

프로필렌의 반응동안 압출 과정에서의 가교 및 분해 유변학

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Rheology of Crosslinking and Degradation of Polypropylene During Reactive Extrusion

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요 약 : Polypropylene 분말을 과산화물 및 다기능성 단량체 존재하에서 230°C에서 압출, 압출물과 사출 시편의 용융흐름지수 및 230°C에서의 선형 점탄성을 측정하였다. 과산화물의 함량이 증가함에 따라 용융흐름지수는 거의 선형적으로 증가하였고, 점성함수는 Newtonian plateau를 보였으며 이로부터 과산화물 처리로 분해와 더불어 분자량 분포가 좁아짐을 짐작할 수 있었다. 한편, PETA(pentaerythritoltriacylate) 및 TMPTA(trimethylolpropanetriacylate) 존재하에서는 압출물의 용융흐름지수는 농도와 더불어 점근적으로 감소하였으며, TAIC(triallylisocyanurate) 및 PBQ(p-benzoquinone)의 경우에는 초기에 감소한 후 일정하게 유지되었다. 다기능성 단량체와 과산화물을 함께 사용했을 때의 용융흐름지수는 과산화물 단독 사용시보다는 작고, 다기능성 단량체 단독 사용시보다는 큰 값을 나타내었다. PETA 및 TMPTA를 사용했을 경우 사출에 의해 용융흐름지수는 수 배 증가하였으나, 과산화물, TAIC 및 PBQ의 경우에는 1.5배 이하로 증가하였다. 점성 곡선으로부터 압출과정의 가교와 사출과정의 사슬 절단반응은 거의 대등한 정도로 일어남을 짐작할 수 있었다.

Abstract : Isotactic polypropylene(PP) powder was extruded in the presence of peroxide and polyfunctional monomer at 230°C. The melt flow index(MI) of extrudate and injection molded specimen, together with the linear viscoelastic properties of melt at 230°C was measured. With the increase of peroxide concentration, MI increased almost linearly, and the viscosity function tended to define a Newtonian plateau, indicative of increased rate of degradation accompanied by narrowed molecular weight distribution. On the contrary, the MI of pellet was reduced asymptotically in the presence of pentaerythritoltriacylate(PETA) and trimethylolpropanetriacylate(TMPTA), and showed a drop at the initial addition of triallylisocyanurate(TAIC) and p-benzoquinone(PBQ). Addition of polyfunctional monomer to peroxide system produced MI lower than the one obtained with the peroxide alone, and higher than the one obtained with polyfunctional monomer alone. By injection, MI increased over se-

veral times with PETA and TMPTA, and by a factor less than 2 with peroxide, TAIC and PBQ. From the viscosity measurements, it was inferred that the extent of crosslinking obtained during extrusion is similar to that of chain scission during injection molding.

INTRODUCTION

Post-reactor modification of polyolefins by peroxide crosslinking or degradation has become a practical technology to control the physical properties of these materials.¹⁻³ In the presence of peroxide, the mechanism of crosslinking is the combination of secondary alkyl macroradical, whereas the degradation is generally explained by the chain scission of tertiary alkyl macroradicals.⁴⁻⁵ Therefore crosslinking becomes dominant reaction in polyethylene(PE)⁶ except at high enough temperature, where thermal degradation becomes dominant.

In polypropylene(PP) crosslinking and chain scission occur simultaneously, and the process is mainly controlled by peroxide concentration and temperature. Chain scission is preferred over crosslinking at lower peroxide concentration and higher temperature,⁶ since it is a monomolecular reaction and has higher activation energy than crosslinking. The peroxide initiated degradation of PP is used for production of controlled-rheology resin with tailor-made properties. However, there would be the optimum temperature for maximum cure. Following earlier works,⁴ when PP was cured in press with t-butyl perbenzoate and dicumyl peroxide initiator, the maximum gel content was obtained at about 165~170°C. The existence of optimum temperature is due presumably to the lower decomposition rate of initiator at low, and chain scission at higher temperature.

Though crosslinking of PP is possible with only peroxide at specific condition, certain additional chemicals called coagents are generally added. These are typically reactive polyfunctional monomers of class of methacrylates or allyl compounds.⁷ Though the mechanism of the action of coagent is not clear, the main effect of these coagent is to im-

prove crosslinking efficiency by minimizing unwanted side reactions such as chain scission and disproportion. Following Odian and Bernstein,⁸ the double bond of the polyfunctional monomer are the sites for trapping macroradicals of PP. Especially, when the PP radical is tertiary alkyl one, coagent reduces disproportionation reaction and augments crosslinking efficiency. In this paper, we report the crosslinking effect of several types of coagent, alone and in combination with peroxide in PP crosslinking during reactive extrusion. The data were analyzed in terms of MI, viscosity(η^*), storage(G'), and loss modulus(G'') of the crosslinked PP.

EXPERIMENTAL

Isotactic polypropylene(PP)(Korea Petrochemicals) with number average molecular weight, $M_n = 39,900$, weight average molecular weight, $M_w = 320,000$, and melt flow index, $MI(2.16 \text{ kg}, 210^\circ\text{C}) = 7.5 \text{ g/10 min}$ was used.

Peroxide and coagents used were 1,3-bis(t-butylperoxy-isopropyl)benzene, pentaerythritoltriacrylate(PETA), trimethylolpropanetriacrylate(TMPTA), triallylisocyanurate(TAIC), and parabenzoquinone(PBQ). First grade of the reagents was used without further purification.

Crosslinking was done in a counter-rotating twin screw extruder at 450 r.p.m., with $L/D = 30$, and $D = 2.5 \text{ cm}$ at 230°C. Peroxide and coagent concentrations were 0.005~0.03 and 0.05~1.0 phr respectively, when they were used alone. The effect of coagent in peroxide system were tested with 0.01, 0.05 and 0.1 phr of peroxide, and 0.2, 0.5 and 1.0 phr coagent concentration.

MI of extrudate and injection molded specimen was measured at 210°C, 2.16kg loading following ASTM D1238. Injection molding(Nissei, plastisi-

zing rate, 49kg/h) was done at 220~230°C, 182cm³/shot with cycle time, 45 sec. Rheometrics Dynamic Spectrometer(RDS-II) with a cone-and-plate fixture was used to measure the rheological properties of the melt at 230°C, 10% strain level. Discs measuring 2.5 cm in diameter were compression molded.

RESULTS AND DISCUSSION

Melt Index

Single Treatment

The MI of extruded pellet and injection molded specimen is given in Table 1. Some calculated values are also contained in the Table for comparison. It can be seen that the MI of specimen is higher than that of extruded pellet at the same peroxide concentration, and both increase almost linearly with the peroxide concentration. The result for pellet is in good agreement with earlier work,¹ done under similar conditions.

The cleavage of polymer chain is primarily accomplished by radicals created by the decomposition of a suitable peroxide, and it is essentially a random process. These radicals preferentially abstract the hydrogen atom attached to the tertiary carbon, which is most vulnerable to chain scission(β -scission).^{4,5} The further increase of MI during injection implies that degradation is undergoing during injection.

When the triacrylates(PETA and TMPTA) are added to the PP resin, the pellet MI is smoothly decreased with its concentration, more with PETA, and less with TMPTA. Upon injection, the MI is increased over several times, more with PETA, and less with TMPTA. It is seen that the relative increase of MI by injection(M_s/M_p) generally becomes more significant with the coagent concentration.

In PBQ and TAIC system, MI shows a drop at 0.05 phr more with PBQ and less with TAIC, whereafter the level is unchanged with its concentration. Upon injection, MI is increased, but by a factor less than 1.5.

Peroxide-Coagent Combination

The effect of coagent in peroxide system is known to augment the crosslinking efficiency of peroxide by minimizing unwanted side reactions such as disproportionation and chain scission, and by resolving steric hinderance.⁷

At the lowest peroxide content(0.01 phr), addition of coagent produces MI lower than the one obtained with peroxide alone, regardless of the coagent type and the amount of coagent used, however, the level is higher than the one obtained with the coagent alone. Peroxide mainly leads to chain scission, whereas coagent to crosslinking of PP. Upon injection MI is increased, but by a factor of 1.3~1.6 in PETA and TMPTA, and 1.1 in PBQ. With the increase of coagent concentration from 0.2 to 0.5 phr, MI is further reduced.

With the increase of peroxide concentration(0.05 phr), MI is increased in PETA and TMPTA, and decreased in PBQ, and it is decreased with increasing concentration of coagent. MI increases by injection, but the increment is reduced when compared with lower peroxide(0.01 phr) content. When the peroxide content is further increased(0.1 phr) in PBQ, MI is further decreased, together with a decrease with PBQ concentration.

RDS Measurement

Though the MI is a quick look at processability it corresponds to a single value of shear rate, which again varies with the viscosity of the material.^{9~11} Namely, at specific conditions of temperature and load, MI of high viscosity material correspond to low shear, and vice versa. In addition, since MI generally corresponds to relatively low shear rate, MI would be a misleading for actual high shear processing depending on molecular weight distribution(MWD). Consequently the non-Newtonian viscosity should be measured in a wide range of shear rate.

Complex viscosity(η^*), storage(G'), and loss modulus(G'') of peroxide(0.01 phr) treated PP, at 230°C are shown in Figs. 1 to 3. It can be seen that the viscosity is decreased throughout the frequencies by peroxide treatment. In addition, the visco-

Table 1. The MI of Peroxide and Polyfunctional Monomer Treated PP

Peroxide	Additive(phr)				MI(g/10min)		$\frac{M_s}{M_p}$	$\frac{M_p}{M_{p.o}}$	$\frac{M_s}{M_{s.o}}$
	PETA	TMPTA	TAIC	PBQ	pellet (M_p)	specimen (M_s)			
-	-	-	-	-	7.5	7.8	1.0		
0.005					10.3	12.8	1.2	1.4	1.6
0.01					17.8	23.6	1.3	2.4	3.0
0.03					43.5	52.5	1.2	5.8	6.7
	0.05				6.1	16.2	2.7	0.8	2.1
	0.2				4.0	15.7	3.9	0.5	2.0
	0.5				2.1	10.3	4.9	0.3	1.3
	1.0				1.4	5.5	3.9	0.2	0.7
		0.05			7.0	16.3	2.3	0.9	2.1
		0.2			5.5	15.8	2.9	0.7	2.0
		0.5			3.4	11.1	3.3	0.5	1.4
		1.0			2.1	6.1	2.9	0.3	0.8
			0.05		6.2	8.3	1.3	0.8	1.1
			0.2		6.2	8.3	1.3	0.8	1.1
			0.5		6.3	7.2	1.1	0.8	0.9
			1.0		6.3	7.1	1.1	0.8	0.9
				0.05	4.8	6.9	1.4	0.6	0.9
				0.2	4.7	6.7	1.4	0.6	0.9
				0.5	4.7	6.7	1.4	0.6	0.9
				1.0	4.6	6.6	1.4	0.6	0.8
0.01	0.2				12.3	16.1	1.3	1.6	2.1
∕	0.5				7.6	11.7	1.5	1.0	1.5
∕		0.2			14.1	19.8	1.4	1.9	2.5
∕		0.5			9.1	14.2	1.6	1.2	1.8
∕				0.2	7.9	8.7	1.1	1.0	1.1
∕				0.5	7.7	8.6	1.1	1.0	1.1
0.05	0.2				20.7	22.3	1.1	2.8	2.9
∕	0.5				17.7	19.9	1.1	2.4	2.6
∕	1.0				14.0	16.4	1.2	1.9	2.1
∕		0.2			22.1	24.9	1.1	2.9	3.2
∕		0.5			19.0	22.1	1.2	2.5	2.8
∕	1.0				15.4	18.2	1.2	2.1	2.3
∕				0.2	5.9	6.5	1.1	0.8	0.8
∕				0.5	5.2	5.9	1.1	0.7	0.8
∕				1.0	5.0	5.8	1.2	0.7	0.7
0.1				0.5	3.4	3.9	1.1	0.5	0.5
∕				1.0	2.7	3.1	1.1	0.4	0.4

note : $M_{p.o} = M_p$ with no addition(7.5)

$M_{s.o} = M_s$ with no addition(7.8)

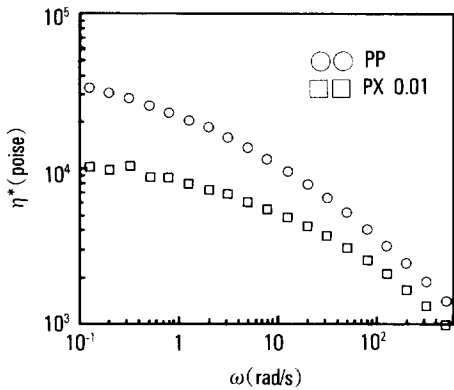


Fig. 1. Complex viscosity of untreated(○) and 0.01 phr peroxide(□) treated PP.

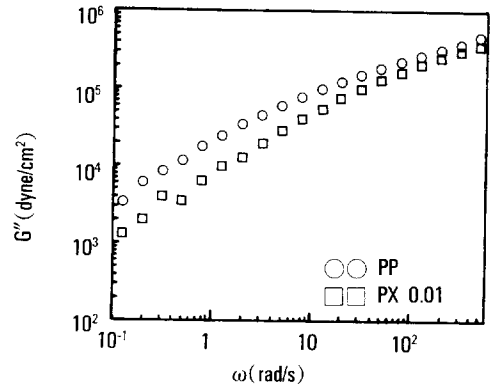


Fig. 3. Loss modulus of untreated(○) and 0.01 phr peroxide(□) treated PP.

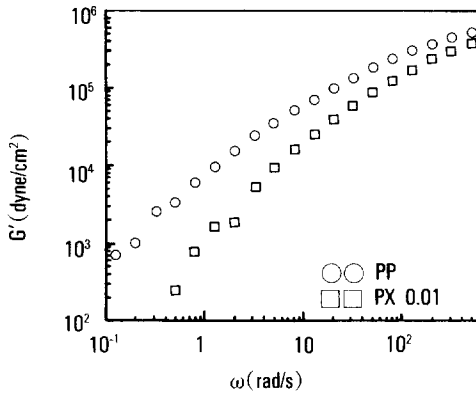


Fig. 2. Storage modulus of untreated(○) and 0.01 phr peroxide(□) treated PP.

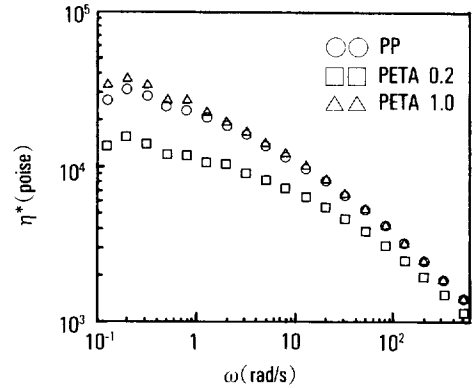


Fig. 4. Complex viscosity of PETA treated PP(untreated : ○, 0.2 : □, 1.0 : △).

sity function tends to define a Newtonian plateau and consequently the shear dependence of the viscosity function has been reduced. With narrower MWD, the viscosity function becomes less shear dependent,⁹ and hence it may be concluded that MWD of PP has been reduced upon peroxide treatment. This result is consistent with earlier work by Tzoganakis et al.¹ During the review process of this paper this has been confirmed from GPC(gel permeation chromatography) measurement. A commercial grade of PP having M_n and M_w very close to the one used in the present experiment was used. Upon treating with 0.03 phr peroxide, M_n increased from about 38,000 to 48,000 and M_w

decreased from 270,000 to 180,000. As a result, polydispersity has been reduced from about 7.1 to 3.8.

G' and G'' decrease upon peroxide treatment. However, the decrease of G' is much more significant(approximately over one order of magnitude) than G'' . In linear viscoelasticity, G' is elastic energy stored, and G'' is the energy dissipated via viscous friction in a cyclic deformation.¹² It follows then that PP loses more of its elasticity than viscosity upon treating with peroxide. Such results can also be observed from the reduced die swell.¹

RDS measurement of coagent treated PP are given in Figs. 4 to 7. With 0.2 phr PETA(Fig. 4), vis-

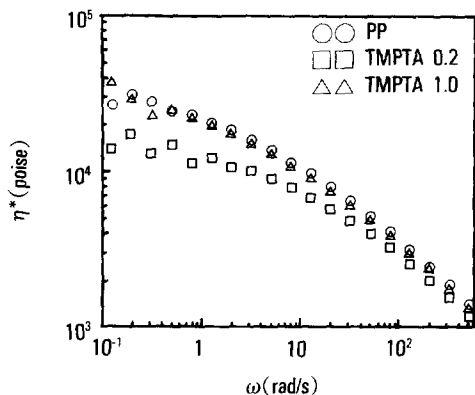


Fig. 5. Complex viscosity of TMPTA treated PP(untreated ; ○, 0.2 ; □, 1.0 ; △).

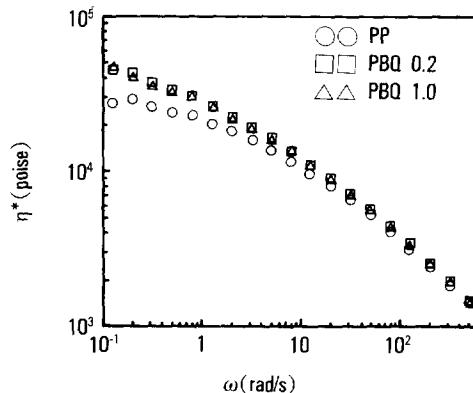


Fig. 7. Complex viscosity of PBQ treated PP(untreated ; ○, 0.2 ; □, 1.0 ; △).

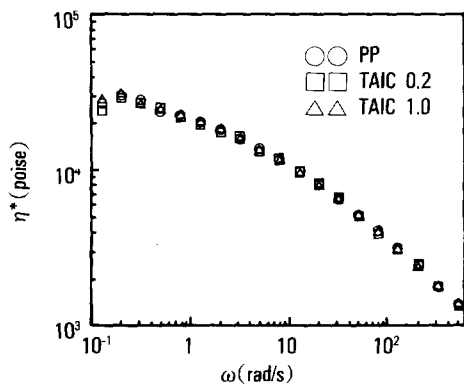


Fig. 6. Complex viscosity of TAIC treated PP(untreated ; ○, 0.2 ; □, 1.0 ; △).

cosity is reduced to about half at low frequency, and it slightly goes over the untreated PP value at 1.0 phr. Basically identical results are obtained with TMPTA, however slightly lower viscosity is obtained than PETA. In TMPTA, viscosity at 1.0 phr is also slightly lower than the untreated PP.

With PBQ, the viscosity is increased, however no recognizable difference is seen between 0.2 and 1.0 phr. Finally, addition of TAIC(0.2 and 1.0 phr) gives marginal decrease of viscosity. To save the space, G' and G'' are not shown, however the relative variation of G' to G'' gave essentially identical trend with that of peroxide, i.e., variation in elasticity(G') was more significant than viscosity(G''). It can be seen that degradation is all the time fol-

lowed by narrowed MWD, like in peroxide treatment. In peroxide treatment, degradation mostly occurs via β -scission of PP chain. With coagent, for example with TAIC, MI is decreased upon extrusion regardless of its concentration, but by injection it would or would not increase over the untreated value, depending on the coagent concentration(see Table 1 for TAIC). The process involves crosslinking(during extrusion) followed by chain scission(disproportionation may occur, but with no effect on M_w). Comparing the viscosity function of untreated and TAIC treated PP, one barely can find the difference in viscosity function. This convinces that the MWD as well as M_w is not really changed by the crosslinking-degradation process.^{14,15}

REFERENCES

1. C. Tzoganakis, J. Vlachopoulos, and A. E. Hamielec, *Polym. Eng. Sci.*, **28**, 170 (1988).
2. P. Hudec and L. Obdrzalek, *Agnew. Makromol. Chem.*, **89**, 41 (1980).
3. M. Dorn, *Adv. Polym. Technol.*, **5**, 87 (1985).
4. I. Chodaok and M. Lazar, *Agew. Makromol. Chem.*, **106**, 153 (1982).
5. E. Borsig, A. Fiedlerova, and M. Lazar, *J. Macromol. Sci. Chem.*, **A16**(2), 513 (1981).
6. Y. Tang, C. Tzoganakis, A. E. Hamielec, and J.

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- Vlachopoulos, *Adv. Polym. Technol.*, **9**, 217 (1989).
7. W. C. Endstra, *Kautschuk Gummit Kunststoffe*, **43**, 790 (1990).
 8. G. Odian and B. S. Bernstein, *J. Polym. Sci., Part A*, **2**, 2835 (1964).
 9. Z. Tadmor and C. G. Gogos, "Principles of Polymer Processing", Wiley-Interscience, New York, 1979.
 10. N. G. McCrum, C. P. Buckley, and C. B. Bucknall, "Principles of Polymer Engineering", Oxford University Press, Oxford, 1988.
 11. A. W. Birley, B. Hawvrth, and J. Batchelor, "Physics of Plastics", Hanser Publishers, Munich, 1991.
 12. R. B. Bird, R. C. Armstrong, and O. Hassager, "Dynamics of Polymer Liquids", Wiley, New York, 1987.
 13. F. P. La Mantia and D. Acierno in "Polymer Processing and Properties", G. Astrita and N. Nicolas eds., Plenum, Capri, 1983.
 14. C. D. Han, "Rheology in Polymer Processing", Academic Press, New York, 1976.
 15. J. E. Mark, A. Eisenberg, W. W. Graessley, L. Mandelkern, and Koenig, "Physical Properties of Polymer", Amer. Chem. Soc, Washington, D. C., 1989.