

Effect of irradiation and LDPE content on crystal formation of PP

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PP의 결정형성에 대한 조사가교와 LDPE 함량의 영향

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Abstract The crystallization behavior of irradiated polypropylene (PP) and the blend is an important parameter for polymer processing. Blends of PP/low density polyethylene (LDPE) with different LDPE contents were prepared by melt mixing in a twin screw extruder. The effect of the LDPE content on the irradiation effectiveness of the PP/LDPE blend with trimethylolpropane-trimethylacrylate (TMPTMA) as a crosslinking co-agent was investigated in conjunction with the LDPE loading in the blend. The non-isothermal crystallization and crystal structure were measured by DSC, X-ray diffraction (XRD), and polarized optical microscopy (POM). A decrease in the melting temperature of PP was observed due to irradiation, which may be due to the PP chain scissioning effect of irradiation. The Ozawa component n represents a rod shaped, disc shaped and sphere-shaped geometry of the crystal if the value corresponds to 2, 3 and 4, respectively. Based on Ozawa analysis, the values of n were 3.8 and 2.3 for the pure PP and PP blends with 30 wt% LDPE, respectively. The fact that the crystal geometry of PP changed from spherical to disc and rod shaped was confirmed by Ozawa analysis and POM. The β form XRD peak of the PP/LDPE blend at 16.1° disappeared after irradiation due to the crosslinking reaction.

요약 전자선 조사 폴리프로필렌과 블렌드의 결정화 거동은 고분자 가공시 중요한 변수중 하나이다. 저밀도폴리에틸렌 (linear low density polyethylene, LDPE) 함량에 따라 폴리프로필렌(polypropylene, PP)/LDPE 블렌드를 이축압출기를 이용하여 제조하였다. 조사에 의한 가교반응을 용이하게 하기위해 가교조제로 trimethylolpropane-trimethylacrylate (TMPTMA)를 PP/LDPE 블렌드 제조시 첨가하였다. PP/LDPE 블렌드의 조사가교 효율에 대한 LDPE 함량의 영향을 평가하였다. 조사시료의 비등온 결정화과정과 결정구조를 DSC, X-선회절분석(X-ray diffraction, XRD), 그리고 편광현미경(polarized optical microscope, POM)을 이용하여 분석하였다. 조사 후 시료의 용융온도가 감소하는 것은 조사에 의한 PP 사슬의 절단에 의한 것으로 판단된다. Ozawa 지수, n 이 4일 때 구형, 3일 때 디스크형, 2일 때 로드형의 결정구조를 나타낸다. Ozawa 분석 결과, 순수 PP의 n 값은 3.8, 30 wt%의 LDPE를 포함하는 시료의 n 은 2.3을 나타내었다. LDPE 첨가와 조사에 의해 PP의 결정구조가 구형에서 disk나 rod형으로 변화하는 것을 Ozawa 분석과 POM을 통해 확인하였다. XRD 스펙트럼의 16.1° 에서 나타나는 β 형 결정구조가 조사 후 시편에서 사라지는데, 이는 가교결합에 의한 것으로 해석할 수 있다.

Key Words : Crosslinking, Crystal Structure, Irradiation, PP/LDPE blend

1. Introduction

Polyolefins are widely used as structural materials because of their relatively low cost and general

availability [1]. Blending of different plastic resins has long been practiced in the manufacturing industry. Among other reasons, blending has been carried out and studied (1) to produce tailor-made blends to meet

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specific processing and performance requirements that cannot be satisfied by single components; (2) for scientific interest; and (3) due to financial incentives. Polypropylene (PP) and polyethylene (PE) are among the binary systems that have attracted significant attention. The huge annual worldwide consumption of PP and PE also has motivated research on various blending issues of these two resins [2].

Radiation processing of polyolefins is an economically viable and versatile way to produce materials with enhanced chemical, mechanical, physical properties [3-6]. The radiation process of PP is of limited use, however, because PP predominantly undergoes chain scissioning when subjected to high energy radiation. In addition to the poor radiation resistance of PP, its poor impact resistance at low temperature further restricts its utilization in industrial domains [7].

Ionizing radiation causes chain scissioning and crosslinking of the polymer chains of PP with roughly equal probability whereas crosslinking is predominant in the case of PE [8]. The toughness and radiation resistance of PP is expected to increase with the addition of PE, as it predominantly undergoes crosslinking under high energy radiation [9,10]. Preparation of PE/PP blends is hindered by the low compatibility of this polymer pair. The compatibility might be improved by adding a compatibilizing agent and electron beam irradiation [11]. Addition of trimethylolpropane-trimethylacrylate (TMPTMA) during sample mixing is used to improve its dispersion within matrix. TMPTMA may reduce the interfacial tension and increase the adhesion force between the polymer phase, allowing finer dispersion and a more stable morphology [12].

Crystallization is a process of formation of crystals from solution or melt. Polymers are not totally crystalline in nature, their crystallinity ranges from 10% to 80% hence they are called semi-crystalline polymers. Crystallization is important in polymer processing because crystallization can affect

mechanical, thermal, optical and chemical properties of polymers. PP when compared with PE has better thermal resistance and rigidity because of its higher melting point and higher crystallinity [13]. Non-isothermal crystallization condition is close to the industrial processing conditions, hence is of great practical importance. Extended Avrami model, Ozawa model is widely used model for analyzing the non-isothermal crystallization process. The non-isothermal kinetics of nucleation and its growth were derived by extending Avrami's equation as proposed by Ozawa,

$$-C(T) = \exp\left[\frac{\chi_c(T)}{a^n}\right]$$

where, n depends on the dimension of growth, and its values range from 2 to 4; χ_c is the cooling function; and $C(T)$ is the conversion at temperature, a is cooling rate [14].

The goal of this study is to characterize a modified PP/PE blend subjected to an irradiation process, and then analyze the effects LDPE content on the non-isothermal kinetics and crystal structure of modified PP. DSC, XRD, and POM are used for characterization and analysis of the crystallization properties of the PP/LDPE blend.

2. Experimental

2.1 Materials and Fabrication

Polypropylene used in this experiment was Block PP (MI 30), supplied by SK Energy. Polyethylene was supplied by LG Chemicals and the type of polyethylene used was low density polyethylene (LDPE). Irganox-1010 was used as an antioxidant and the amount used was 1 phr (part per hundred resins) for all samples. Trimethylolpropane-trimethylacrylate (TMPTMA, Sigma Aldrich) was used as a co-agent for crosslinking. The PP/LDPE blend was prepared and tested in order to check the effect of LDPE on the crosslinking and crystallization kinetic of PP by

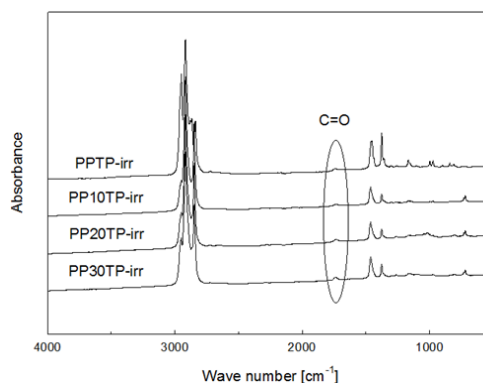
electron beam irradiation. Table 1 summarizes the constituents of the samples. All the constituent samples were weighed as per required and were mixed for 30 minutes before being fed into a twin extruder. The temperature setting of the twin extruder was 190/190/190/190/160/130 °C and the rpm was 130. After compounding, the samples were pressed as sheets with dimensions of 1 mm x 120 mm x 120 mm at 190 °C. These samples were then exposed to electron beam irradiation with 500 KV and 4 Mrad.

2.2 Measurements

Fourier transformation Infrared (FT-IR) spectroscopy was used to analyze the chemical structure of the modified polypropylene. The chemical structures of the samples were recorded in absorbance mode making use of a Perkin Elmer Spectrum 100 FT-IR spectrometer, with air as reference. The remaining gel after the extraction in xylene was prepared as a thin sheet and infrared light was passed through it to measure its absorbance. Thermal analysis was conducted with a TA Q20 differential calorimeter (TA Instruments, Newcastle, DE, USA). A sample weighing between 0.002g to 0.004g was sealed inside an aluminum pan; with aluminum as the reference, DSC was carried out in a nitrogen atmosphere. Samples were heated to 250 °C at a rate of 10 °C/min and cooled to 40 °C with different rates, 1, 3, 5 and 10 °C/min. The samples were again heated to 250 °C with the same rate. Polarized optical microscopy was used to observe the crystal size and geometry of the samples. The samples were heated to 200 °C at 10 °C/min and then cooled to 120 °C with same rate and hold at 120 °C. X-ray diffraction (XRD) was carried out by using a Rigaku X-ray generator (CuK α radiation with $\lambda = 0.15406$ nm) at room temperature. The diffractograms were scanned in 2θ ranges from 5 to 40° at a rate of 2° · min⁻¹.

3. Results and Discussions

In order to verify the crosslinking reaction, infrared spectra of irradiated samples are shown in [Fig. 1]. All the samples were extracted in xylene at 140 °C for 12 hours and they were dried at 150 °C for 1 hour. Irradiated sample left gel after extraction while non-irradiated samples dissolved. These extracted gels were then hot pressed into thin films and FT-IR tests were conducted. The TMPTMA crosslinking reaction was confirmed from the intensity of 1700 cm⁻¹ for the -C=O group in the FT-IR spectrum. The crosslinking co-agent used has a carbonyl group and the presence of the carbonyl group in the extracted sample suggests crosslinking of the sample.



[Fig. 1] FT-IR spectra of PP/LDPE blends after irradiation.

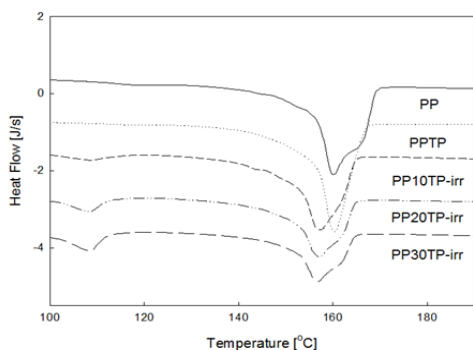
Gel content and melt flow index (MI) of the samples also suggested the crosslinking occurred after irradiation. Non-irradiated samples completely dissolved in xylene during extraction while irradiated sample remained with gel formation. Higher gel content of the sample with high LDPE composition can be related to higher crosslinking of samples. Similarly decrease in melt flow index of sample denotes obstruction of melt flow from the capillary which is due to formation of complex network within the polymer. This complex network formation is ascribed to crosslinking which obstructed polymer chain movement. Gel content and MI are listed in [Table 1].

[Table 1] Summaries for formulation and cross-linking amount

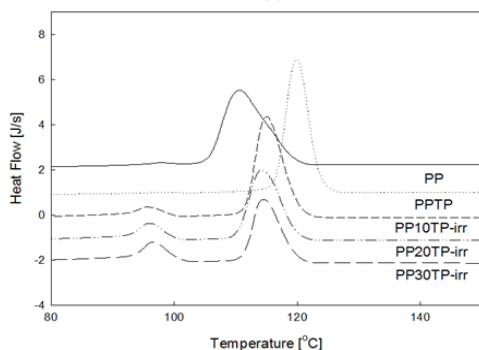
Sample	Name	PP (wt%)	LDPE (wt%)	Gel content(%)	Melt Index (g/10min)
PP		100	0	-	30.0
PPTP		100	0	-	-
PP10TP		90	10	-	23.7
PP20TP		80	20	-	18.8
PP30TP		70	30	-	17.0
PPTP-irr		100	0	23.0	-
PP10TP-irr		90	10	25.1	11.5
PP20TP-irr		80	20	25.6	7.6
PP30TP-irr		70	30	30.6	5.8

* Phr: parts per hundred resins, irr- represents irradiated sample,
 ** All samples include Irganox-1010 (1 Phr)

The heating and cooling curves of the irradiated samples are shown in Fig. 2. The samples were heated twice to investigate the change in their enthalpy and melting points. Thermal properties of the PP/LDPE blend achieved after both scans are listed in [Table 2].



(a)



(b)

[Fig. 2] DSC heating (a) and cooling (b) curves of PP/LDPE blends before and after irradiation

[Table 2] Thermal properties of the modified PP

Sample Name	Cooling		Second heating
	T _c (°C)	ΔH _c (J/g)	
PP	110.6	72.6	160.2
PPTP	119.0	67.9	160.3
PP10TP	119.0	49.6	162.1
PP20TP	113.7	51.0	160.0
PP30TP	117.6	32.6	161.6
PPTP-Irr	116.6	51.3	154.9
PP10TP-Irr	115.1	47.8	157.2
PP20TP-Irr	115.5	54.1	156.4
PP30TP-Irr	114.4	41.2	156.7

T_m:Melting temperature, ΔH_f:Fusion enthalpy, T_c: Crystallization temperature, ΔH_c: Crystallization enthalpy

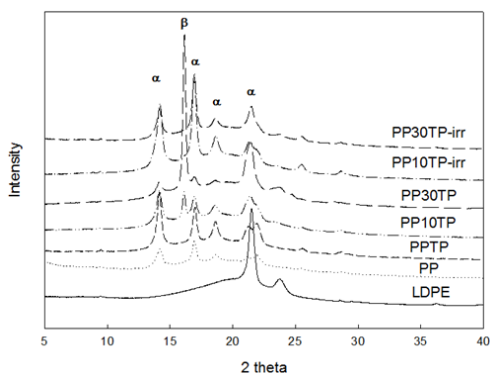
As shown in Fig. 2, when PP/LDPE blends were heated two well separated peaks could be seen, and these are ascribed to the melting points of LDPE and PP. Higher melting temperature corresponds to PP and lower melting temperature corresponds to LDPE. This demonstrates that blends of PP and LDPE are basically incompatible. There were some significant changes in PP after blending and irradiation. From the Table 2 it can be noted that the melting points of all the irradiated samples were slightly decreased in the second scan. The decrease in the melting point can be attributed to the thermal history and re-crystallization of the samples [15]. The decrease in T_m could be the result of chain scissioning, which decreases the number of tie molecules in the amorphous regions and consequently weakens the lamellar connections [16].

Fig. 2 (b) shows the crystallization curves of the irradiated samples. An increase in crystallization temperature was observed for all irradiated sample compared to the pure PP. According to the results of Y. An et. al [17], because the addition of TMPTA will lead to form some crosslinking sites in PP phase, the crosslinking sites, acting as nucleating agent, can promote the crystallization of PP. Therefore, in the case with LDPE, the crystallization temperatures of PP in PPTP and PP/LDPE blends increase. The changes in melting points and crystallization temperature suggest

that the sample has undergone some molecular and crystal structure change. This is due to degradation/crosslinking or branching of the samples.

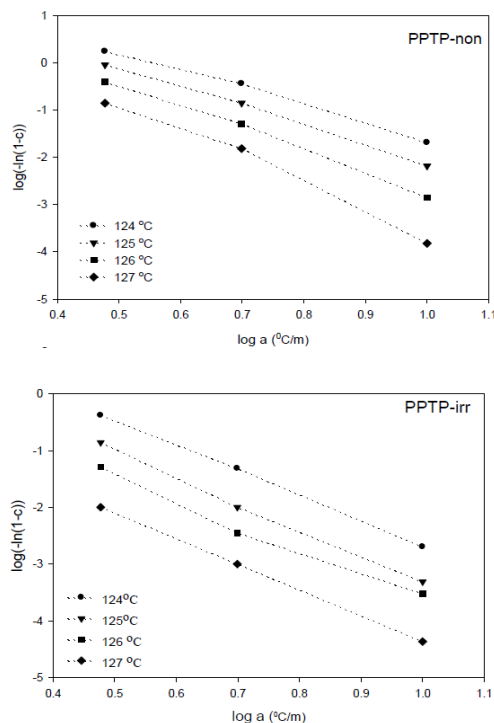
PP could crystallize in three polymorphic forms, α (monoclinic), β (pseudo-hexagonal), and γ (triclinic), depending on the composition of PP and crystallization conditions [17]. The XRD peaks at 14.0, 16.8, 18.5, 21.0, and 21.8° correspond to the α (110), α (040), α (130), α (111), and $\alpha\alpha$ (131) planes, respectively. Fig. 3 shows the XRD patterns of the PP/LDPE blends before and after irradiation. The diagrams of all PP samples are characteristic of the monoclinic α form of PP. It is interesting to note that, whereas the XRD patterns of the PP/LDPE blends exhibit a new reflection at 16.1°, characteristic of the β form of PP. On the other hand, this reflection does not appear in the corresponding irradiated samples. The phase transformation from the β form to the stable α form has been extensively studied [18,19]. S. Borysiak [25] reported that in the presence of shearing force, the $\beta \rightarrow \alpha$ phase transformation is easier and, as a consequence, a decrease in the amount of the β form is observed. The same behavior observed in the XRD pattern of the crosslinked PP/LDPE blend reported by S. Bouhelal et. al. [19]. Our observations suggest that the $\beta \rightarrow \alpha$ phase transformation is easier when the chain mobility is restricted by crosslinking reaction.

In order to analyze the crystallization process non-isothermal crystallization analysis was made.



[Fig. 3] XRD curves of PP/LDPE blends before and after irradiation

Ozawa model which is the extension of Avrami model of non-isothermal crystallization was studied. The logarithmic form of Ozawa model is expressed as $\log [-\ln (1-C(T))] = \log \chi (T) - n \log a$. The Ozawa model can provide parameters with clear physical meanings to characterize the crystallization rate from DSC data. $\log [-\ln (1-C(T))]$ vs. $\log a$ is shown on Fig. 4 and Ozawa component is listed in Table 3. The lines of Ozawa plot of samples were nearly parallel indicating that Ozawa model is suitable for describing the crystallization kinetics. The Ozawa component n can be calculated as the regression line of the plot. The Ozawa component n represent rod shaped, disk shaped and sphere shaped geometry of the crystal if value corresponds to 2, 3 and 4 respectively. This suggests that the crystals of pure PP are sphere in geometry. After the addition of LDPE and TMPTMA the value of n decreased. Also, with the increasing LDPE content the n value further decreased. Similarly, after irradiation the n value decreased compared to respective non-irradiated samples. The



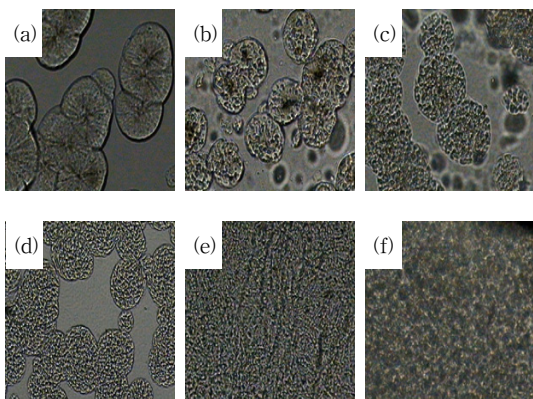
[Fig. 4] Plot of $\log [-\ln (1-C(T))]$ vs. $\log a$ of PPTP based on Ozawa model.

presence of LDPE in the blend and irradiation as heterogeneous nucleating agent and can hinder the chain mobility and diffusion of PP chains during crystallization process. Also, the decrease in mobility may results from the complex 3D network formation in PP chain due to irradiation which crosslink the polymer chain.

[Table 3] Ozawa indexes for the modified PP

Sample name	Non Irradiated	Irradiated
PP	3.8	-
PPTP	3.1	3.1
PP10TP	3.4	3.3
PP20TP	2.9	2.8
PP30TP	2.5	2.3

This decrease in n value of blend from 4, changing the geometry of crystals of blends to rod and disk shape from sphere is further supported by polarized optical microscope (POM) image. The crystal image from POM is shown in Fig. 5. Crystals which were fine and clearly observed in POM were changing shape after addition of LDPE and irradiation. For the irradiated samples because of early crystallization and change of crystal into rod shape crystals were not properly observed in POM image.



[Fig. 5] POM image of PP/LDPE blends: (a) Pure PP, (b) PPTP, (c) PP10TP, (d) PP30TP, (e) PP10TP-irr, (f) PP30TP-irr.

4. Conclusion

The FT-IR analysis supported that some cross-linking phenomena occurred with the presence of a carbonyl group (C=O) at 1700 cm^{-1} . Also, gel content and melt flow index showed some crosslinking effect. Thermal degradation suggested some scissioning/degradation phenomena in the PP/LDPE matrix after irradiation while an increase in complex viscosity at low frequency and introduction of shear thinning property suggested complex network formation, indicating cross-linking/branching. The $\beta \rightarrow \alpha$ phase transformation was observed in case of irradiated PP/LDPE samples and the addition of LDPE and irradiation changed crystal geometry. Crystals of PP which were sphere in shape were changed into disk and rod shaped after addition of LDPE and irradiation. Because the change of crystallization kinetic can be effected in industrial applications and processing condition, we need the further work for those things.

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Polymer Structure & Engineering, Polymer Processing, Polyolefin