High-Melt-Strength Polypropylene with Electron Beam Irradiation in the Presence of Polyfunctional Monomers

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SYNOPSIS

High-melt-strength polypropylene (PP) was achieved with irradiation by an electron beam generated from an accelerator in the presence of polyfunctional monomers (PFM). Among 16 PFMs, the relatively shorter molecular chain bifunctional monomers such as 1,4-butanediol diacrylate (BDDA) and 1,6-hexanediol diacrylate (HDDA) were the most effective for enhancing the melt strength of PP. The concentration and dose of the HDDA to obtain the high melt strength PP in irradiation under nitrogen gas atmosphere were 1.5 mmol/ 100 g PP and 1 kGy, respectively. DSC measurement and dynamic mechanical analysis showed that the thermal behavior of the high-melt-strength PP was different from that of the original PP. Crystallinity and crystallization temperature during cooling after heating were lower and higher in high melt strength PP than original PP, respectively. Elongational viscosity at 180°C of the high-melt-strength PP showed a remarkable increase at a certain elongational time with constant strain rate, demonstrating the typical property of high-melt-strength samples. This implies that a few higher molecular chains of PP, formed by intermolecular combination of its chain by HDDA in irradiation, give higher melt strength to induce entanglement of molecular chains. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Electron beams generated from an accelerator are very convenient for improving polymer materials by crosslinking, grafting, and degradation.[1] The radiation crosslinking of polymer materials occurs sufficiently even at room temperature. The crosslinking is due to formation of network structure by recombination of radicals formed in polymer materials by irradiation. This technology has been applied for crosslinking of insulation cables to improve heat stability. Currently, there is a growing technology toward recycling of waste polymer for conservation of resources. Radiation technology is used to decompose polytetrafluoroethylene (PTFE)[2] and butyl rubber wastes[3] for recycling.

In current technology, for production of polyethylene and polypropylene foams, foaming agent such as azodicarbonamide is kneaded to those polymers. Then, crosslinking structure is induced to the polymer by irradiation. When the polymer is heated at a temperature higher than the decomposition temperature of foaming agent, foam product is formed by making a lot of bubbles in polymer by nitrogen gas introduced by decomposition of a foaming agent. In this technology, to prevent melt flow during foaming at high temperature, high-melt-strength property of polymer is led by crosslinking during irradiation. But, the crosslinked materials are difficult to recycle to heat molding material because they cannot melt for crosslinking. The melt strength required during foaming at high temperature for preparation of polyethylene and polypropylene foams is achieved by adding long branch structure into main chains.[4,5] Since the polymer having branch chain melts at high temperature, the polymer can be recycled by remelting. It is reported that branch

Table I Modification in Enhancing of Melt Strength by PFM

PFM	Melt Strength (gf)	Functionality
Control	1.1	
Lauryl acrylate[a]	1.0	Monofunctional monomers
Cetyl acrylate[b]	0.7	
Stearryl acrylate[a]	1.0	
1,4-butanediol diacrylate (BDDA)[b]	7.0	Bifunctional monomers
1,6-hexanediol diacrylate (HDDA)[c]	6.6	
1,6-hexanediol dimethacrylate (HDDMA)[a]	3.4	
1,9-nonanediol diacrylate (NDDA)[a]	3.6	
Diethyleneglycol diacrylate (DEGDA)[c]	2.0	
Triethyleneglycol diacrylate (TEGDA)[c]	1.7	
Tetraethyleneglycol diacrylate (TEGDA)[c]	1.9	
Ethyleneglycol dimethacrylate (EGDMA)[c]	6.8	
Triethyleneglycol dimethacrylate (TEGDMA)[c]	2.6	
Neopentylglycol dimethacrylate (NPGDMA)[c]	3.0	
Trimethylolpropane triacrylate[c]	2.8	Trifunctional monomers
Trimethylolpropane trimethacrylate[c]	2.6	
Tetramethylolmethane tetraacrylate[c]	2.9	Tetrafunctional monomer

Monomer conc., 1.5 mmol/100 g PP; dose, 5 kGy.
[a] Supplier: Kyoeisha Chemical Co., Ltd.
[b] Supplier: Ohsaka Organic Chemical Industrial Co., Ltd.
[c] Shinnakamura Chemical Industrial Co., Ltd.

structures of polyethylene and polypropylene are formed at high doses (50 kGy) before gel formation in irradiation under nitrogen gas atmosphere using electron beam.[4] In previous papers,[6-8] we reported, in our investigation on irradiation effect of medical device material, that polypropylene is degraded by oxidation in two stages: during irradiation and during storage after irradiation. Thus a larger dose is not preferable for modification of PP using irradiation. Moreover, it was found that crosslinking with polyfunctional monomers improves physical properties of polymer materials at a lower dose.[9,10] In this article, on the basis of the these findings, studies on improvement of melt strength of the polypropylene by irradiation in the presence of polyfunctional monomers have been carried out.

EXPERIMENTAL

Materials

Polypropylene (PP) produced by Chisso Petrochemical Corporation was used for preparation of high-melt-strength PP in irradiation. The PP contained antioxidant (0.2 wt %) of phenol type but does not contain nucleating agent to improve transparency and toughness, in order to avoid effect of additive on the melt strength. Polyfunctional

monomers (PFM) used are shown in Table I. These monomers were used without purification for the experiments in irradiation.

Preparation of High-Melt-Strength PP and Irradiation

The PFM was added to the PP powder (100 μm) and the mixture was stirred for 2 h at room temperature. After stirring, the mixture was stored for 2 days at room temperature to help penetration of PFM into the interior part of PP. The sample was introduced in a polyester bag (20 × 20 cm) for irradiation. Then, the sample was irradiated with an electron beam at a beam current of 1 mA and an acceleration energy of 2 MeV generated by a Cockroft–Walton type accelerator (maximum voltage and current of 2 MeV and 30 mA, respectively). After irradiation, the sample was heated for 30 min at 80°C and then, further heated for 1 h at 130°C to react of residual radicals. This sample was used to evaluate the melt strength and elongational viscosity.

Melt Strength and Elongational Viscosity

PP heat treated after irradiation was pelletized to 2 mmϕ × 3 mm using a extruder (maximum diam-
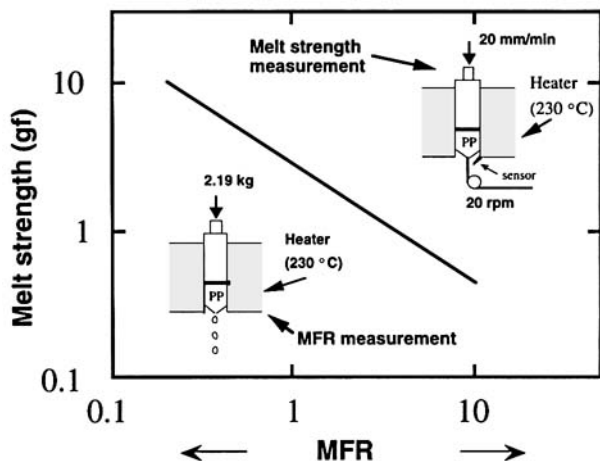
Figure 1 Calibration curve of relationship between melt strength and MFR of PP.

eter, 20 mm) at 200°C. Equipment schematics for measurement of melt strength and melt flow index (MFR) are shown in Figure 1. The PP pellets were introduced into the heated cell and then melt strength (gf) was measured by a Capilograph (Toyoseiki Co. Ltd.) having orifice of 2.095 mm diameter at 230°C. Extrusion rate was 20 mm/min and take up velocity was 20 mm/min. MFR was estimated by measuring weight of PP flowed for 10 min from orifice of 2.095 mm diameter under 2.16 kg at 230°C, by a Melt Flow Indexer (Toyoseiki Co. Ltd.). Melt strength linearly decreased with increasing MFR. The melt strength of the PP improved by irradiation was estimated by measuring MFR from the calibration curve in Figure 1.

In order to measure elongational viscosity, PP irradiated in the presence of HDDA was moulded into a rod of 3.0 to 4.0 mm diameter and length 33 mm by a Capilograph (Toyoseiki Co. Ltd.). Elongational viscosity was measured at several constant strain rates at 180°C by using a Meissner type rheometer (Toyoseiki Co. Ltd.) having a pair of rotating clamps. A range of strain rate was 0.05 to 0.3 s^{-1}.

Differential Scanning Calorimeter (DSC) and Dynamic Mechanical Analysis (DMA)

For the thermal analysis of high-melt-strength PP obtained by irradiation, a Perkin-Elmer Model DSC-1B was used. The measurement was carried out at a heating rate of 10°C/min under nitrogen gas. A 5-mg sample was placed in an aluminum pan before being put in the sample cell. For the first run, the cell was heated from room temperature to 200°C and then cooled at a rate of 10°C/min for crystallization up to 50°C. A second run was made im-

mediately after the first run was completed using the same conditions as before.

A torsion pendulum-type apparatus, Rhesca RD 1100 (Rhesca Co. Ltd.) was used for observation of molecular motion in the high-melt-strength PP. The measurement was carried out at a frequency of 0.2–1.0 Hz over a temperature range of −150 to 140°C.

RESULTS AND DISCUSSION

Effect of PFM on the Melt Strength of PP

The PFM is effective in giving network structure for polymeric materials at a lower dose because of its higher reactivity.[8,9] This structure is useful for improvement of physical properties such as heat stability and tensile strength. In this case, a relatively higher concentration such as 2 to 5 parts per hundred resin (phr) of PFM is necessary for improvement of polymeric materials. It is expected that reduced concentrations of PFM added to PP would induce enhancement of the melt strength by formation of higher molecular chain components and long branch structure without network structure by irradiation. Table I shows melt strength of PP improved by various PFMs in irradiation. It can be seen that bifunctional monomers is effective in improving melt strength of PP. On the contrary, trifunctional and tetrafunctional monomers are not preferable for enhancing of melt strength of PP. For these monomers, gels of 2% to 5% of PP are obviously observed. Irradiation of 5 kGy in monofunctional monomer may be too low for improvement of melt strength of PP because of its lower activity. Effect of chain length in the bifunctional monomers on the melt strength of PP is shown in Figure 2. Relatively shorter chain monomers such as BDDA and HDDA are better than longer chain monomers for improvement of melt strength of PP.
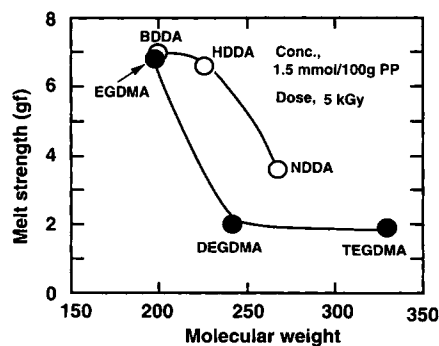

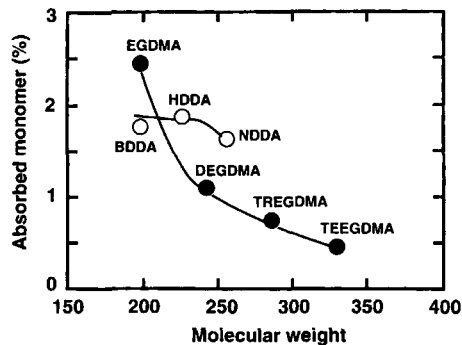**Figure 2** Effect of molecular chain length of PFM on melt strength of PP.

Figure 3 Monomer absorption of PP sheet. Absorption temp., 25°C; Absorption time, 24 h.

The melt strength of PP is higher with acrylate monomer than with methacrylate at the same molecular weight. This is because the reactivity of acrylate monomer is higher than that of methacrylate.[10] To elucidate the effect of monomer chain length on melt strength, PP sheet was immersed in PFM at 25°C for 24 hs. The results are shown in Figure 3. The shorter chain monomers such as EGMA, BDDA, and HDDA are well absorbed in the PP sheet. This result correspond with the improved melt strength described in Figure 1. From these findings, since shorter chain monomers penetrate well into PP sheet, it is considered that these monomers react effectively with the PP chain upon irradiation.

Effect of Monomer Concentration and Atmosphere during Irradiation on the Melt Strength

Crosslinking by irradiation of polymer materials are effective for improvement of its heat stability so that PFM is often used to reduce dosage required to achieve crosslinking of polymer materials. Figure 4 shows the relationship between melt strength of PP and dosage in different atmospheres. According to these results, the melt strength of PP increases with irradiation in the presence of HDDA. This means that irradiation is essential for enhancing melt strength of PP. The irradiation in air requires higher doses because oxygen retards reaction of HDDA with the PP. With irradiation in nitrogen gas, the melt strength increases remarkably at a dose of 1 kGy, and then become constant. Irradiation in the absence of PFM requires higher doses of more than 50 kGy for improvement of PP melt strength.[4] Hence, it is concluded that addition of PFM is preferable to get high-melt-strength PP at lower doses. Monomer concentration is an important factor on
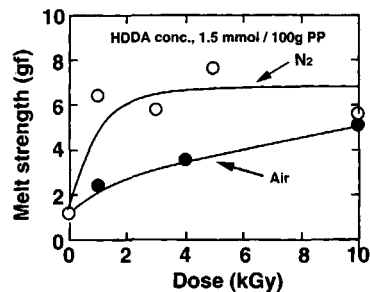

Figure 4 Effect of atmosphere on melt strength in irradiation.

melt strength during irradiation. Figure 5 shows the effect of monomer concentration on the melt strength in irradiation in air and nitrogen gas. Maximum melt strength of PP obtained with irradiation in nitrogen gas and air were found at concentrations of 1.5–2 and 2.5–3 mmol/100 g PP, respectively. The maximum melt strength of PP irradiated in nitrogen atmosphere is slightly larger than PP irradiated in air. From Figure 3, PP absorbed 8 mmol of HDDA per 100 g PP. This means that approximately 20% of the monomer before irradiation contributed to increasing the melt strength of PP and 80% of the monomer may form homopolymer. At higher monomer concentration, melt strength of PP is reduced. In this case, the monomers may lead toward production of homopolymer rather than reaction with PP, because so much monomer surrounds the radicals formed during irradiation. Accordingly, from these findings, it was clarified that lower concentrations such as 1.5–2 mmol/100 g PP is favorable for improvement of melt strength of PP.

Thermal Analysis of High-Melt-Strength PP

It was reported earlier[11] that in the radiation sterilization of medical devices, melt temperature in the crystalline part of the PP was obviously reduced at doses such as 50 kGy, by a degradation process oc-
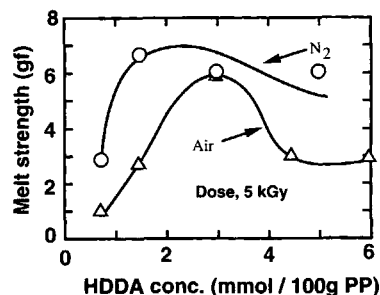

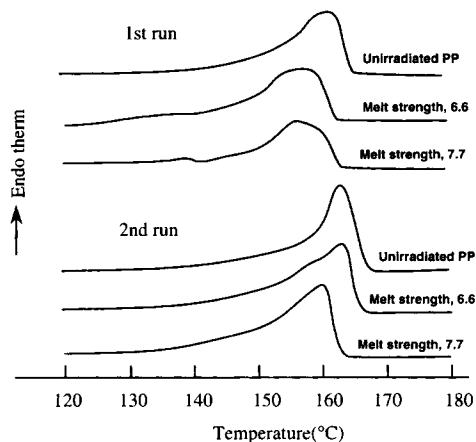**Figure 5** Effect of atmosphere on melt strength in different monomer concentrations.

Figure 6 DSC curves of various melt strength PPs.

Figure 7 Crystallization temperature of different PPs during cooling after heating.

curring on the crystal boundary. Since in this current experiment, a lower dose such as 5 kGy is used, melt behavior of PP by DSC measurement is hardly changed by irradiation. Hence, if the melt behavior of PP modified by irradiation in presence of PFM changed compared with that of unirradiated PP, it is assumed that HDDA is added by graft polymerization onto PP chains during irradiation. Figure 6 shows DSC curves of different high melt strength PPs prepared by irradiation in the presence of HDDA. In the first run, the melting peak shifts toward lower temperature with increasing melt strength and becomes broader. In the second run, unirradiated PP shows a narrower peak compared with the first run owing to rearrangement of molecular chains during slow cooling after melting in the first run. The high-melt-strength PPs have broader peaks in melting even in the second run, indicating that crystallization during cooling after the first run of PP is due to larger molecules formed by HDDA grafted to the PP, as discussed later. The crystallization temperature of PP during cooling after melting in the first and second run is shown in Figure 7. Unirradiated PP and PP with added HDDA have crystallization peaks at 115°C and 128°C, respectively. The crystallization temperature of unirradiated PP is far different from that of the irradiated PP in the presence of HDDA. The PP with HDDA added gives a microcrystal, since crystallization occurs from a higher temperature as compared to the unirradiated sample.

To elucidate the morphology of high-melt-strength PP obtained by irradiation, dynamic viscoelastic properties were determined. Figure 8 shows the mechanical loss (logarithmic decrement) and shear modulus (G') as a function of temperature in the second run. The mechanical loss of the PP shows
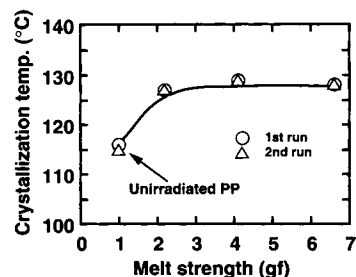
three processes,[12] α, β, and γ relaxations. At high-temperature, α-relaxation is used to determine the crystallinity of the sample, the higher the α-relaxation, the sample is more crystallized. The β-relaxation is related to the amorphous fraction and is associated with the glass transition (T_g) state of the polymer. An increase in the β-relaxation indicates a decrease in the crystallinity. The low-temperature γ-relaxation is due to local motion of various chemical groups in the polymer chain. Shear modulus G', on the other hand, was found to decrease with decrease in crystallinity. As shown in Figure 8, it can be seen that for high-melt-strength PP, peak level of β-relaxation is slightly higher and α-relaxation is shifted toward lower temperature as compared with those of the original PP, respectively. The G' is lower in high-melt-strength PP than in the original PP at higher temperature than glass temperature. From these findings, it is confirmed that crystallinity of the high-melt-strength PP is lower than that of the
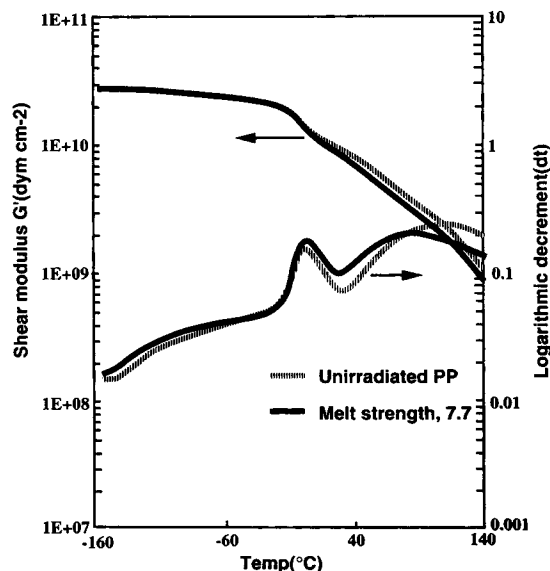

Figure 8 Dynamic viscoelastic properties of PP in the 2nd run.

original PP since crystallization during cooling after the first run is retarded by HDDA added to PP with irradiation.

Elongational Viscosity of High-Melt-Strength PP

To elucidate the role melt properties play in moulding and spinning of polymer materials, elongational viscosity in the molten state is often measured to evaluate processability of polymer. It was reported that high molecular weight PP and branch PP had higher elongational viscosity.[4,13] Figures 9(a) and 9(b) show elongational viscosities with various strain rates at 180°C for unirradiated PP (melt strength, 1.1) and PP irradiated in the presence of HDDA (melt strength, 7.7), respectively. The elongational viscosity of the unirradiated PP [Fig. 9(a)] is substantially linear and unchanged at different strain rates because it is straight chain to use in injection moulding, while for the irradiated PP, the elongational viscosity is nonlinear with time. For the faster strain rate (0.20752 s^{-1}), elongational viscosity increases more rapidly at an earlier stage. On the contrary, slower strain rates such as 0.09067 and 0.03596 s^{-1} give higher elongational viscosity at a later stage than the faster strain rate. Low density polyethylene[13] and PP having long branch[4] have the same properties.

Next, to confirm the incremental increase of the elongational viscosity and melt strength of PP by PFM, gel-permeation chromatography (GPC) and low-angle laser light scattering (LALLS) measurements were carried out. The GPC–LLS is useful to determine high molecular weight components and long chain branches formed by irradiation for enhancing melt strength and elongational viscosity of PP. The relationship between molecular weight and radius of gyration in 1,2,4-trichlorobenzene of high-melt-strength PP obtained by irradiation is almost similar to that of the original PP (before irradiation). Thus, long chain branches on the main chain of PP do not form. Further, higher molecular weight components formed by HDDA upon irradiation were not evident. Although high melt strength PP was boiled in xylene for 6 h, a gel fraction was not observed. However, as shown in Figure 6, 7, and 8, irradiated PP showed thermal behavior different from the original one and have properties of high melt strength and high elongational viscosity. Increase of elongational viscosity in the molten state results from entanglement of polymer chains. It has been reported that a few longer molecular chain lead to higher elongational viscosity by entanglement of polymer chains.[13–15] Hence, it is deduced that some
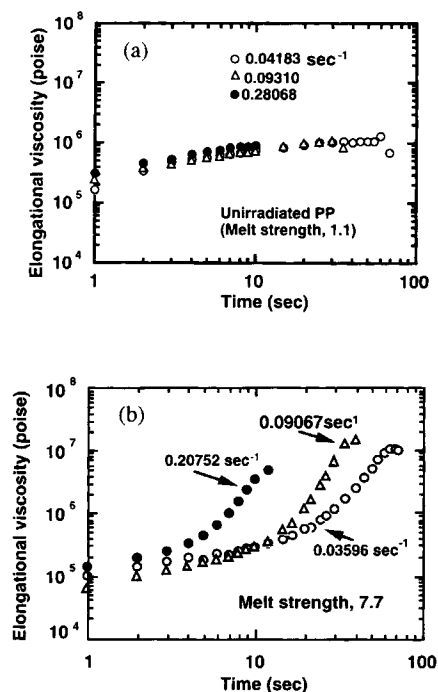

Figure 9 Elongational viscosity of unirradiated PP (a) and PP irradiated (b) in the presence of HDDA.

longer chains formed by HDDA, not detected by GPC–LLS, give high melt strength by entanglement of PP chains. Longer molecular chains of two or three times the original PP may be formed by intermolecular combination of PP chain by HDDA in irradiation. In this case, network structure of PP by crosslinking does not form owing to use of lower doses and lower PFM concentration.

CONCLUSION

To improve melt strength, PP was irradiated in the presence of PFM. High concentrations of PFM in irradiation led to a network structure of PP by crosslinking. On the other hand, lower concentrations such as 1.5 mmol give higher melt strength to the PP without crosslinking at a lower dose, 1 kGy. BDDA and HDDA of bifunctional monomers were the most effective for enhancing the melt strength of PP. Thermal behavior of high-melt-strength PP prepared by this method was different from that of the original PP. High-melt-strength PP was obtained at a lower dose by using PFM. Hence, the high-melt-strength PP prepared by this new technology, instead of the radiation crosslinked PP in current technology, could be applied for production of foam in the near future. Since it would be possible

to reuse this PP by remelting, it would be useful for reduction of environment pollution by waste plastics.

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