absorbed dose and grafting temperature. The order of dependence of grafting rate of grafting parameters was determined by variation of r_{p0} with monomer concentration and absorbed dose. The reaction kinetics were represented by equations: $\frac{dG_o}{dt} = k[M_G]^{1.76}[D_G]^{1.03}$ and $\frac{dG_o}{dt} = k[M_V]^{1.21}[D_V]^{1.66}$ for grafting of GMA and VBC, respectively. The kinetics of the reaction in the two grafting systems was found to be controlled by the monomer concentration and absorbed dose. However, GMA grafting showed higher dependence on the monomer concentration whereas VBC grafting demonstrated higher dependence on the amount of trapped radicals, i.e., absorbed dose. Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) were used to provide evidence for the formation of graft copolymers in both of the grafting systems.

Keywords: Activation energy, Grafting kinetics, Radiation-induced grafting, Radical polymerization, Reaction mechanism.

1. Introduction

Nylon-6 possesses excellent physico-mechanical properties [1], elasticity, chemical and thermal stability and are applied in various household and industrial applications [2]. Modification of nylon-6 by graft copolymerization technique can further enhance its properties to be applied for specific applications in various fields including immobilization of acrylamide onto nylon films to enhance their water adsorption capacity [3]. Timus et al. [4, 5] explained that thermal behaviour and anti-dripping properties of nylon-6 can also be improved by grafting of acrylic monomers such as acrylic acid and methacrylic acid. Grafting of 2-hydroxyethyl methacrylate improved the dyeability of nylon [6], whereas the incorporation of vinylbenzyltrimethyl ammonium chloride imparted flame retardancy to nylon [7]. Moreover, high selectivity and permeation fluxes were obtained after acrylic acid or its derivatives were grafted onto nylon-6 [8, 9]. Based on studies by Mascia and Hashim [10], large improvements in solvent resistance were also obtained by grafting methacrylic acid onto nylon.

Nylon is also used as a substrate for the synthesis of various functional/ionic polymers. For example, grafting of vinylbenzyl chloride (VBC) and subsequent amination was used to prepare fibrous adsorbent for adsorption of boron from solutions and preparation of cation exchange nylon 6 capillary-channeled polymer fibres by graft polymerization [11, 12]. Miyazawa et al. [13] commented that modification of nylon by radiation-induced grafting (RIG) with vinylbenzyl trimethylammonium chloride and sodium styrene sulfonate was used to confer desired ion exchange properties to it in a single step.

Despite the facile modification of nylon by RIG and its use in a large number of applications, scarce reports can be found on the kinetics of grafting reactions involving nylon modification with this method. Thus, it is essential to understand the kinetics of grafting of two versatile monomers that allow post-grafting functionalization such as glycidyl methacrylate (GMA) and vinylbenzyl chloride (VBC) both of which, produce nylon graft copolymer precursors suitable for hosting a large number of a functional group for various applications. Comparisons between these two different grafting systems are needed to provide an understanding of the relationship between the grafting parameters and the level of modification taking place in nylon substrate. This would allow identifications of monomer favouring the desired application and the aspects to reduce the monomer consumption and improve grafting economy.

The aim of this study is to investigate the kinetics of RIG of GMA and VBC onto nylon-6 fibres. The relationship between the grafting parameters (concentration of monomer, radiation dose and temperature) and the grafting yield (DG) for both grafting systems were established. The success of grafting reaction was confirmed using FTIR spectroscopy and SEM.

2. Experimental

2.1. Materials

VBC (mixture of 3- and 4-isomers, 97% contains 700–1100 ppm nitromethane as an inhibitor, 50–100 ppm tert-butylcatechol as an inhibitor) and GMA with purity of 97% were supplied by Sigma-Aldrich. The monomers were used as received. Nylon-6 fibres with a molecular weight in the range of $1.59–2.84\times10^6$ and moisture content of 3.5% were obtained from Reliance Sdn. Bhd. Methanol of reagent grade was purchased from Merck and used without further purification.

2.2. Radiation-induced grafting of monomer onto nylon-6

The RIG of monomers onto nylon-6 fibres was carried out in a two-step procedure involving irradiation with Electron Beam accelerator (EB) and subsequent reaction with monomer under controlled conditions as shown in Fig. 1.

The Pristine fibres samples were placed in PE bags, which were filled with N_2 gas to replace the air before they were sealed. The sealed PE bags with the samples were irradiated using an Electron Beam (EB) accelerator operated at 1.0 MeV and 10 mA. The PE bags containing samples were irradiated with doses of 50, 100 and 300 kGy.

Monomer solutions were diluted with methanol to desired concentrations, flushed with N_2 gas and introduced to irradiated samples placed in glass reactors. The temperatures of the grafting mixtures (fibres and monomer mixtures) were maintained at desired values and the reactions were allowed for different time intervals up to 4 h. The grafted samples were removed and washed with methanol several times to remove the unreacted monomer and any homopolymer. The clean grafted samples were dried at 40 °C for 24 h. The grafting yield (DG) resembling the weight increase was determined by:

$$DG(\%) = \frac{W_1 - W_0}{W_0} \times 100 \tag{1}$$

where, W_0 and W_1 are the weights of pristine and final grafted nylon-6 fibre samples, respectively.

Figure 2 shows a schematic representation for RIG of GMA and VBC monomers onto fibres. The grafting of GMA and VBC onto samples were carried out in two-steps started by irradiation of nylon-6 fibres with EB accelerator and subsequent grafting.

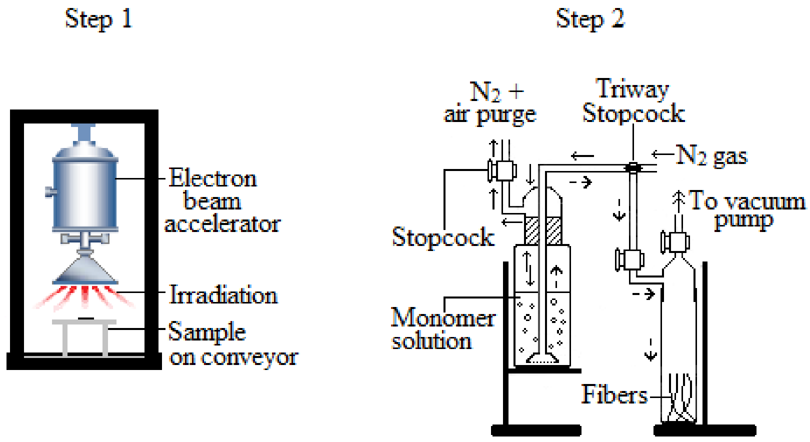

Fig. 1. Two-step procedures using electron beam irradiation and grafting reaction.

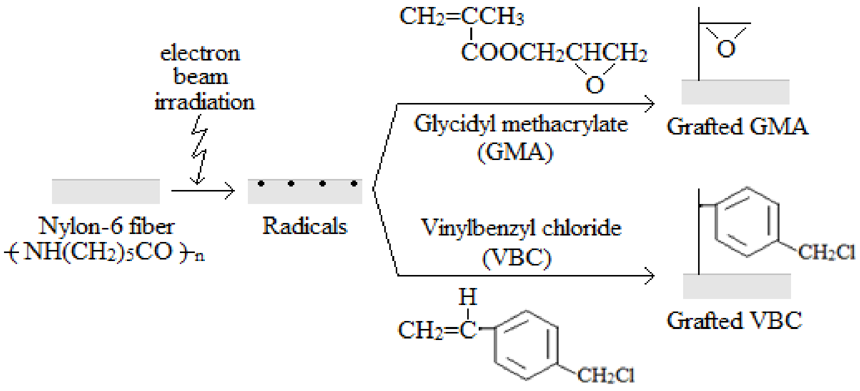

Fig. 2. Schematic representation for grafting of GMA and VBC onto nylon-6 fibers.

2.3. Fourier transform infrared (FTIR) and scanning electron microscopy (SEM)

The changes in chemical structure were investigated using Fourier transform infrared coupled with attenuated total reflection (FTIR-ATR). The analysis was performed on a Perkin Elmer spectrometer (Spectrum RX I) in the wave number range of 500-4000 cm^{-1}. The spectra were obtained using a number of the scans of 10 at a resolution of 4 cm^{-1}. Scanning electron microscope (SEM) images of samples were taken on the FEI Quanta 4000 after coating with 4-5 nm Au and images of the samples were obtained at 20.0 kV.

2.4. Kinetic analysis

The kinetics of the grafting reactions at various grafting parameters were obtained using the following equation [14]:

$$\mathrm{DG}(\%) = \frac{r_{p0}}{\gamma} ln[1 + \gamma(t - t_0)] \qquad (2)$$

where rp_0 is initial polymerization rate, γ is characteristic radical recombined rate and t_0 is the delay time. The Arrhenius equation shown below was used to determine the activation energy.

$$k = Ae^{\frac{-Ea}{RT}} \qquad (3)$$

where k is the rate constant, A is the pre-exponential factor, R is the gas constant (8.314 J K^{-1}mol^{-1}) and T is the absolute temperature (K). The slope ($-E_a/R$) of the ln (r_{p0}) plot vs. the temperature (1/T) is used to calculate the E_a.

3. Results and Discussion

3.1. Concentration of monomer

Figure 3 shows the variation of the grafting yield with time at different monomer concentrations GMA and VBC grafting systems. The grafting yield for GMA and VBC at all monomer concentration were found to increase at the beginning of grafting reaction and started to level off after 2 and 3 hours, respectively. These results reveal that the increase in the monomer concentration allow more monomer molecules to diffuse to the grafting sites in irradiated substrates leading to higher DGs. Interestingly, the DG for GMA grafting system was found to be more than 5 times higher than that for VBC grafting despite the use of same monomer concentrations in both GMA and VBC grafting systems.

This suggests that GMA is more reactive than VBC. This likely because of GMA has a higher polarity than VBC, which also has a benzene ring exerting resonance stabilization effect. Thus, there is effective utilization of the radicals formed on the nylon-6 substrates in the initiation of more graft growing chains with GMA at a higher rate than VBC leading to higher DG. According to Nava-Ortiz et al. [15] and Ikeda et al. [16], such high DG in GMA grafting system is consistent with the results reported in the literature. The relatively lower DG obtained from the VBC grafting system is found in agreement with the literature [17, 18].

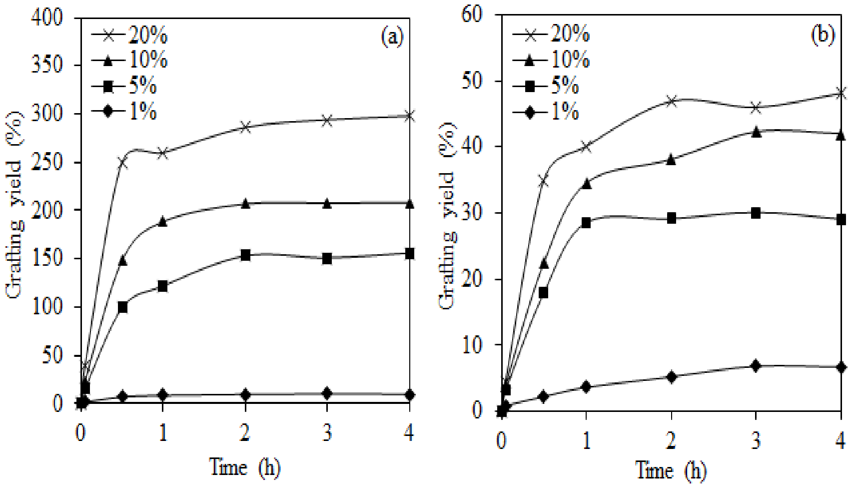

Fig. 3. Variation of grafting yield at different concentrations of monomer with time for GMA: (a) VBC, (b) Reaction parameters: solvent, methanol; reaction temperature, 30 °C absorbed dose, 100 kGy.

The relationship between initial polymerization rate and the concentration of monomers is shown in Fig. 4. The dependence of the initial polymerization rate (d*G*/d*t*) on the concentration of monomer was derived from the slope of the plot. The reaction order for the polymerization of GMA and VBC onto the irradiated substrate was 1.76 and 1.21, respectively. The grafting kinetics is represented with the following expressions:

$$\frac{dG_o}{dt}\alpha[M_G]^{1.76} \quad (4)$$

$$\frac{dG_o}{dt}\alpha[M_V]^{1.21} \quad (5)$$

where, M_G and M_V are monomer concentrations for GMA and VBC, respectively.

The result indicates that the dependency of GMA grafting system on monomer concentration was relatively higher compared to VBC grafting system. The higher value of exponent recorded for GMA grafting system also indicates that the rate of initiation and chain propagation with GMA was higher leading to higher DG.

This suggests that the grafting of GMA and VBC onto nylon-6 substrate is controlled by monomer diffusion to the grafting sites. The effect of monomer concentration on grafting rate that was found in this study is similar with other grafting systems such as acrylic acid/poly (ethylene/tetrafluoroethylene) [19] and acrylic acid/poly (tetrafluoroethylene/hexafluoropropylene) film [20], having reaction orders of 1.2 and 1.25, respectively.

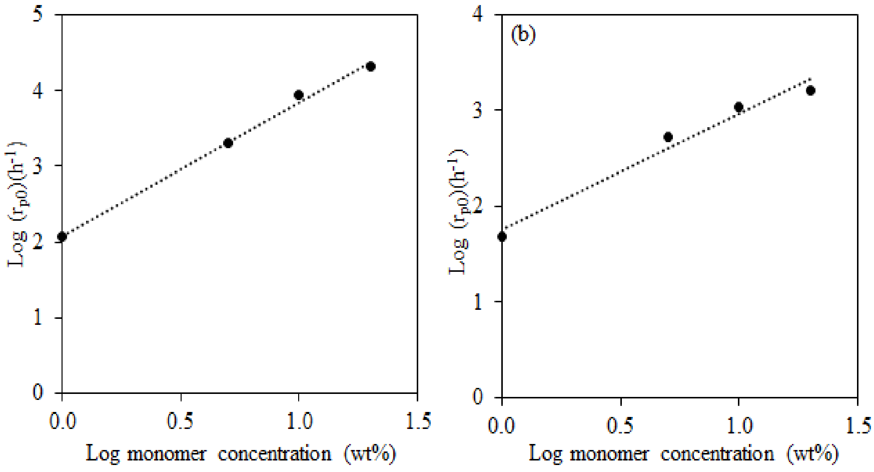

Fig. 4. Plot of an initial polymerization rate (*r_{p0}*) vs. concentration of monomer for GMA: (a) VBC, (b) Grafting systems. Data are calculated according to Eq. (2).

3.2. Irradiation dose

Figure 5 displays plots for the variation of grafting yield with time at different irradiation doses for GMA and VBC grafting systems. The DG for GMA and VBC at all irradiation doses were found to increase at the beginning of the reaction and started to level off after 2 hours.

Since the concentration of radicals produced on the polymer substrate is dependent on the irradiation dose, the increased in DG is caused by a riichse in the amount of radicals generated in the polymer substrate with higher doses.

It is worth mentioning that grafting is initiated by the trapped radicals in the amorphous region, which initiates the grafting reaction and allows graft growing chains to propagate [19, 21]. After most radicals are consumed, the grafting reaction becomes slow and this likely occurred in the first hour of reaction [21, 22].

The termination reaction of the growing chains noticeably occurred after the third hour. Although the irradiation dose applied for GMA and VBC grafting system was same, the GMA grafting system is found to give a DG more than 3-times higher than VBC. This further confirms the earlier observation that GMA is more reactive than VBC.

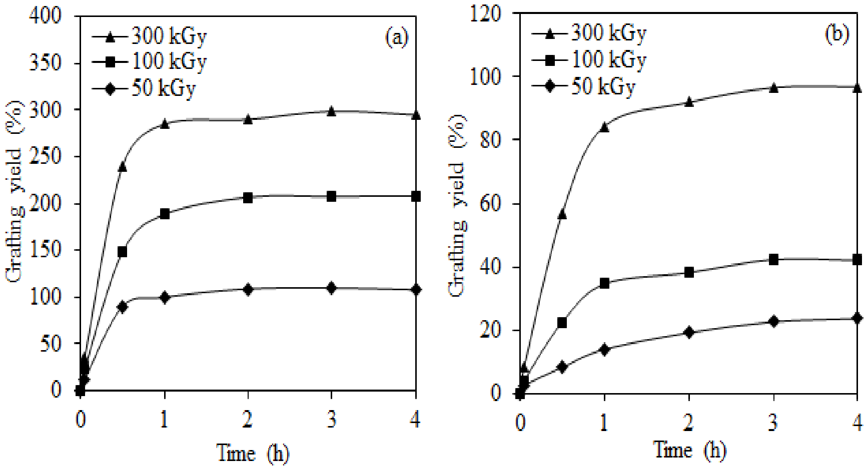

Fig. 5. GMA variation of grafting yield with time for grafting of GMA: (a) VBC, (b) At different irradiation doses. Reaction parameters: solvent, methanol; monomer concentration, 10 wt%; reaction temperature, 30 ºC.

The plot of the polymerization rate vs. irradiation dose is presented in Fig. 6. The slope of the plot was used to obtain the order of dependence of the dG_o/dt on the irradiation dose. The reaction orders for the polymerization of GMA and VBC onto polymer substrate were found to be 1.03 and 1.66, respectively. The reaction is represented by following kinetic equations:

$$\frac{dG_o}{dt}\alpha[D_G]^{1.03} \quad (6)$$

$$\frac{dG_o}{dt}\alpha[D_V]^{1.66} \quad (7)$$

where, D_G and D_V are absorbed dose for GMA and VBC, respectively.

As can be seen, the dose exponent for VBC grafting system is higher than that of GMA grafting system. Therefore, the dependency of the VBC grafting system on the absorbed dose is much higher than GMA grafting system.

The dependency on irradiation dose in this study is shown to be high and this can be attributed to the difference in the types and structures of the polymer substrates [20-23]. Since the conditions to form trapped radicals onto nylon-6 fibres were the same for the two grafting systems. Therefore, the high dependency on the absorbed dose for VBC grafting system is likely to be related to its lower reactivity compared to GMA. Dilli and Garnett [24] stated that the VBC monomer has an aromatic ring with higher molecular weight and this aromatic compound could scavenge the radicals under the influence of resonance stabilization effect. Therefore, the low reactivity of VBC towards radicals reduced the macroradical initiation leading to lower DG. Such results suggest that both GMA and VBC grafting systems follow the free radical mechanism that depends on the amount of trapped radicals and their level of involvement in the initiation of the graft growing chains. It can be concluded that grafting of both monomers is not only depending on the monomer concentration but also on the absorbed dose. Thus, the overall kinetic equation for grafting of GMA onto nylon-6 fibres with reference to Eqs. (4) and (6) can be given in the following expression:

$$\frac{dG_o}{dt}\alpha k[M_G]^{1.76}[D_G]^{1.03} \quad (8)$$

Equation (8) can be rewritten and given in the following equation:

$$\frac{dG_o}{dt} = k[M_G]^{1.76}[D_G]^{1.03} \quad (9)$$

Similarly, the equation for graft polymerization of VBC onto nylon-6 fibres with reference to Eqs. (5) and (7) can be given in the following expression:

$$\frac{dG_o}{dt}\alpha k[M_V]^{1.21}[D_V]^{1.66} \quad (10)$$

Equation (10) can be rewritten and given in the following equation:

$$\frac{dG_o}{dt} = k[M_V]^{1.21}[D_V]^{1.66} \quad (11)$$

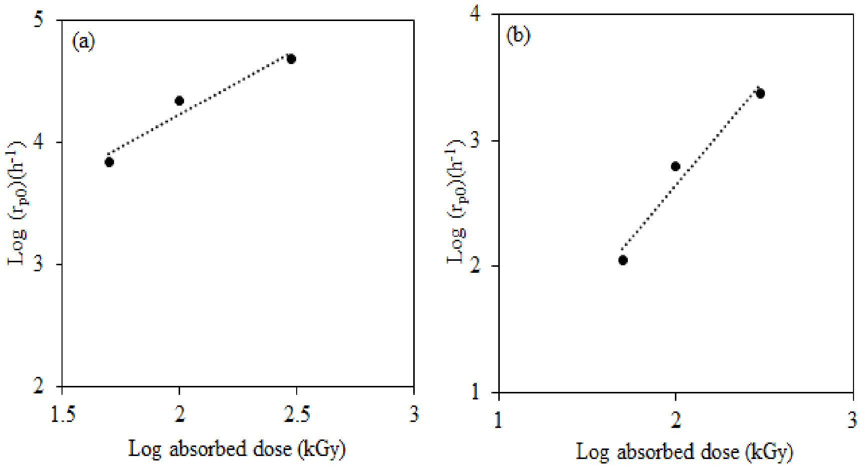

Fig. 6. Plots for initial polymerization rate (r_{p0}) vs. irradiation dose for GMA: (a) VBC, (b) Grafting system. Data are calculated according to Eq. (2).

3.3. Grafting temperature

Figure 7 shows the variation of the grafting yield with time at different reaction temperatures for the GMA and VBC grafting systems. The DG increased intensely at the beginning of grafting reaction and started to level off after 2 hours. This can be understood based on the facts that temperature increases the reactivity of the radicals and enhances the diffusion of the monomer to the grafting sites. Therefore, the rate of initiation and propagation were improved leading to a higher rate of grafting.

Figure 8 shows the Arrhenius plots for GMA and VBC grafting systems. The slope of the Arrhenius plot is used to calculate the activation energy based on Eq. 3. The activation energies for GMA and VBC grafting systems were 34.5 kJ/mol and 60.3 kJ/mol, respectively. The GMA grafting system recorded lower activation energy with high DG and this was due to higher reactivity of GMA and the consequent higher initiation rate [25]. The higher activation energy coupled with the relatively low DG obtained from the VBC grafting system was possibly due to the resonance stabilization effect caused by an aromatic ring of VBC that can scavenge some radicals during the process of initiation [17, 26].

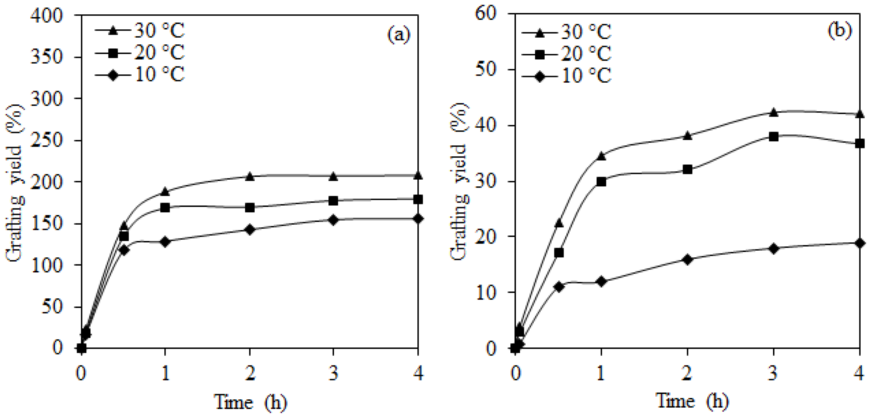

Fig. 7. Variation of the grafting yield at different temperatures with time for GMA: (a) VBC, (b) Grafting systems. Reaction parameters: solvent, methanol; concentration of monomer, 10 wt% and irradiation dose, 100 kGy.

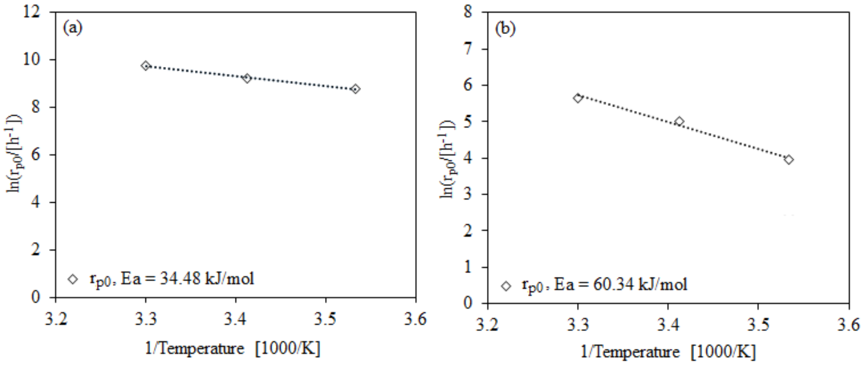

Fig. 8. Arrhenius plots for an initial polymerization rate (r_{p0}) vs. 1/Temperature for GMA: (a) VBC, (b) Grafting systems. Data are calculated according to Eq. (2) and the activation energy is obtained from the slope.

3.4. Evidence of grafting

SEM of poly(VBC) grafted fibres with the reference to the pristine fibres and pure poly(GMA) are presented in Fig. 9. As can be seen, the incorporation of poly(GMA) and poly(VBC) onto nylon-6 fibres brought a remarkable increase in the diameters of the fibres. The diameter of the pristine fibres was increased from 15 µm as shown in Fig. 9(a) to 28 µm after poly(GMA) grafting as in Fig. 9(b) and to 25 µm by incorporation of poly(VBC) as in Fig. 9(c). This confirms the successful grafting of GMA and VBC onto nylon-6 fibres.

The FTIR spectra of original fibres, poly(GMA) and poly(VBC) grafted nylon-6 fibres are presented in Fig. 10.

The peaks related to pristine nylon-6 fibres at 3300 cm^{-1}, 3086 cm^{-1}, 2931 cm^{-1}, 2859 cm^{-1}, 1645 cm^{-1} and 1544 cm^{-1} are representing the hydrogen-bonded NH stretching, NH Fermi resonance, CH_2 asymmetric stretching, CH_2 symmetric stretching, amide I and amide II, respectively [18]. The intensity of these peaks was reduced after grafting of monomers onto the fibres. The FTIR spectrum of poly(GMA) grafted nylon-6 fibres revealed that the peak at 1728 cm^{-1} is due to C=O stretching and peaks at 1150 and 1135 cm^{-1} are assigned for C-O- stretching of the ester. Nasef et al. [27] explained that the peaks at 950, 908 and 855 cm^{-1} are resembling the epoxy group of the GMA. The spectrum associated with poly(VBC) grafted nylon-6 fibres showed peaks at 1264 cm^{-1} representing the C-Cl group and the bands at 838, 702 and 676 cm^{-1} from the *p*-substituents on the aromatic ring [18]. The FTIR results further provide strong evidence of the successful grafting of both GMA and VBC onto nylon-6 fibres.

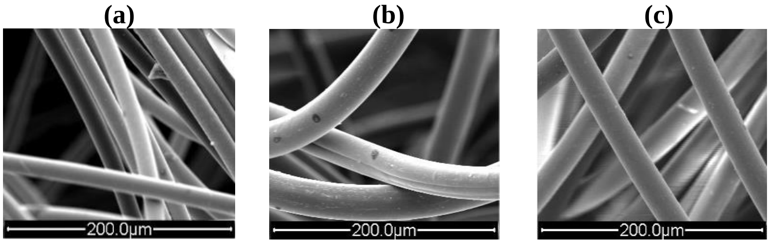

Fig. 9. SEM of: (a) Pristine fibres, (b) GMA grafted fibres with grafting yield of 200%, (c) VBC grafted fibres with grafting yield of 130%.

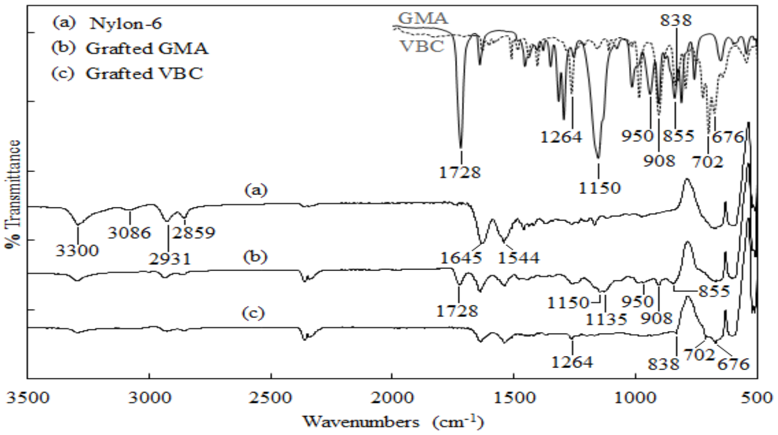

Fig. 10. FTIR spectra of pristine fibres: (a) GMA grafted fibres, (b) VBC grafted fibres, (c) With reference to the spectra of pure GMA and VBC.

4. Conclusions

The kinetics of radiation grafting of two interesting grafting systems of GMA/nylon and VBC/nylon diluted with methanol was successfully evaluated. The results reveal that the initial rate of polymerization and overall grafting yield increased with the increase in the concentration of monomer, absorbed dose and reaction temperature for both grafting systems. The activation energy for GMA/nylon-6 and VBC/nylon-6 were found to be 34.5 kJ/mol and 60.3 kJ/mol, respectively. These results suggest that higher grafting yield can be obtained using GMA/nylon-6 grafting system where grafting yield for GMA grafting system was found to be 5 times higher than VBC grafting system despite the use of same grafting conditions in both grafting systems.

Acknowledgement

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Nomenclatures

A	Pre-exponential factor
D_G	Absorbed dose for GMA
D_V	Absorbed dose for VBC
E_a	Activation energy
k	Reaction rate constant
M_G	Monomer concentrations for GMA
M_V	Monomer concentrations for VBC
R	Gas constant (8.314 J K^{-1}mol^{-1})
r_{p0}	Initial polymerization rate
T	Absolute temperature in K
t_0	Delay time
W_0	Weights of initial grafted
W_1	Weights of final grafted
γ	Characteristic radical recombination rate

Abbreviations

ATR	Attenuated total reflection
DG	Grafting yield
EB	Electron beam
FTIR	Fourier transform infrared
GMA	Glycidyl methacrylate
MOSTI	Ministry of science, technology and innovation
PE	Polyethylene
PVDF	Poly(vinylidene fluoride)
RIG	Radiation induced grafting
SEM	Scanning electron microscope
VBC	Vinylbenzyl chloride

References

1. Pramanik, N.K.; Haldar, R.S.; Bhardwaj, Y.K.; Sabharwal, S.; Niyogi, U.K.; and Khandal, R.K. (2009). Radiation processing of Nylon 6 by e-beam for improved properties and performance. *Radiation Physics and Chemistry*, 78(3), 199-205.
2. Lim, J.G.; Gupta, B.S.; and George,W. (1989). The potential for high performance fiber from nylon 6. *Progress in Polymer Science*, 14(6), 763-809.
3. Haruvy, Y.; Rajbenbach, L.A.; and Jagur-Grodzinski, J. (1986). Grafting of acrylamide to nylon-6 by electron beam preirradiation. IV. Sorption of water in nylon grafted acrylamide membranes. *Journal of Applied Polymer Science*, 32(4), 4649-4656.

4. Timus, D.M.; Popov, A.-M.; Brasoveanu, M.M.; Babes, A.; and Bradley, D.A. (1997). Some preliminary studies of the thermal behaviour of electron beam grafted polyamides. *Applied Radiation and Isotopes*, 48(10-12), 1657-1662.
5. Timus, D.M.; Cincu, C.; Bradley, D.A.; Craciun, G.; and Mateescu, E. (2000). Modification of some properties of polyamide-6 by electron beam induced grafting. *Applied Radiation and Isotopes*, 53(4-5), 937-944.
6. Kaur, I.; Barsola, R.; Misra, B.N.; and Chauhan, G.S. (2000). Radiochemical graft copolymerisation of 2-hydroxy ethylmethacrylate onto polyamide-6, 6-nylon. *Defence Science Journal*, 50(4), 425-433.
7. Kolhe, S.M.; and Kumar, A. (2007). Radiation-induced grafting of vinyl benzyl trimethyl ammonium chloride onto nylon-6 fabric. *Radiation Physics and Chemistry*, 76(5), 901-906.
8. Huang, R.Y.M.; and Xu, Y.F. (1989). Pervaporation separation of acetic acid-water mixtures using modified membranes. Part II. Gamma-ray-induced grafted polyacrylic acid (PAA)-Nylon 6 membranes. *Journal of Membrane Science*, 43(2-3), 143-148.
9. Haruvy, Y.; Rajbenbach, L.A.; and Jagur-Grondzinski, J. (1982). Grafting of acrylamide to nylon-6 by the electron beam preirradiation technique. II. Kinetic aspects and film permeability. *Journal of Applied Polymer Science*, 27(7), 2711-2723.
10. Mascia, L.; and Hashim, K. (1997). Carboxylic acid functionalization of nylon 6 by radiation grafting and conversion to zinc salts: Effects on physical properties. *Colloid and Polymer Science*, 275(7), 689-697.
11. Ting, T.M.; Nasef, M.M.; and Hashim, K. (2016). Evaluation of Boron adsorption on new radiation grafted fibrous adsorbent containing N-methyl-D-glucamine. *Journal of Chemical Technology and Biotechnology*, 91(7), 2009-2017.
12. Jiang, L.; and Marcus, R.K. (2017). Microwave-assisted, grafting polymerization preparation of strong cation exchange nylon 6 capillary-channeled polymer fibers and their chromatographic properties. *Analytica Chimica Acta*, 977, 52-64.
13. Miyazawa, T.; Asari, Y.; Miyoshi, K.; Umeno, D.; Saito, K.; Nagatani, T.; and Yoshikawa, N. (2009). Development of novel ion-exchange membranes for electrodialysis of sea water by electron-beam-induced graft polymerization. II. Graft polymerization of vinyl benzyltrimethylammonium chloride and sodium styrenesulfonate onto nylon-6 film. *Bulletin of the Society of Sea Water Science, Japan.*, 63(3), 175-182.
14. Niemoller, A.; and Ellinghorst, G. (1987). Radiation initiated grafting on fluoro polymers iii. grafting of n-vinylpyrrolidone in aqueous solution on poly(vinylidene fluoride) films by accelerated electrons. *Micromolecular Materials and Engineering*, 148(1), 1-18.
15. Nava-Ortiz, C.A.B.; Burillo, G.; Bucio, E.; and Alvarez-Lorenzo, C. (2009). Modification of polyethylene films by radiation grafting of glycidyl methacrylate and immobilization of β-cyclodextrin. *Radiation Physics and Chemistry*, 78(1), 19-24.
16. Ikeda, K.; Umeno, D.; Saito, K.; Koide, F.; Miyata, E.; and Sugo, T. (2011). Removal of boron using nylon-based chelating fibers. *Industrial and Engineering Chemistry Research*, 50(9), 5727-5732.

17. Hwang, M.-L.; Song, J.-M.; Ko, B.-S.; Sohn, J.-Y.; Nho, Y.-C.; and Shin, J. (2012). Radiation-induced grafting of vinylbenzyl chloride onto a poly(ether ether ketone) film. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 281, 45-50.
18. Ting, T.M.; Nasef, M.M.; and Hashim, K. (2015). Modification of nylon-6 fibres by radiation-induced graft polymerisation of vinylbenzyl chloride. *Radiation Physics and Chemistry*, 109, 54-62.
19. Hegazy, E.-S.A.; Dessouki, A.M.; El-Assy, N.B.; El-Sawy, N.M.; and El-Ghaffar, M.A.A. (1992). Radiation-induced graft polymerization of acrylic acid onto fluorinated polymers. I. Kinetic study on the grafting onto poly(tetrafluoroethylene-ethylene) copolymer. *Journal of Polymer Science Part A: Polymer Chemistry*, 30(9), 1969-1976.
20. Hegazy, E.-S.A.; Ishigaki, I.; Dessouki, A.M.; Rabie, A.; and Okamoto, J. (1982). The study on radiation grafting of acrylic acid onto fluorine-containing polymers. III. Kinetic study of preirradiation grafting onto poly(tetrafluoroethylene-hexafluoropropylene). *Journal of Applied Polymer Science*, 27(2), 535-543.
21. Rohani, R.; Nasef, M.M.; Saidi, H.; and Dahlan, K.Z.M. (2007). Effect of reaction conditions on electron induced graft copolymerization of styrene onto poly(ethylene-co-tetrafluoroethylene) films: Kinetics study. *Chemical Engineering Journal*, 132(1-3), 27-35.
22. Cardona, F.; George, G.A.; Hill, D.J.T.; and Perera, S. (2003). Comparative study of the radiation-induced grafting of styrene onto poly(tetrafluoroethylene-co-perfluoropropylvinyl ether) and polypropylene substrates. I: Kinetics and structural investigation. *Polymer International*, 52(5), 827-837.
23. Nasef, M.M.; Saidi, H.; and Dahlan, K.Z.M. (2011). Kinetic investigations of graft copolymerization of sodium styrene sulfonate onto electron beam irradiated poly(vinylidene fluoride) films. *Radiation Physics and Chemistry*, 80(1), 66-75.
24. Dilli, S.; and Garnett, J.L. (1967). Radiation-induced reactions with cellulose. III. Kinetics of styrene copolymerization in methanol. *Journal of Applied Polymer Science*, 11(6), 859-870.
25. Seko, N.; Bang, L.T.; and Tamada, M. (2007). Syntheses of amine-type adsorbents with emulsion graft polymerization of glycidyl methacrylate. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 265(1), 146-149.
26. Herman, H.; Slade, R.C.T.; and Varcoe, J.R. (2003). The radiation-grafting of vinylbenzyl chloride onto poly(hexafluoropropylene-co-tetrafluoroethylene) films with subsequent conversion to alkaline anion-exchange membranes: optimisation of the experimental conditions and characterisation. *Journal of Membrane Science*, 218(1-2), 147-163.
27. Nasef, M.M.; Abbasi, A.; and Ting, T.M. (2014). New CO_2 adsorbent containing aminated poly(glycidyl methacrylate) grafted onto irradiated PE-PP nonwoven sheet. *Radiation Physics and Chemistry*, 103, 72-74.