Available online at www.sciencedirect.com
ScienceDirect

Polymer 47 (2006) 6592–6597

polymer

www.elsevier.com/locate/polymer

Melt complex viscosity and molecular weights for homo-polypropylene modified by grafting bifunctional monomers under electron beam irradiation

Do-Hung Han*, Jae-Hyuk Jang, Byung-Gi Cho, Byung-Nam Kim, Gil-Soo Seo

School of Chemical Engineering and Technology, Yeungnam University, 214-1 Daedong, Gyongsan, Gyongbuk 712-749, Republic of Korea

Received 9 March 2006; received in revised form 7 July 2006; accepted 17 July 2006
Available online 4 August 2006

Abstract

High melt viscosity polypropylene was manufactured by grafting bifunctional monomers, HDDA (1,6-hexanediol diacrylate) and TPGDA (tripropyleneglycol diacrylate), onto homo-polypropylene under an electron beam irradiation. Melt complex viscosity (η^*) of modified polypropylene was sensitive to irradiation dose and monomer content. The melt viscosity of the polypropylene modified with TPGDA increased to 132,290 Pa s (at 190 °C and 0.1 rad/s of frequency) from 5039 Pa s for virgin homo-polypropylene. TPGDA monomer could give higher melt viscosity at low dosages than HDDA monomer, probably due to the structural feature of TPGDA with three numbers of methyl groups.

Modified polypropylene with high melt complex viscosity had a broad molecular weight distribution with remarkable shift to higher molecular weight leading to high values of both $\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_w$. Melt viscosity of modified polypropylene could be properly correlated by the equation $\eta^* = k_t(\overline{M}_w/\overline{M}_n)^{\alpha}(\overline{M}_z/\overline{M}_w)^{\beta}$, where the term $(\overline{M}_z/\overline{M}_w)$ gave a dominant effect for the estimation of η^*.

Keywords: Homo-polypropylene; High melt viscosity; Electron beam

---

1. Introduction

Polypropylene exhibits such good properties as high mechanical strength, inertness for various chemical reagents, non-toxicity, high transparency, high glossiness, etc. However, homo-polypropylene has been restricted to its application in such processes as forming, vacuum molding, blow molding, and extrusion coating, due to its low melt strength. High melt strength of polypropylene (HMS-PP) can be substituted for polystyrene of foamed products and for polyethylene phthalate of high-pressure bottle, widening its marketability. Especially, HMS-PP is environmentally intimate material with a prohibition of any toxic gas discharge during incineration. Moreover, HMS-PP can be recycled since it is melted from an imperfect crosslinking of polymer chains.

It was found that HMS-PP could be manufactured by several ways: by using Methalosen catalyst or Zigler–Natta catalyst [1], by adding organic peroxide, crosslinking reagent and acrylic monomer [2], and by using electron beam irradiation [3], wherein, the electron beam irradiation can form radicals on the end-groups of polymer chains leading to the formation of long branches through sequential grafting between radicals and monomers.

In general, structure of HMS-PP can have long branches on linear polypropylene or entanglement of huge molecules [4–7]. It has been found that electron beam irradiation is capable of grafting several kinds of monomers onto polypropylene for improvement of its melt strength [8–10]. It is indicated that crystalline polypropylene is susceptible to oxidative degradation through two steps, during irradiation and during storage after irradiation, under electron beam irradiation [8,11–13]. Yoshii et al. [7] found that with electron beam irradiation of 0–10 kGy, bifunctional monomers such as HDDA, BDDA and EGDMA could exhibit high melt strength of polypropylene by testing 16 kinds of functional monomers.

It has been known that the molecular weight distribution (MWD) is dependent on temperature, oxygen pressure and induction period after thermal treatment [14]. MWD of isotatic polypropylene shifts to higher molecular weight during the

---

* Corresponding author. Tel.: +82 53 810 2518; fax: +82 53 810 4631.
E-mail address: dhhan@yumail.ac.kr (D.H. Han).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.07.027

induction period in air. Whereas, in the degradation of polyethylene, the degree of molecular weight increases proportionally to the length of the induction period at very low pressures of air. These results are due to two simultaneous processes, i.e., a radical intermolecular recombination, which leads to a molecular weight increase, and a decrease in intermolecular weight. Seavey et al. [15] presented methodologies to quantify the relationships among MWD, steady-shear non-Newtonian viscosity (i.e., flow curve), and melt index of three linear low-density polyethylenes, employing three models [16–18]. Llorens et al. [19] described a method for determining the polydispersity index $I_{p2} = \overline{M}_z/\overline{M}_w$ of the molecular weight distribution (MWD) of linear polymeric materials from linear viscoelastic data.

This study focusses on electron beam irradiation of graft monomers, 1,6-hexanediol diacrylate (HDDA) and tripropyleneglycol diacrylate (TPGDA), onto homo-polypropylene for manufacturing high melt viscosity polypropylene. And, it will be suggested that the melt viscosity of modified polypropylene quantitatively correlates with average molecular weights ($\overline{M}_w$, $\overline{M}_n$, $\overline{M}_z$).

2. Experimental parts

2.1. Materials

Virgin polymer used for improvement of melt viscosity is the homo-polypropylene with 3.0 of melt index manufactured by Korean Petroleum Chemical Ind. Co., Ltd. HDDA and TPGDA (Aldrich Co.) added to the polymer are of first grade and used without further purification. Antioxidant is phenol type of Irganox 1010.

2.2. Preparation of HDDA or TPGDA – grafted polypropylene

Bench kneader with twin screw kneads homogeneously the mixture of homo-polypropylene, monomer and antioxidant at 180 °C for 30 min. Amounts of added monomers are 1.5 mmol or 3.0 mmol per 100 g of HPP and added antioxidant is 1 wt%. The kneaded mixture is left in air for several hours for the purpose of homogeneous impregnation of aqueous monomer into polypropylene. Hot pressing at 180 °C makes a disc-shaped sample with 10 mm diameter and 1 mm thickness. These samples are mainly used for the measurement of complex melt viscosity by means of ARES (Advanced Rheometric Expansion System: Rheometric Scientific Co.).

Commercial electron beam accelerator (ELV-0.5, BINP, Russia) irradiates the samples under a nitrogen circumstance with several dosages controlled by changing the beam current and conveyor speed. The irradiated samples are stored in a dry oven at 80 °C for 1 h to eliminate residual radicals.

2.3. Measurement of melt viscosity

ARES (Advanced Rheometric Expansion System, Rheometric Scientific Co.) measures melt complex viscosities of both homo-polypropylene and modified polypropylene at temperatures between 160 °C and 230 °C under nitrogen circumstance with 0.1 rad/s of frequency and 15% deformation, using parallel plates of 20 mm in diameter and with a gap height of 1 mm.

To compare melt complex viscosities of both homo-polypropylene and modified polypropylene under the same condition, virgin homo-polypropylene is also kneaded in bench kneader in addition with 1 wt% of antioxidant as mentioned earlier.

2.4. Measurements of molecular weight distributions, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_z$

GPC (Gel Permeable Chromatograph, Alliance 2000, Waters Co.) measures molecular weight distribution (MWD) and several kinds of average molecular weights ($\overline{M}_w$, $\overline{M}_n$, $\overline{M}_z$) with column (Water Styragel) temperature of 140 °C and mobile phase solution of TCB with 0.92 ml/min flow rate. Where, the polymers are dissolved in 0.5% TCB solution and the standard material is polystyrene.

3. Results and discussion

3.1. Melt viscosities of modified homo-polypropylenes

In this study, melt viscosity of homo-polypropylene (HPP) is the melt complex viscosity measured by means of ARES, where measuring temperatures are between 160 °C and 230 °C with 10 °C of interval each at 0.1 rad/s of frequency. The viscosity at zero-shear presents well the property of polymer, especially for polymer with entangled chains or long-branched chains. In this study, the zero-shear viscosity was analogized by the complex viscosity evaluated at the 0.1 rad/s of low frequency.

As shown in Fig. 1, the melt complex viscosity of unmodified HPP, which was thermally treated by kneading process, ranges from 5039 Pa s to 3026 Pa s at 180–230 °C. Melt viscosity of HPP that was treated only thermally with the addition of 1.5 mmol of HDDA considerably increased compared to

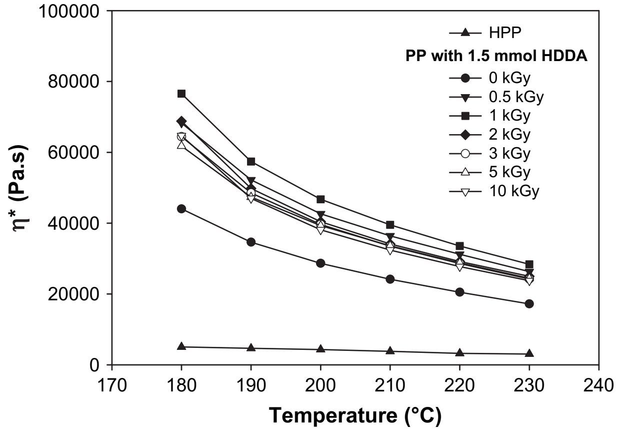


Fig. 1. Effect of dosage and temperature on the melt complex viscosity (η^*) of HPP grafted with 1.5 mmol of HDDA.

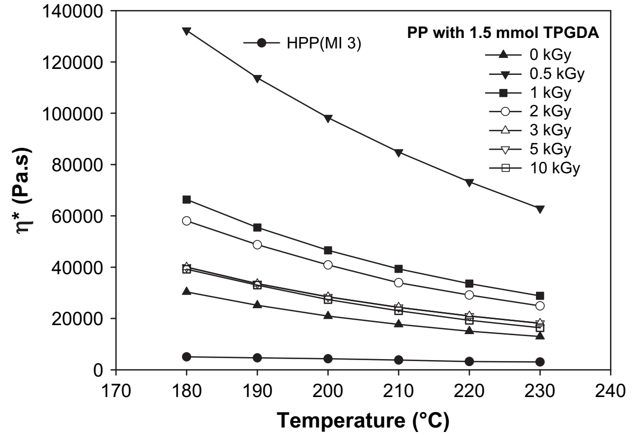
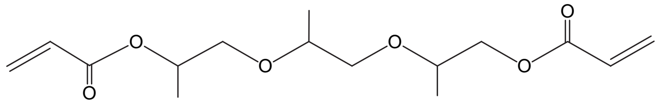
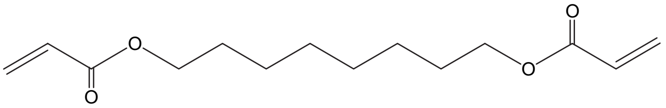


Fig. 2. Effect of dosage and temperature on the melt complex viscosity (η^*) of HPP grafted with 1.5 mmol of TPGDA.



(a) TPGDA ($C_{15}H_{24}O_6$, M_w=300.54)



(b) HDDA ($C_{12}H_{18}O_4$, M_w=226.2718)

Fig. 4. Molecular structures of (a) TPGDA and (b) HDDA.

virgin HPP, e.g., 44,001 Pa s for the treated polypropylene at 180 °C. Electron beam irradiation can further enhance melt viscosity of HPP with the highest value around 1.0 kGy (76,555 Pa s at 180 °C) and then it slightly decreases at dosages above 2 kGy.

HPP grafted by TPGDA instead of HDDA remarkably improves its melt complex viscosity that is much more sensitive to the irradiated dosages than HDDA-grafted HPP, as shown in Fig. 2. Under no irradiation of electron beam, the melt viscosity of modified HPP, which was only thermally treated with 1.5 mmol of TPGDA, is nearly sixtimes more than the virgin HPP. With 0.5 kGy of irradiation dosage, the melt complex viscosity remarkably increases, showing 132,290 Pa s at 180 °C, whereas the melt viscosities of HPP considerably decrease above 1 kGy.

Further addition of 3.0 mmol of TPGDA exhibits highest melt viscosity at 1.0 kGy but the melt complex viscosity is much lower than 1.5 mmol TPGDA addition at 0.5 kGy, as shown in Fig. 3. However, at dosages except 1 kGy, the melt viscosities of the polypropylene modified with 3.0 mmol of TPGDA are superior to the addition of 1.5 mmol of TPGDA. It is inferred that more addition of monomer in HPP requires higher dosage for accomplishment of high degrees of grafting.

Structures of HDDA and TPGDA are similar to each other giving the same number of C=O and C=C groups, but TPGDA has additional three branches of methyl groups ($-CH_3$) (Fig. 4). Therefore, electron beam irradiation can give more chance for the formation of radicals in TPGDA than in HDDA since methyl groups in TPGDA change to radicals $-CH_2$• and =CH•. This can lead to a formation of long-branched chains on polymer chains and simultaneously to a homo-polymerization between radicals. Therefore, the TPGDA-modified HPP was likely to exhibit higher melt viscosity than HDDA-modified HPP.

Melt viscosities of the HPPs modified with HDDA or TPGDA are compared with HMS-PPs made by Montell and by Chisso Co., respectively (Fig. 5). Melt viscosities of the HPP modified with TPGDA or HDDA are comparable to Montell's product. However, the modified HPP with TPGDA or HDDA has higher melt viscosity than Chisso's HMS-PP. From Figs. 1 and 4 we observe that all polypropylenes modified with HDDA between 0.5 kGy and 10 kGy exhibit higher melt viscosity than Chisso's HMS-PP. Montell Co. and Chisso Co. tried to make HMS-PP without addition of any monomer, wherein an organic peroxide (Chisso [2]) or an electron beam (Montell [3]) played a role in chain-scission of linear

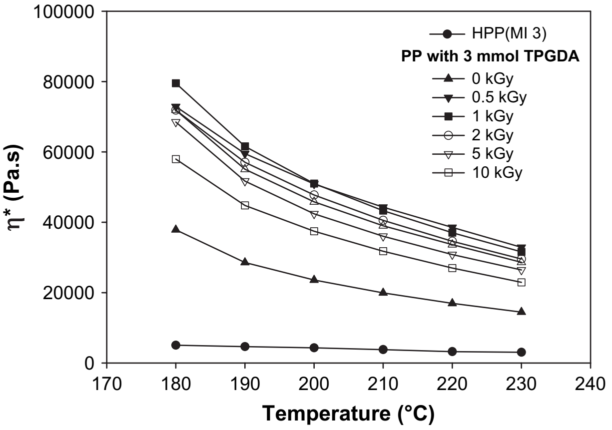


Fig. 3. Effect of dosage and temperature on the melt complex viscosity (η^*) of HPP grafted with 3.0 mmol of TPGDA.

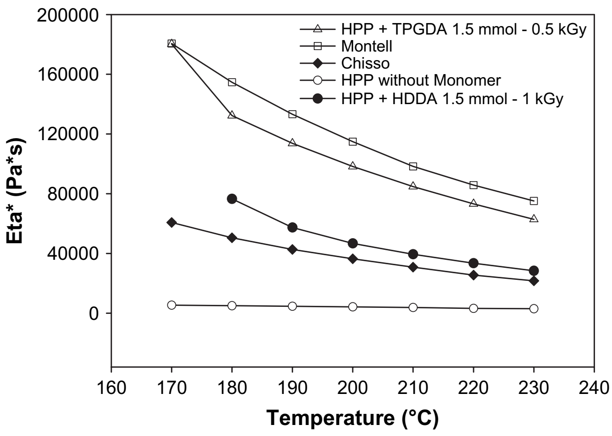


Fig. 5. Comparison of HDDA- and TPGDA-grafted HPP with other HMS-PP.

polypropylene, leading to the joining of the chain fragments to linear chains and forming the desired substantially branched, high molecular weight of polypropylenes.

In our experimental results, the melt complex viscosities of modified HPP were very sensitive to dosage, monomer content and monomer structure. Enhancement of melt viscosity can arise from pure grafting reaction under suppression of both homo-polymerization and chain-scissions in polymer. High dosage and high content of monomer can lead to both high degradation and high degree of homo-polymerization, resulting in a decrease of melt viscosity.

3.2. Molecular weight distributions and average molecular weights

Figs. 6 and 7 show molecular weight distribution (MWD) for HPP modified with TPGDA and HDDA, respectively. As shown in the figures, MWD of virgin homo-polypropylene without any thermal treatment exhibits a single peak with a narrow width. On the other hand, MWD of HPP modified under electron beam irradiation became comparably broader.

MWD of HPP modified at 0.5 kGy with the addition of 1.5 mmol of TPGDA, which gives highest melt viscosity, considerably shifts to high molecular weights with a broadest MWD (Fig. 6). In addition, MWD of HPP modified at 0.5 kGy with 1.5 mmol of HDDA, which also gives comparably high melt viscosity, is very similar to MWD of TPGDA-modified HPP (Fig. 7). HPP modified by higher dose of 10 kGy with 1.5 mmol of TPGDA or 1.5 mmol of HDDA exhibits bimodal peak of MWD with additional peak at several thousands of weight-average molecular weight ($\overline{M}_w$) (Figs. 6 and 7). The virgin homo-polypropylene only thermally treated also exhibits bimodal peak of MWD with additional peak at several thousands of weight-average molecular weight. Such additional peak can arise from chain-scission of polymer, consequently leading to a decrease of melt viscosity.

At higher monomer content of 3.0 mmol and 0.5 kGy dosage, the MWD exhibits an additional small peak around ten thousand of $\overline{M}_w$ and shifts a little to higher $\overline{M}_w$ in comparison with virgin homo-polypropylene (Figs. 6 and 7). This additional peak may occur from homo-polymerization at excess addition of monomer rather than chain-scission of polymer due to very low irradiation dosage.

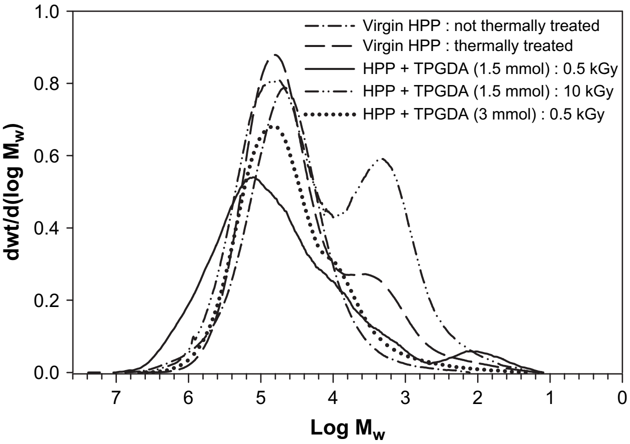


Fig. 6. Molecular weight distribution for the polypropylene modified with TPGDA.

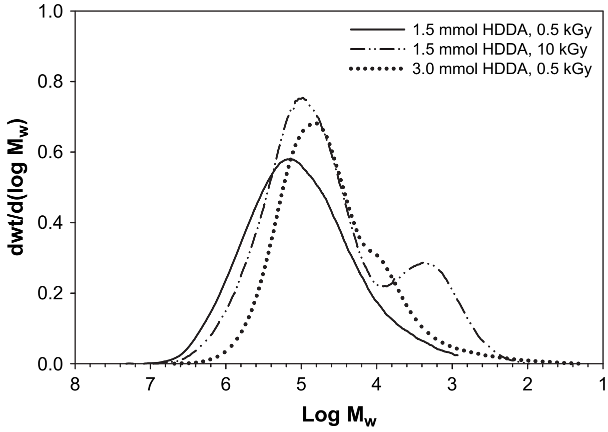


Fig. 7. Molecular weight distribution for the polypropylene modified with HDDA.

Other studies indicated that polymer could be oxidatively degraded with oxygen at high temperature, decreasing both $\overline{M}_w$ and $\overline{M}_n$ and shifting MWD to low molecular weights [20]. Homo-polymerization between monomers could arise from enclosing radicals by excess monomers [7].

3.3. Correlation between melt viscosity and average molecular weights

It has been found that high melt viscosity of modified HPP can be accomplished by the formation of long branches on polymer chains or by entanglement of polymer chains with ultra-high molecular weight [4,20]. Melt viscosity related to such structural features may be correlated with several kinds of average molecular weights such as $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_z$. In general, higher $\overline{M}_w/\overline{M}_n$ of polymer has wider molecular weight distribution and more branches on main chains. In addition, higher $\overline{M}_z/\overline{M}_w$ values exhibit more ultra-high molecular weight of molecules in polymer since high molecular weight of molecules are much more sensitive to z-average molecular weight ($\overline{M}_z$) than weighted-average molecular weight ($\overline{M}_w$).

Table 1 shows that the modified HPP with high melt viscosity exhibits large values of both $\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_w$. Whereas, unmodified homo-polypropylene exhibits considerably low values of both $\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_w$.

In this study, the following equation could make it possible to correlate between melt viscosity and average weights for modified HPP.

$$\eta^* = k_t \left(\frac{\overline{M}_w}{\overline{M}_n}\right)^{\alpha} \left(\frac{\overline{M}_z}{\overline{M}_w}\right)^{\beta} \qquad (1)$$

Experimental data for the six kinds of samples modified at 0.5 kGy and 10 kGy determine the values of k_t, α and β in Eq. (1), as shown in Table 1. All data in Table 1 exhibit

Table 1
Average molecular weights of modified polypropylenes (3.0 MI) and complex viscosities at 0.1 rad/s of frequency and at 190 °C

Sample[a]	M_n	M_w	M_z	M_w/M_n	M_z/M_w	η* (190 °C) experimental	η* (190 °C) calculated[b]
1	37,199	101,158	270,786	2.719	2.677	4656	27,137
2	4264	237,305	1,958,178	55.653	8.252	113,740	117,707
3	50,548	143,584	475,653	2.841	3.313	32,987	35,339
4	25,044	309,234	1,348,253	12.348	4.360	52,194	51,523
5	56,702	225,514	933,586	3.977	4.140	46,961	46,933
6	30,383	236,998	1,171,807	7.800	4.944	61,574	59,461
7	6942	316,115	1,893,362	45.537	5.989	133,220	78,858

[a] (1) Unmodified virgin HPP; (2) 1.5 mmol of TPGDA and 0.5 kGy; (3) 1.5 mmol of TPGDA and 10 kGy; (4) 1.5 mmol of HDDA and 0.5 kGy; (5) 1.5 mmol of HDDA and 10 kGy; (6) 3 mmol of TPGDA and 0.5 kGy; (7) Montell's HMS-PP.

[b] Calculated by using Eqs. (1) and (3a)–(3c).

high melt viscosity compared to virgin HPP as indicated in Figs. 1–3. Melt complex viscosities at 0.1 rad/s of frequency (η*) between 180 °C and 230 °C with 10 °C of increment (six number of temperatures) are adapted for the correlations with total number of 30 data with the exception of samples 1 and 7.

From linearization of Eq. (1),

$$\log \eta^* = \log k_t + \alpha \log(\overline{M}_w/\overline{M}_n) + \beta \log(\overline{M}_z/\overline{M}_w) \tag{2}$$

The following correlations for constants are obtained from Fig. 8.

$$\log k_t = 5.99878 - 1.10743 \times 10^{-2}\,\mathrm{T} \tag{3a}$$

$$\alpha = 1.54451 \times 10^{-1} - 6.76450 \times 10^{-4}\,\mathrm{T} \tag{3b}$$

$$\beta = 3.35823 \times 10^{-2} + 6.31726 \times 10^{-3}\,\mathrm{T} \tag{3c}$$

where the linearity in Eqs. (3a)–(3c) is good with temperature, and k_t is inversely proportional to temperature and α is nearly independent of temperature and β slowly increases with temperature (Fig. 9). Inverse relation of k_t with temperature is due to a decrease of the melt viscosity of the polymer with temperature. The correlated values of α and β between 180 °C and 220 °C are changed by 0.03–0.06 and 1.2–1.4, respectively. Therefore, the term $\overline{M}_z/\overline{M}_w$ in Eq. (1) plays a dominant role in the calculation of the complex melt viscosity. This means that the formation of high molecular chains in a modification of polymer is very important to give high melt viscosity.

Fig. 9 compares the η* values calculated from Eqs. (2) and (3a)–(3c) with the experimental values of η* between 180 °C and 230 °C, showing a good correlativity for the modified polypropylenes. From Fig. 9 and the final column in Table 1, deviations between calculated η* and measured η* are very little for HPP modified with TPGDA or HDDA regardless of dosage, whereas the calculated values of η* for polypropylene manufactured by Montell Co., Ltd. are lower than the measured values. In unmodified virgin homo-polypropylene, the calculated values of η* are considerably different with the measured values. Therefore, Eqs. (1) and (3a)–(3c) are likely to be proper to estimate the melt viscosity of the modified HPP with comparably high melt viscosity.

Eqs. (3a)–(3c) were determined by using experimental data with the exception of Montell and virgin PP samples, probably resulting in a large discrepancy between calculated values and experimental ones. It is well known that virgin polypropylene

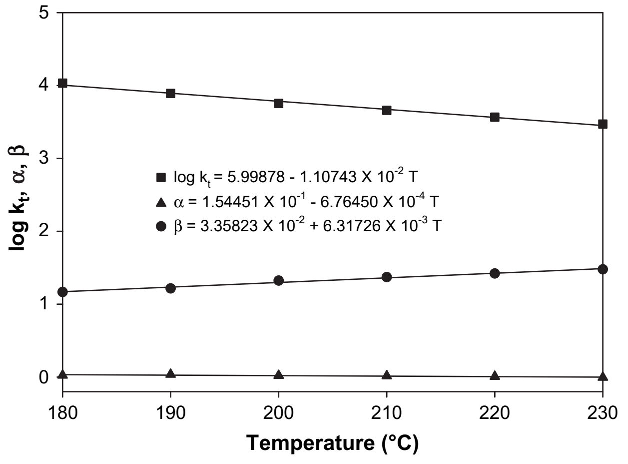


Fig. 8. Dependence of temperature on log(k_t), α and β calculated from the experimental data of η* for PP modified at 0.5 and 10 kGy with TPGDA by means of Eq. (2).

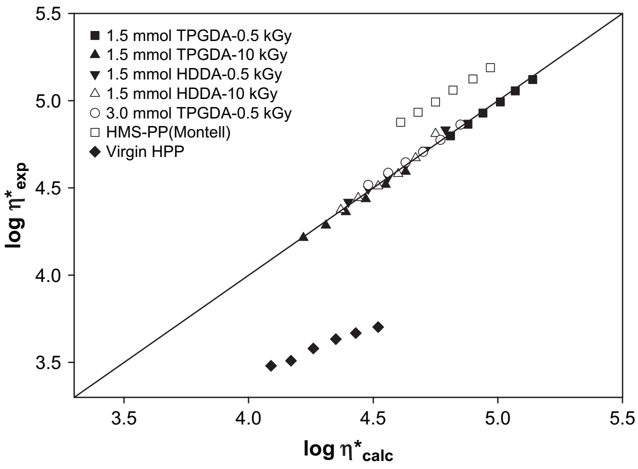


Fig. 9. Comparison of η* calculated from Eqs. (2) and (3a)–(3c) with experimental η* for the modified PP.

has a linear polymer chain differing from the modified polypropylenes that have high molecular chains.

Whereas, Montell sample was modified by only recombination of the chain fragments, which were generated by chain-scissions under electron beam irradiation without any addition of functional monomer, leading to the formation of high molecular weight branches. Where, irradiation dosages were much higher than in this study, for example 10, 60 and 80 kGy; such high dosages could cause much chain-scission in polymer, resulting in a large decrease of melt viscosity. From these facts, it can be concluded that Montell sample might have different structural configurations compared to the polypropylene modified by electron beam irradiation with the addition of a functional monomer.

4. Conclusion

- A grafting of bifunctional monomers, HDDA and TPGDA, onto HPP can considerably enhance melt viscosity of HPP under low dosages of electron beam irradiation.
- High values of melt viscosities accomplish with low irradiation dose and comparably with low composition of monomer under suppression of both oxidative degradation and homo-polymerization.
- TPGDA can enhance the melt viscosity of polypropylene more than HDDA and the melt viscosity of polypropylene modified with TPGDA is considerably sensitive to irradiation dose, probably resulting from structural feature of TPGDA with three numbers of methyl groups.
- Modified polypropylene with extremely high value of melt viscosity has a broad molecular weight distribution that remarkably shifts to high molecular weight.
- Modified polypropylene with high melt viscosity has large values of both $\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_w$, and the melt complex viscosity can be correlated by the equation $\eta^* = k_t(\overline{M}_w/\overline{M}_n)^{\alpha}(\overline{M}_z/\overline{M}_w)^{\beta}$ with a good correlation.

Acknowledgements

This research was supported by the Yeungnam University research grants in 2004.

References

[1] Houvinen P, Harilin A, Jääskeläinen P, Karbasi A, Manner N. International Patent, Publication No. WO99/016797, Applicant Borealis A/S; 1998.
[2] Saito J, Kawazoe S, Kikukawa S. Japan Patent, Publication No. 1994-157666, Applicant Chisso Corp.; 1992.
[3] Scheve BJ, Mayfield JW, DeNicola Jr AJ. US Patent 5591785, Applicant Montell North America Inc.; 1995.
[4] Weng W, Hu W, Dekmezian AH, Ruff C. Macromolecules 2002;35:3838.
[5] Wong B, Baker WE. Polymer 1997;38:2781.
[6] Sugimoto M, Masubuchi Y, Takimoto J, Koyama K. J Appl Polym Sci 1999;73:1493.
[7] Yoshii F, Makuuchi K, Kikukawa S, Tanaka T, Saitoh J, Koyama K. J Appl Polym Sci 1996;60:617.
[8] Yoshii F, Sasaki T, Makuuchi K, Tamura N. J Appl Polym Sci 1986; 31:1343.
[9] Cho BG. The study on improvement of high melt strength for polypropylene with addition of functional monomer, M.S. thesis (major advisor: D.H. Han), School of Chemical Engineering and Technology, Yeungnam University, Korea; 2001.
[10] Jang JH. Improvement of melt strength of homo polypropylene with addition of functional monomers and foaming of modified polypropylene, M.S. thesis (major advisor: D.H. Han), School of Chemical Engineering and Technology, Yeungnam University, Korea; 2003.
[11] Yousefi A, Katbab AA. Radiat Phys Chem 1994;44:645.
[12] Mezghani K, Philips P. Polymer 1995;36:2407.
[13] Zhrah AK, Yoshii H, Makuuchi K, Ishigaki I. Polymer 1989;30:1425.
[14] Iring M, László-Hedvig S, Kelen T, Tüdős F, Füzes L, Samay G, et al. J Polym Sci Symp 1976;75:55.
[15] Seavey KC, Liu YA, Khare NP, Bremner T, Chen CC. Ind Eng Chem Res 2003;42:5354.
[16] Bersted BH. J Appl Polym Sci 1975;19:2167.
[17] Bersted BH, Slee JD. J Appl Polym Sci 1977;21:2631.
[18] Bremner T, Rudin A. J Appl Polym Sci 1990;41:1617.
[19] Llorens J, Rudé E, Marcos RM. Polymer 2003;44:1741.
[20] Sugimoto M, Masubuchi Y, Takimoto J, Koyama K. J Polym Sci Part B Polym Phys 2001;39:2692.