Graft Copolymerization of N-Vinylimidazole on Poly(Ethylene Terephthalate) Fibers in a Swelling Solvent Using Azobisisobutyronitrile as Initiator

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In this study, poly(ethylene terephthalate) (PET) fibers were grafted in dimethylformamide (DMF) with n-vinylimidazole (n-VI) using azobisisobutyronitrile (AIBN) as an initiator. Variations of percentage grafting with time, temperature, monomer and initiator concentrations as well as monomer and initiator diffusions were investigated. It was observed that the percentage of grafting and grafting efficiency increased as time and temperature rose up to a certain value, and then they levelled off. The percentage of grafting was found to rise with increasing monomer and initiator concentrations, and then decrease. Monomer and initiator diffusions into PET fibers were shown to follow a similar trend and increased the percentage of grafting. Optimum conditions for grafting were found to be [n-VI] = 0.5 M, [AIBN] = 1.5 x 10^{-3} M, T = 70 °C and t = 3 days. The rate of grafting was found to be proportional to 1.4 and 0.7 powers of monomer and initiator concentrations, respectively. The overall activation energy for grafting was 22.2 kcal/mol. Further changes in the properties of grafted PET fibers such as intrinsic viscosity, water absorption capacity, fiber diameter and elongation percentage were determined. Grafted fibers were characterized by FTIR spectroscopy and scanning electron microscopy.

Key Words: Graft copolymerization, n-vinylimidazole, radical polymerization, swelling, PET fiber.

Introduction

Poly(ethylene terephthalate) (PET) fibers are highly crystalline, hydrophobic in nature and do not contain chemically reactive groups. Hence, this material is not easily penetrated by dyes of large molecular dimensions and cannot combine with dye anions or cations. Furthermore, they suffer from static build up and low moisture regain. One of the most common ways used to improve these undesirable features is grafting vinyl monomers onto it. In this manner, the PET fibers acquire some desired properties depending on the monomer used for grafting. Vinyl monomers can be grafted onto PET fibers either by radiation or by chemical means. Of the methods for grafting, the chemical initiation method has been found to be the best fitting for the purpose owing to the low degradation of the base polymer and high radical yield.

A large number of papers have appeared on the grafting onto PET fibers by the chemical initiation method[1−14]. However, since PET fiber is a hard substrate containing no chemically reactive groups, low

graft yields have been obtained in comparison with other fibers. In a heterogeneous polymer-monomer system, diffusion controls the chain growth and chain termination in the internal structures of the polymer. One way of facilitating diffusion is to open up the physical structure of the polymer to allow the monomer and initiator to enter in sufficient quantities. Many solvents have been recommended as separate swelling agents before graft copolymerization was carried out[1,15−21].

In this study, we have carried out the polymerization reactions in dimethyl formamide (DMF), which was also used as a swelling agent ($\delta = 12.14$) for PET ($\delta = 9.5$-12.0) previously by Hsieh et al.[1]. Dambatta and Ebdon[22], and Bamford and Schofield[23] also reported that the rate of polymerization of n-VI in DMF is higher than in other solvents such as methanol and ethanol.

Recently, interest in polymer and copolymers containing the imidazole ring has been growing because of their useful properties. The ability of imidazoles to form complexes with metals and bind dyes, the hydrophilicity of its polymers and their polyelectrolyte behavior have stimulated interest in imidazole-containing polymers for potential industrial uses[22,24−28].

There are also some studies investigating the graft copolymerization of n-VI onto Kapton[29,30] (polyimide of Du Pont), Teflon-FEP[31] (copolymer of tetraflouroethylene with hexafluoropropylene) and polyethylene[32] films. However, there is no research concerning the grafting of n-VI onto either PET films or fibers.

As a part of our studies on the swelling-assisted graft copolymerization of vinyl monomers onto PET films and fibers[17−21], the present paper deals with a view of evaluating the optimum grafting conditions and properties of n-VI grafted PET fibers.

Experimental

Materials

PET fibers (126 denier, 28 filament) were kindly supplied by SASA Fiber Co. (Adana, Turkey). The PET fiber samples were soxhlet-extracted for 12 h with acetone and then with water and dried to a constant weight at 50 °C in a vacuum oven, and kept in a desiccator until use. N-vinylimidazole, (n-VI) monomer (Merck) was used after vacuum distillation at 15 mmHg at 65 °C. The initiator, AIBN (Merck), was recrystallized by precipitating twice from methanol and dried in a vacuum oven for 2 days. All the other reagents were Merck products and they were used as received.

Grafting Reactions

PET fibers of known mass (i.e. 130 mg) were dipped into a 100 mL polymerization tube containing 8 mL of n-VI solution dissolved in DMF at a known concentration, and the tube was placed in an oil bath adjusted to the polymerization temperature, and nitrogen gas was allowed to pass through the solution for 45 min. After the thermal equilibrium was established, the required amount of AIBN (dissolved in 2 mL methanol) was added, and the polymerization was carried out under a nitrogen atmosphere for a specified period of time. At the end of the predetermined polymerization time, the fiber samples were removed from the polymerization tube and subjected to soxhlet-extraction for 6 h with methanol and distilled water, respectively. They were then vacuum dried at 50 °C for 72 h and weighed.

The grafting yield percentage was calculated from the weight gain of the fibers as follows:

$$\text{Grafting Yield } (\%) = [(w_g - w_i)/w_i] x 100 \tag{1}$$

where w_i and w_g denote the weights of the ungrafted and n-VI grafted PET fibers, respectively.

At the end of the grafting procedure, homopoly(n-VI) formed in the grafting medium was precipitated by the addition of excess acetone. Grafting efficiency (GE) was calculated as follows:

$$GE(\%) = [(\text{weight of graft})/(\text{weight of graft} + \text{weight of homopolymer})] \times 100 \qquad (2)$$

The rate of grafting (R_g) was found by using the formula[31]

$$R_g = [(w_g - w_i)x1000]/[MxtxV] \qquad (3)$$

where M is the molecular mass of the monomer, t is the polymerization time (s), and V is the volume (mL) of the overall reaction medium.

Characterization

Ungrafted and n-VI grafted PET fibers were conditioned at 20.0 ± 0.1 °C in a medium having a relative humidity of 65% for 24 h in order to evaluate the moisture regain value. The moisture regain capacity of PET fibers was calculated from the weight gain.

Diameters of the fibers were measured using a Kyowa Microlux-11 microscope at a magnification of X 400. The measurements were carried out using at least five samples taken from different regions of the grafted fibers.

Intrinsic viscosity measurements of ungrafted and n-VI grafted PET fibers were carried out in m-cresol using a Ubbelohde capillary flow viscometer mounted in a water bath maintained at 25.0 ± 0.1 °C.

FTIR spectra of ungrafted and n-VI grafted PET fibers were recorded using a Mattson Model 1000 FTIR spectrophotometer with KBr disks.

Results and Discussion

Effect of Polymerization Time on Grafting

Grafting of PET fibers was carried out at various polymerization times, keeping the monomer, initiator and temperature constant at 0.5 M, 1.5×10^{-3} M and 70 °C, respectively. As shown in Figure 1, grafting yield percentage first rose with increasing polymerization time; it then levelled off, reaching to a saturation grafting value of 2.7%. As the polymerization time increases, the number of monomer and initiator molecules that diffuse onto the PET fiber surface also increases, and this results in a higher grafting yield percentage. The levelling off of grafting may be attributed to the saturation of active PET back-bone by homopoly(n-VI), which forms a diffusion barrier on the fiber surface, as is reflected in the grafting efficiency curve in Figure 1. However, the diffusion of the monomer becomes difficult due to the increase in the medium viscosity. Similar results were observed in the graft copolymerization of acrylamide[12,18,19] (AAm), methyl methacrylate[11] (MMA) and glycidyl methacrylate[29] on PET fibers.
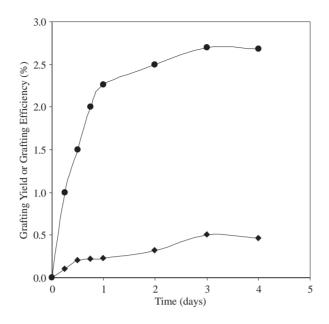
Figure 1. Change of grafting yield (●) and grafting efficiency (♦) with time. [AIBN] = 1.5 x 10^{-3} M, [n-VI] = 0.5 M, T = 70 °C.

Effect of Temperature

The effect of temperature on the graft copolymerization of n-VI onto PET fiber was studied within the range of 60-100 °C keeping monomer, initiator, and polymerization time constant (Figure 2). As reflected in the graph, a sharp increase in the grafting yield value of 2.7% was obtained and then this almost levelled off. The enhancement in the grafting yield with increasing temperature may be attributed to: (1) the enhancement of PET fiber swellability; (2) an increase in the mobility of the initiator and monomer; (3) an increased rate of diffusion for the initiator and monomer from the solution phase to the PET back-bone; (4) an increased number of active sites in the reaction medium; and (5) an increased rate of initiation and propagation steps. The levelling off of the grafting yield after 70 °C was due to the increase in the formation of homopoly(n-VI), as is reflected in the grafting efficiency curve in Figure 2.

Influence of Monomer Concentration

The variation of grafting yield with the concentration of n-VI was investigated by carrying out polymerization at six different n-VI concentrations (Figure 3). As is evident, grafting yield sharply rises with increasing n-VI concentration up to 0.5 M, achieves 2.7% grafting yield, and then decreases with further increases in n-VI concentration. As the n-VI concentration rises, the diffusion of monomer into the PET fiber phase increases and leads to an increment in the grafting yield. The decrease in the grafting yield at higher n-VI concentrations may be associated with the adsorption of monomer on the PET surface in excessive amounts, which prevents diffusion of the initiator molecules inside the fibers and thereby lowers the polymer add-on. Similar behavior was reported in the grafting of AAm onto PET film[18].
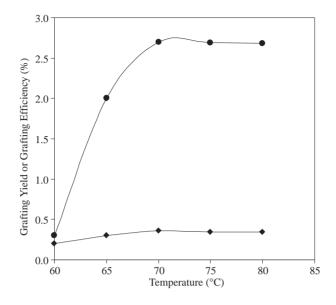
Figure 2. The effect of temperature on grafting yield and grafting efficiency. (●) grafting yield, (◆) grafting efficiency, [AIBN] = 1.5 x 10^{-3} M, [n-VI] = 0.5 M, t = 3 days.

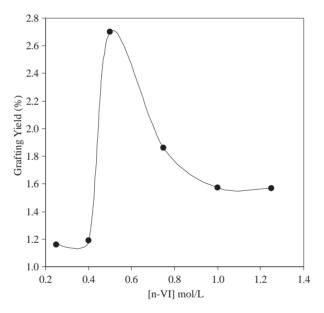**Figure 3.** The variation of grafting yield with monomer concentration. [AIBN] = 1.5 x 10^{-3} M, T = 70 °C, t = 3 days.

Influence of Initiator Concentration

The results presented in Figure 4 indicate that the percentage of grafting increases with AIBN concentration in the 0.5 x 10^{-3} M to 1.5 x 10^{-3} M range, and then decreases with any further increase in the AIBN concentration. The enhancement of grafting by increasing the AIBN concentration to a certain limit implies that free-radical species produced by the dissociation of AIBN molecules may participate essentially in the abstraction of H atoms from the PET back-bone, yielding a PET macroradical capable of initiating grafting. As the initiator concentration increased above 1.5 x 10^{-3} M, the termination reactions of the

growing polymer chains combination of the free-radical species, the termination process with the polyester macroradicals (including crosslinking reactions) and the decrease in the half-life of AIBN molecules[33] prevail over the initiation process. This typical behavior was observed in many studies[2,3,18,26].
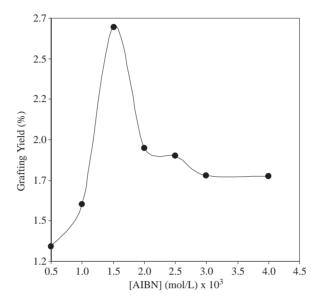

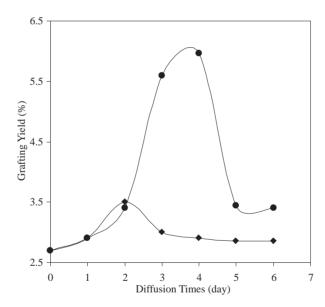**Figure 4.** The effect of initiator concentration on grafting yield. [n-VI] = 0.5 M, T = 70 °C, t = 3 days.

Figure 5. The effects of monomer (♦) and initiator (●) inclusions on grafting yield. [AIBN] = 1.5 x 10^{-3} M, [n-VI] = 0.5 M, T = 70 °C, t = 3 days.

Effect of Monomer and Initiator Inclusions

Pretreated PET fibers were dipped into 0.5 M n-VI and 1.5 x 10^{-3} M AIBN solutions for 1-6 days at 20 °C before graft copolymerization experiments were carried out (Figure 5). The overall graft yield increased with increasing monomer and initiator inclusion times. Saturation grafting yield values were reached at 2 days

(3.5%) and 4 days (6.0%) for the monomer and initiator inclusions, respectively. These results are consistent with earlier studies of the grafting of various hydrophilic monomers on PET fiber[18] and films[17,20,21].

Kinetics of Grafting

In a grafting system of n-VI, AIBN and PET fiber, the relation of the rate of grafting (R_g) with the monomer and initiator concentrations can be written as[33]

$$R_g = k[n-VI]^m[AIBN]^n \tag{4}$$

where m and n can be experimentally determined.

The change in the initial rate of grafting with n-VI concentration, between 0.25 and 0.50 M, by keeping the AIBN concentration constant, is given in Figure 6. The slope of the $\log R_g$ vs $\log[\text{n-VI}]$ graph reflects that the rate of grafting is proportional to the 1.4 power the of n-VI concentration.

Likewise, the initial rate of grafting was determined for AIBN concentrations of 0.5×10^{-3} M-1.5×10^{-3} M, keeping the n-VI concentration constant (Figure 7). The slope of the $\log R_g$ vs. $\log[\text{AIBN}]$ graph given in Figure 7 shows that the rate of grafting was proportional to the 0.7 power of the AIBN concentration. Thus, from these experimental results, the grafting rate of n-VI and PET fibers using AIBN initiator can be written as

$$R_g = k[n-VI]^{1.4}[AIBN]^{0.7} \tag{5}$$

The overall activation energy was calculated to be 22.2 kcal/mol from the Arrhenius plot of $\log R_g$ vs. $1/T$ (Figure 8).
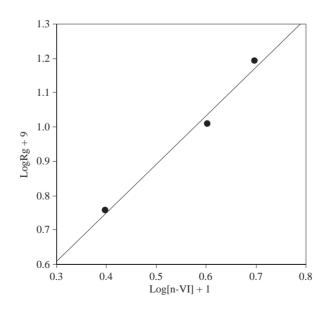

Figure 6. The change of rate of grafting with monomer concentration. [AIBN] = 1.5×10^{-3} M, T = 70 °C, t = 3 days.
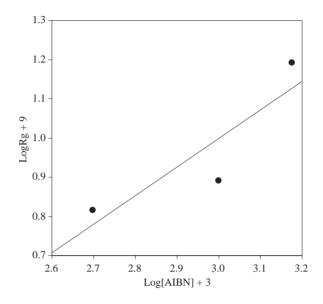
Figure 7. The change of rate of grafting with initiator concentration. [n-VI] = 0.5 M, T = 70 °C, t = 3 days.
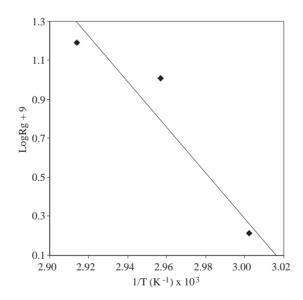

Figure 8. The effect of temperature on the rate of grafting. [AIBN] = 1.5 x 10^{-3} M, [n-VI] = 0.5 M, T = 70 °C, t = 3 days.

Although there are reports in the literature on the grafting of various vinyl monomers onto PET fibers and films using different initiators, there are no kinetic data concerned with the grafting of n-VI onto PET fibers using an AIBN initiator. It was reported by various authors that the dependence of rate of grafting on monomer and initiator concentrations varies with the types of monomers and initiators used for grafting[5,17,20,35−38].
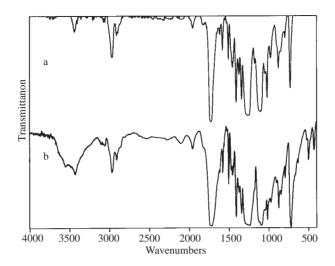
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Figure 9. FTIR spectra of (a) ungrafted PET fiber, (b) n-VI grafted (6.0%) PET fiber.

Evaluation of Some Properties of n-VI Grafted PET Fibers

Moisture Regain

The change in moisture regain with grafting yield percentage is given in Table 1. Moisture regain values of the fibers increased from 0.41 to 1.19% as the grafting percentage of n-VI was increased to 6.0%. This threee fold increase in the moisture regain values of the fibers can be attributed to the hydrophilic nature of the grafted monomer and the opening up of the PET matrix due to grafting. A similar trend was reported in the literature[10,18,34−38].

Table 1. Moisture regain results of n-VI Grafted PET fibers.

Grafting Yield (%)	Moisture Regain (%)
0.0	0.41
1.0	0.68
1.5	0.76
2.3	0.97
2.7	1.10
3.4	1.17
6.0	1.19

Intrinsic Viscosity

Limit viscosity numbers, $[\eta]$, of ungrafted and n-VI grafted PET fibers were determined in m-cresol at 25.0 °C $\pm$ 0.1 °C and the results obtained are tabulated in Table 2. $[\eta]$ was shown to increase with increasing grafting yield, which is evidence of grafting. Similar results were reported for the graft copolymerization of various vinyl monomers onto PET fibers[18] and PET films[17,20].

FTIR Spectrum

The FTIR spectrum of ungrafted PET fiber (Figure 9a) shows distinctive absorptions at 1724 cm^{-1}, 1400-1600 cm^{-1}, 2967-2909 cm^{-1} and 3060 cm^{-1} that are typical of C=O, C=C, aliphatic C-H and aromatic C-H stretchings, respectively. In addition to the above absorptions of PET, characteristic absorption peaks of poly(n-VI) at 1635 cm^{-1} (C=N stretching), 1225 cm^{-1} (C-N stretching in the imidazole ring) and 1108 cm^{-1} (C-N stretching)[36] caused broadening in the FTIR spectrum of n-VI grafted PET fiber (Figure 9b) due to an overlapping of the peaks.

Table 2. Intrinsic viscosity data of n-VI grafted PET fibers.

Grafting Yield (%)	$[\eta]$ (dl/g)
0.0	0.06
1.9	0.12
2.7	0.29
6.0	0.34

Tensile Properties

Studies concerning the mechanical properties of PET are limited[4,40−43]. Table 3 lists the percentage elongation of the n-VI grafted PET fibers obtained using an Instron Model 1185. n-VI grafted PET fibers showed increases in the percentage elongation with rising grafting yield and achieved 65% elongation with 6.0% grafting yield. The plasticizing effect of the newly polymerized molecules in the amorphous regions of PET may have contributed to the higher elongation at break. Therefore, mechanical test results are further proof of grafting.

Table 3. Mechanical test results of n-VI grafted PET fibers.

Grafting Yield (%)	Elongation at Break (%)
0.0	44
1.0	50
1.5	55
1.9	57
6.0	65

Diameters of Grafted Fibers

The change in the diameters of PET fibers with the grafting yield is shown in Table 4. Fiber diameter increases as grafting yield rises. This may be attributed to the possible accumulation of grafted chains in between the polymer chains. Similar results were reported for the AAm grafted PET fibers using cerium ammonium nitrate initiator[12,18].

Microstructure of Grafted Copolymers

The scanning electron micrographs of ungrafted and n-VI grafted (6.0%) PET fibers are depicted in Figure 10. The ungrafted PET fiber surface (Figure 10a) has a smooth and relatively homogeneous appearance.

The grafted side chain, poly(n-VI), seems to form microphases attached to the PET back-bone in the graft copolymer (Figure 10b) which is further proof of grafting.

Table 4. Diameters of n-VI grafted PET fibers.

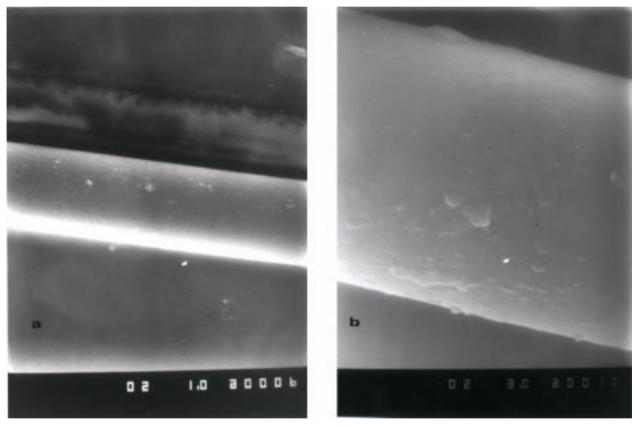| Grafting Yield (%)	Diameter (μm)
0.0	15.8
1.5	20.0
2.3	23.0
6.0	26.2

Figure 10. SEM micrographs obtained from (a) ungrafted (1000 X), and (b) n-VI grafted (3000 X) PET fibers.

Conclusions

From our studies on the grafting of n-VI onto PET fiber using AIBN initiator the following conclusions may be drawn: 0.5 M n-VI concentration and 1.5×10^{-3} M AIBN concentration, 3 days of polymerization time and 70 °C polymerization temperature were found to be the optimum conditions for grafting. The rates of grafting were found to be 1.4 and 0.7 powers of monomer and initiator concentrations, respectively, and the overall activation energy for grafting was determined to be 22.2 kcal/mol. The intrinsic viscosity, diameter, moisture regain and elongation percentage values of n-VI grafted PET fibers were observed to increase as grafting yield rose.

Acknowledgment

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