Two-step Radical Grafting onto Polypropylene Fiber Initiated by Active Species Prepared through the Irradiation of Electron Beam

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Graft polymerization is one of the surface modification methods for organic solid. When organic solids are irradiated by electron beam (EB), activation sites can be generated in the polypropylene and monomer reacts at the active site to grafted chains. First-step polymerization proceeded during EB irradiation. And then, the fiber was heated at high pressure to promote second step grafting with high propagation rate. The generated chains have bimodal distribution in molecular weight and high molecular weight component gradually increased with polymerization pressure for second grafting. The molecular weight of grafted chains and their distribution are evaluated from those for the extracted solution polymers. Temperature dependence of grafting efficiency gave us thermodynamic parameters for the grafting polymerization.

Keywords: electron beam grafting, survived radical, ultrahigh pressure, two-step polymerization

1. Introduction

Graft polymerization is one of the surface modification methods for organic solid. When the fiber was irradiated by electron beam (EB), activation sites can be generated in the crystalline region and amorphous region in the matrix. If EB irradiated onto fiber in the monomer solution, monomers react immediately with the active site to

grafted chains at the boundary of crystalline (first-step polymerization). The unpaired electrons in crystalline are so stable that they survived more than 100 hours at -78 °C [1]. The radical could migrate to the boundary of crystalline by repeating chain transfer reaction between polymer chains at elevated temperature. Once the radical reach on the boundary, they can initiate

Scheme 1. Two-step polymerization using “survived” radicals.

Table 1. Activation volume ($\Delta V^\ddagger$) for the propagation reaction of methyl acrylate[1].

Pressure (MPa)	$\Delta V^\ddagger$ (cm ³ / mol)
≤ 180	-21.4
190-270	-22.9
270-400	-3.6
≥ 400	-12.8

grafting. In this study, the irradiated fibers were heated under high pressure. Generally the propagation reaction of monomers could be accelerated at high pressure because of negative activated volume [2]. So, we checked of two-step polymerization can be promoted through the molecular weight distribution of resulting chains as shown in Scheme 1.

2. Method

2.1. Electron-Beam induced Grafting

PP nonwoven fabrics were immersed into methanol containing a certain amount of methyl acrylate (MA), 30 – 70 wt%. After nitrogen bubbling in the solution, it was shield in polyethylene bag. Electron beam was irradiated through the bag and the dose was from 40 to 200 kGy by Area Beam Type Electron Beam Processing System (EPS) Curetron® EBC250-20-35 (NHV Corporation). Electron beam processing systems are useful and powerful tools in industrial applications, such as the production of cross-linked wire, rubber tire, heat shrinkage film and tubing, curing, degrading of polymers, sterilization and environmental applications.

After initial polymerization at room temperature, the second step polymerization was operated at ambient pressure or higher pressure, 100-500 MPa, and at 30-60 °C. The pressure was applied with Servo Pressure800 HPV-80C20-SA (Sugino Machine Ltd.). Generally speaking, rate constant of a reaction, k , is a function of pressure as shown in eq. (1).

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^\ddagger}{RT} \quad (1)$$

where $\Delta V^\ddagger$ is a volume difference between reactants and transient complex and is called as an

activation volume of the reaction. As shown in Table 1, $\Delta V^\ddagger$ for the propagation reaction of methyl acrylate are negative, so the reaction could be accelerated at elevated pressure. In radical polymerization, molecular weight of the product is proportional to the propagation rate constant, k_p , so the polymers obtained at higher pressure must have high molecular weights.

After second reaction degree (DG) of grafting was determined as follows,

$$\text{Degree of Grafting} = \frac{w_2 - w_1}{w_1} \times 100 \quad (2)$$

where w_1 and w_2 are the weights of PP nonwoven fiber before and after grafting, respectively.

2.2. Gel Permeation Chromatography (GPC)

The molecular weight and their distribution are almost same with grafted chain because propagation rate does not depend on the fixation of opposite end [3]. We measured the molecular weight distribution of the extracted solution polymer to estimate those for grafted chains.

Molecular weight distributions were assessed by Gel Permeation Chromatography (GPC) in tetrahydrofuran at 40 °C using a two PSt gel columns [TSKgel GMH_{HR}-M×2; 7.8 mm i.d. × 300 mm each; flow rate 1.0 mL/min] connected to a Tosoh CCPM-II pump and an RI-8012 and UV-8000 for refractive index and UV detector, respectively. Mn and Mw/Mn were calculated from GPC curves on the basis of a polystyrene calibration.

2.3. High-resolution 3D X-ray microscopy

In order to study the evolution of grafting for individual fibers, a small volume of the material is illuminated with X-rays. For this purpose, the 3-D XRD microscope, nano3DX (Rigaku Corp.), was used in the transmission geometry. The energy of the monochromatic X-rays is 40 keV (Cu target). The view area is 900 × 700 μm², and the thickness of the samples is 900 μm. By rotating the sample around an axis perpendicular to the beam, a number of grains give rise to diffraction spots on a two-dimensional (2-D) detector. The exposure time was 11 or 45 min. At the

Figure 1. Degree of grafting for EB-grafted polypropylene fibers as a function of irradiation dose and applied pressure for second polymerization. (a) [MA] = 70 wt%, (b) [MA] = 50 wt% and (c) [MA] = 30 wt%.

given experimental conditions, spatial resolution was $1.35 \mu\text{m}/\text{pixel}$.

3. Results and discussion

3.1. High pressure polymerization

Figure 1 shows degree of grafting as a function of irradiated dose and pressure for second step polymerization. When monomer concentration is high enough, e.g. 70 wt%, the

Figure 2. Reconstructed 3D X-ray microscope images for MA-grafted PP nonwoven fabric (degree of grafting: 427 %): (a) irradiated side and (b) back side of the fabric.

degree of grafting increased with the irradiated dose and the polymerization pressure. At lower concentration of monomer, 50 and 30 wt%, the degree of grafting showed maximum around 300 MPa, it decreased at more elevated pressure.

3.2. High-resolution 3D X-ray microscopy

MA-grafted PP nonwoven fabrics was observed with high-resolution 3D X-ray microscopy. Figure 2 shows reconstructed 3D X-ray microscope images for MA-grafted PP nonwoven fabric (degree of grafting: 427 %). Diameters of fibers were more than $50 \mu\text{m}$ at the irradiated side. The thickness of fiber gradually decreased with the depth and the diameters were around $23 \mu\text{m}$ at the other side, and which is close to those for native fibers ($19 \mu\text{m}$).

Figure 3 shows high-resolution X-ray microscope image for cross-sectional view for the same fabric with Figure 2. With increasing exposure, density resolution was 0.17 g cm^{-3} at the given experimental conditions. The densities of polypropylene and poly(methyl acrylate) are 0.9 g cm^{-3} and 1.22 g cm^{-3} , respectively [4]. If grafted chain grew at the separated space, the microscopy could detect the density gap, 0.32 g/cm^{-3} . There is slight bright rim for each fiber but the amount is not enough to satisfy high degree of grafting. The results indicate that the grafting proceeds just not only on the surface of fiber, but also interior of fiber. The later reaction contains the diffusion of

Figure 3. High-resolution X-ray microscope image for cross-sectional view of MA-grafted PP nonwoven fabric (degree of grafting: 427 %). Electron beam was irradiated from left to right.

monomer through fiber. The process might disturb by compression at high pressure.

3.3. 10^5 Molecular weight 10^1 Retention time / min

d molecular weight distribution of grafted chains

After second polymerization at ambient pressure (0.1 MPa), the reaction mixture was consisted of two components; unreacted monomer and polymers with molecular weight around 10,000 as shown in Figure 4. On the other hand, another polymer component was obtained around 1,000,000 through second step polymerization at high pressures. As shown in Table 1, the activation volumes are negative for propagation reaction of methyl acrylate. Then, the high-molecular-weight (HMW) components were certainly born under high pressure, and low-molecular-weight (LMW) component was polymerized during and after EB irradiation at ambient pressure.

The weight fraction of HMW components increased with an elapse of time for second step polymerization as shown in Table 2. The results show HMW components produced at second step polymerization and active species produced by the electron beam irradiation could “survive” more than several hours within a fiber matrix to initiate post polymerization. Previously two kinds of grafted chain were promoted through two

Figure 4. GPC curves for soluble components in reaction mixtures. [MA]: 70 wt% and irradiated dose: 200 kGy. Polymerization pressure were 0.1 MPa (solid line), 100 MPa (dotted line), 300 MPa (broken line) and 500 MPa (chain line).

sequential irradiations [5]. The second irradiation can degrade the first graft and matrix polymer. In this procedure, we irradiated electron beam onto native fiber just before grafting, so the process can reduce the risk mentioned above.

The molecular weights of HMW components were higher than that for the component polymerized at ambient pressure but they were almost identical at elevated pressures as shown in Figure 5. Since the

Table 2. Weight fractions in solution polymers as a function of reaction time for second step polymerization.

Time (min)	DG (%)	Yield (%)	Weight content (%)	
			LMW polymer	HMW polymer
10	2.50	2.87	100	0
20	6.10	4.16	74.9	25.1
30	12.3	4.34	36.4	43.6
60	42.9	14.5	11.1	88.9

* Initial concentration of MA was 70 wt%. Grafting was initiated through 40-kGy EB irradiation. Polymerization pressure was 500 MPa.

Figure 5. Relation between weight-average molecular weight and polymerization pressure. ○: 40 kGy, △: 50 kGy, □: 100 kGy, ▽: 150 kGy, and ◇: 200kGy. Initial concentration of methyl acrylate was 70 wt%.

rate constant for propagation reaction still increases with the polymerization pressure for solution polymerization, the saturation phenomena might be related monomer diffusion through fiber matrix. The long lifetime of unpaired electrons under high pressure [6] gives us clear vision for this apparent increase of initiation efficiency under at high pressure.

3.4. Thermodynamic analysis

Graft efficiency was evaluated as follows:

$$\text{Graft efficiency} = \frac{W_2 - W_1}{m} \times 100 \quad (3)$$

where m is weight of feed monomer. Polymerization rates, R_p , were evaluated from the gradient of graft efficiency as a function of polymerization time. The rate constants, k , were calculated from eq. (4).

$$R_p = k[M][P\cdot] \quad (4)$$

where $[M]$ is a concentration of monomer and $[P\cdot]$ the concentration of growing chains. $[P\cdot]$ was evaluated experimentally through the coupling reaction between EB-irradiated PP fabric and di(phenyl)-(2,4,6-trinitrophenyl) iminoazanium (DPPH). Actual number of unpaired electrons must be higher than one estimated with DPPH because DPPH cannot

Figure 6. Arrhenius plots of the rate constants of MA grafting onto polypropylene fibers through EB irradiation: ○; 0.1 MPa, △; 100 MPa, □; 300 MPa and ▽; 500 MPa.

penetrate into the crystalline region of PP fiber. However, the reacted sites are seem to be identical with the sites initiated grafting polymerization of methyl acrylate.

Figure 6 shows the Arrhenius plots of the rate constants for the grafting of methyl acrylate onto PP fiber through EB irradiation. From the linear relationship, the thermodynamic parameters were evaluated through following equations:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (6)$$

$$E_a = \Delta H^\ddagger + 2RT \quad (7)$$

$$A = e^{-2 \frac{N_B T}{h} \frac{RT}{P}} \exp \left(\frac{\Delta S^\ddagger}{R} \right) \quad (8)$$

where E_a is activation energy, " $G^\ddagger$ " activation Gibbs energy, " $H^\ddagger$ " activation enthalpy and " $S^\ddagger$ " the activation entropy. As shown in Table 3, activated enthalpy for propagation of grafted chain was almost independent of polymerization pressure and they were around 60 kJ mol⁻¹. The value was smaller than those for the propagation reaction for solution polymerization of methyl acrylate, 82.5 kJ mol⁻¹ [7]. The activated entropy increased from -96.4 J mol⁻¹ K⁻¹ to -17.6 J mol⁻¹ K⁻¹ with the applied pressure. The trend was basically same with solution polymerization

Table 3. Thermodynamic parameters of graft polymerization of methyl acrylate onto polypropylene nonwoven fabric at 333 K.

Pressure MPa	"H" kJ mol ⁻¹	"S" J mol ⁻¹ K ⁻¹	"G" kJ mol ⁻¹	"V" cm ³ mol ⁻¹
0.1	59.8	-96.4	91.9	-16.6
100	60.0	-46.9	75.6	-17.4
300	61.0	-23.4	68.8	-19.1
500	56.9	-17.6	62.7	-20.8

[8]. Interesting point in the thermodynamic analysis, the activated volume for grafting was less dependent on the applied pressure than those for solution polymerization [9]. The rate-determining state for grafting onto the fiber may be "rigid" and their structure is less influenced by applied pressure.

4. Conclusion

Methyl acrylate was grafted onto polypropylene nonwoven fabric through electron beam irradiation. The molecular weight and their distribution are estimated from those for the extracted solution polymers. Gel permeation chromatography analysis showed that the active species survived within the polypropylene fiber for several hours. The survived species could initiate another grafting by changing reaction condition. High-resolution 3D X-ray microscopy and thermodynamic parameter suggested that the grafting proceed at the surface and interior of fibers.

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