

Graft Copolymerisation of N-Vinyl Pyrrolidone onto Polypropylene Copolymer in Melt: Effect of Grafting on Thermomechanical Properties and Paint Adhesion

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ABSTRACT: N-vinyl pyrrolidone (NVP) was grafted onto a polypropylene copolymer (PP) in melt in a Brabender Plasticorder and single screw extruder. The effect of variation of dicumyl peroxide (DCP) and lupersol (LUP) concentrations alone and with 20 wt % NVP concentration in the Brabender Plasticorder on Melt Flow Index (MFI) and final torque values was studied. Variation of NVP concentration (1–10 wt %) at a fixed DCP concentration on percent grafting (G) and MFI was also studied in the single screw extruder. The graft copolymers (PP-g-NVP) obtained by reaction of PP with NVP were Soxhlet extracted with isopropanol to remove homopolymer, dried, and finally characterized by Fourier transform infrared (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The PP-g-NVP (0–30 wt %) was used as an additive with PP, extruded in the single screw extruder, molded, and the

mechanical properties and paint adhesion was measured. MFI values increased and torque values decreased with an increase in initiator concentration, indicating the dominance of the peroxide-initiated scission reaction over grafting. DCP gave higher grafting compared to LUP. When NVP concentration was increased, MFI values increased initially due to more scission, and then decreased, indicating more graft copolymer formation. Mechanical properties increased by incorporation of PP-g-NVP as an additive than PP-g-NVP alone. Paint adhesion increased by the presence of PP-g-NVP as additive especially with polyurethane primer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2173–2180, 2003

Key words: graft copolymerization; crystallization; polypropylene copolymer

INTRODUCTION

Polypropylene and copolymers have wide applicability in the marketplace due to their low cost and good mechanical properties. Graft copolymerization of polar monomers onto polypropylene and copolymers (PP) offers an effective means for introducing desirable properties such as adhesion, dyeability, paintability, and compatibility into the polymer without adversely affecting the nature of polymer backbone.¹ Graft copolymerization of vinyl monomers onto PP,² synthesis of polyolefins graft copolymers, and block copolymers by reactive extrusion have been reviewed.^{3,4} Polypropylene and its derivatives have been recently reviewed by Borsig.⁵ Graft copolymerization was achieved by using solution,^{6,7} melt,^{8–12} solid state,^{13,14} photochemical,^{15–17} γ irradiation in supercritical CO₂,¹⁸ etc., using peroxide initiators. Various monomers also used for graft copolymerization have been maleic anhydride,^{8,9,11,19,20} acrylic acid,^{17,21} α -methyl styrene,^{22,23} polysiloxysilane,²⁴ functional peroxides,²⁵ oxazoline,²⁶ glycidyl methacrylic ac-

id,^{27,28} poly(oxyalkylene)imide,²⁹ and *p*-phenylene-bis-maleamic acid,³⁰ onto polyolefins. N-vinyl pyrrolidone (NVP) was functionalized onto polyethylene by melt grafting.³¹ The graft copolymerization reaction carried out in melt is a cost-effective single-step process as there is no solvent required and it helps in producing graft copolymers without construction of an entirely new facility compared to traditional copolymerization processes.³²

In the present work, graft copolymerization of PP with NVP in the melt with two peroxide initiators in a Brabender Plasticorder and single screw extruder have been studied. The detailed characterizations of these graft copolymers and their effect on mechanical properties and paint adhesion are also reported.

EXPERIMENTAL

Materials and methods

Polypropylene copolymer (PP), MFI 3.16 g/10 min at 230°C with a ethylene content of 8 wt %, was produced in our company, Indian Petrochemicals Corporation Limited, Vadodara, India. In the literature low ethylene (<10 wt %) is also considered as PP, so we have abbreviated polypropylene copolymer as PP.³ NVP was obtained from Fluka Chemicals, Switzer-

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land; dicumyl peroxide (DCP) from Aldrich Chemicals, Milwaukee, WI; and Lupersol-101 [2,5-di-(tert-butylperoxy)-2,5-dimethyl hexane] (LUP) from Lucidal, a division of Pennwalt Corporation, Buffalo, NY, was used as received. Acetone and methanol of analytical reagent grades from Ranbaxy Chemicals Ltd., S A S Nagar, India, were used without purification.

Graft copolymerization of NVP onto PP in Brabender Plasticorder

Graft copolymerization of PP with NVP was carried out in a melt mixing head of Brabender Plasticorder at 180°C with a screw speed of rpm 50. PP granules (18 g) were added into the mixing head through loading shoot and left for 1–2 min to reach equilibrium in molten state. Then, the required amount of DCP, Lupersol, and NVP was added, and melt mixed for 5 min. Variation of DCP and LUP concentrations 0–0.5/100 g of PP (wt %) at a fixed NVP concentration (20 wt %) was studied.

Graft copolymerization of NVP onto PP in single screw extruder

Graft copolymerization was also carried out in a single screw extruder by premixing initiator and monomer, and added to molten PP. The effect of variation of NVP concentration (0–10 wt %) at a fixed DCP (0.1 wt %) concentration with a temperature profile of 175–195–205–195°C and screw speed of rpm 50 was studied.

The graft copolymers (PP-g-NVP) obtained above in the Brabender Plasticorder and single screw extruder were cut into 3–5 mm size granules, dried at 60°C for 8 h. They were Soxhlet extracted with isopropanol for 36 h to remove homopolymer, and dried again under vacuum at 60°C for 8 h to a constant weight. The amount of NVP grafted onto PP and homopolymer was estimated gravimetrically.

$$\text{Percent grafting (G)} = (W_1 - W_0)100/W_0$$

$$\text{Percent homopolymer (HP)} = (W_2 - W_1)100/W_0$$

where W_0 is the weight of PP, W_1 the weight of graft copolymer (PP-g-NVP) after Soxhlet extraction, and W_2 the weight of graft copolymer (PP-g-NVP) along with homopolymer.

Addition of PPgNVP with PP

The graft copolymer (PP-g-NVP₃) prepared in the single screw extruder with a percent grafting of 3.7 wt % was used as additive (0–30 wt %) along with PP, and extruded in the single screw extruder under above identical conditions as done in graft copolymerization.

The extrudates were palletized, dried, and compression molded into films and 3 mm sheets in a compression molding machine at 210°C with a pressure of 150 psi, and their thermomechanical properties were evaluated.

Characterization and evaluation

The infrared (IR) spectra of compression-molded films were recorded on a Fourier transform infrared (FTIR) spectrophotometer. Melting (T_m), crystallization (T_c) temperatures, heat of fusion during melting (ΔH_m), and crystallization (ΔH_c) were recorded on a modulated 2910 differential scanning Calorimeter (DSC) from TA instruments. The samples (5–10 mg) were heated under a nitrogen atmosphere from ambient to 200°C at a heating rate of 10°C/min, held for 5 min, and cooled to room temperature. Thermogravimetric analysis (TGA) thermograms were recorded on a Hi Res TGA 2950 Thermogravimetric Analyzer from TA Instruments with a heating rate of 10°C/min under N₂ atmosphere from 0 to 600°C to measure initial decomposition temperature (IDT), half decomposition temperature (T_{50}), and final decomposition temperatures (FDT). The mechanical properties of 3 mm test specimens such as notched Izod impact strength (IS) (kg cm/cm) tensile strength (TS) (kg/cm²), tensile modulus (TM) (kg/cm²), and MFI (g/10 min at 230°C/2.16 kg) were measured according to ASTM D-638, D-256, and 1238L, respectively. The paint adhesion test was measured by the cross-cut adhesion test (ASTM D-3359, method B) with or without using a primer. The percent paint removed are indicated as follows: 0B, >65%; 1B, 35–65%; 2B, 15–35%; 3B, 5–15%; 4B, <5%; 5B, 0%; adhesion or none.

RESULTS AND DISCUSSION

Graft copolymerization of PP with NVP was studied in the Brabender Plasticorder and single screw extruder in melt and the conditions were optimized. The effect of variation of DCP, LUP, and NVP concentrations on MFI, torque, and thermomechanical properties are discussed below.

Studies in Brabender Plasticorder

Effect of DCP and LUP concentrations on MFI, and torque

The effect of variation of initiators—namely, DCP and LUP concentrations (0.05–0.5 wt %)—on MFI and final torque is given in Figures 1 and 2. The MFI values increased and torque values decreased with an increase in initiator concentration. MFI values increased from 3 to 70 and 22 g/10 min, respectively, for DCP and LUP, indicating more scission in DCP. The final

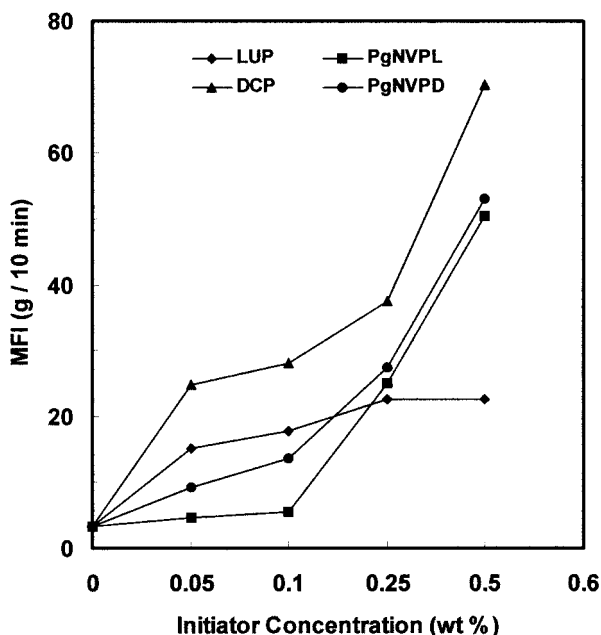


Figure 1 Effect of variation of initiators and NVP concentration on MFI in the Brabender Plasticorder. PgNVPL: LUP + NVP (20 wt %); PgNVPD: DCP + NVP (20 wt %).

torque values given in Figure 2 decreased continuously from 750 to 450 and 325, respectively, for LUP and DCP. The decrease in torque was more in DCP than LUP due to more scission in the former. More scission was also indicated by their higher MFI values

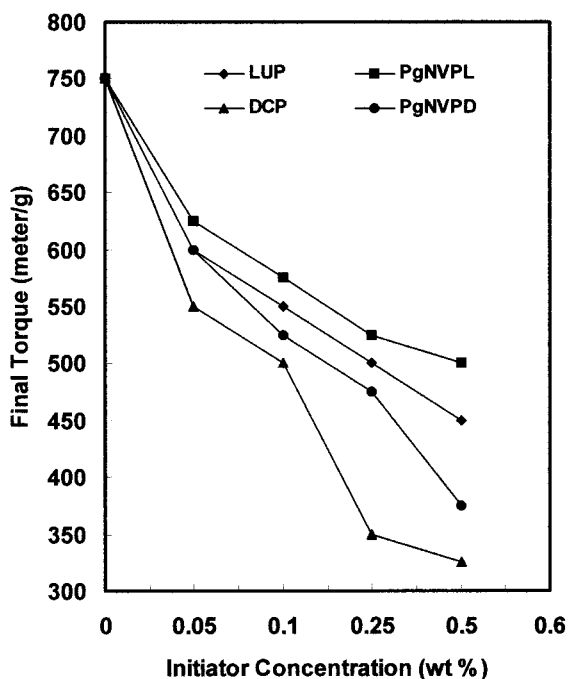


Figure 2 Effect of variation of initiators and NVP concentration on final torque in the Brabender Plasticorder. PgNVPL: LUP + NVP (20 wt %); PgNVPD: DCP + NVP (20 wt %).

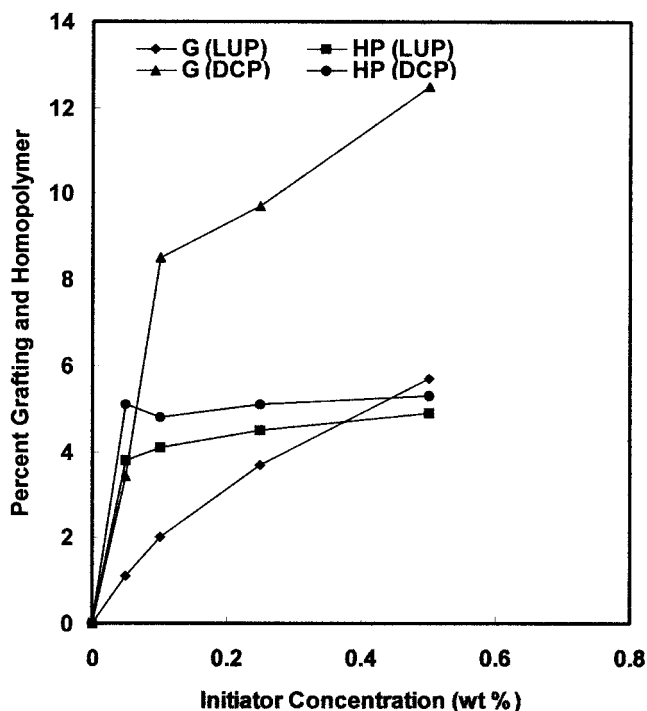


Figure 3 Effect of variation of initiators and NVP concentration on percent grafting and homopolymer in the Brabender Plasticorder. G (LUP): grafting obtained with lupersol; G (DCP): grafting obtained with DCP; HP (LUP): homopolymer obtained with lupersol; HP (DCP): homopolymer obtained with dicumyl peroxide.

for DCP (70) compared to 22 for LUP. A shorter half life ($t_{1/2}$) of the initiator gives a higher transient radical concentration for the same concentration of initiators. As DCP has a shorter half life of 9.2–0.25 min compared to LUP, having 14–0.30 min at 150–200°C, the initially formed radicals cause more β -scission in PP with DCP than LUP, leading to an increase in MFI and a decrease in torque values.³

Effect of DCP, LUP, and NVP on MFI and torque

The effect of variation of the initiators DCP, and LUP concentrations (0.05–0.5 wt %) at a fixed concentration of NVP (20 wt %) on MFI and torque are given in Figures 1 and 2. The MFI values increased with an increase in initiator concentration from 3 to 50 and 45, respectively, for DCP and LUP. The increase in MFI when NVP and DCP were added together was less (50) than the MFI obtained when DCP was added alone (70) to PP. The torque values decreased with an increase in initiator concentration with 20 wt % NVP concentration. The torque values decreased from 750 to 540 and 400, respectively, for LUP and DCP. These torque values obtained are higher when NVP and initiator are added together than the torque values obtained for initiator alone (Fig. 2). The higher torque values and lower MFI values obtained when initiator

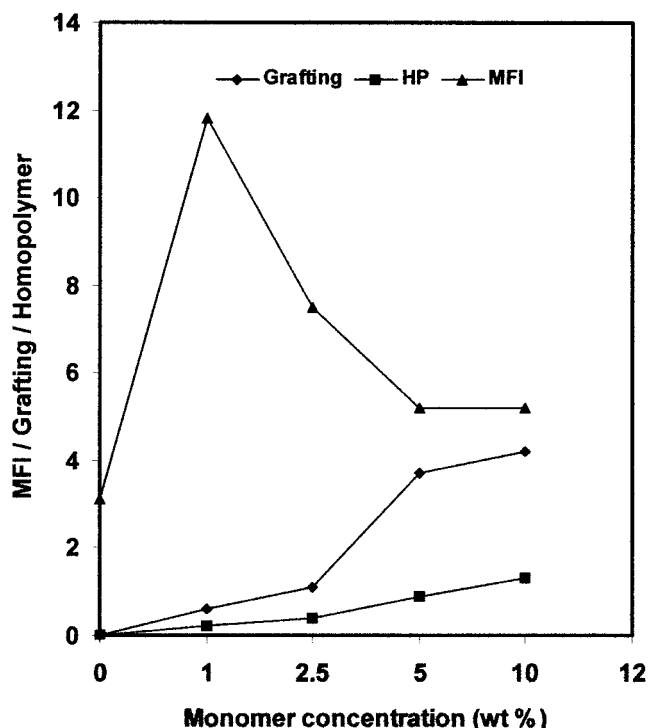


Figure 4 Effect of variation of NVP at a fixed DCP concentration on MFI, grafting, and homopolymer in the single screw extruder.

and NVP are added together showed that there is a graft copolymerization. Between these two initiators DCP gave higher MFI values and lower torque values compared to LUP when the initiator and NVP added together. The final torque values are always lower than the initial torque value of 750 for PP, indicating the dominance of peroxide-initiated chain scission than grafting.

Percent grafting

The effect of variation of the initiators DCP and LUP concentrations at 20 wt % NVP concentration on percent grafting and homopolymer is given in Figure 3.

The idea of taking excess NVP (20 wt %) is to allow the complete reaction of initiator radicals (0.5 wt %) with NVP. Above this concentration of monomer under melt conditions in a closed batch, the reaction gives more of homopolymer than graft copolymer. The percent grafting increased with an increase in initiator concentration of both initiators. Maximum grafting of 5.7 and 12.5 wt % was obtained for LUP and DCP at 20 wt % NVP and 0.5 wt % initiator concentration. The increase in grafting with increase in initiator concentration is expected due to an increase in free initiator radicals at higher concentration, which facilitates grafting the NVP radicals to attack at free radical sites of PP. The higher grafting in DCP is due to time of graft reaction for DCP, which was 1.03 min³¹ compared to 0.27²⁵ min for LUP. The homopolymer also increased with an increase in initiator concentration but the increase was less at higher initiator concentration due to the formation of more graft copolymer. As DCP gave a higher percent grafting, further studies were carried out in the single screw extruder with the same initiator.

Studies in single screw extruder

Effect of NVP concentration

The effect of variation of the monomer NVP concentration from 1 to 10 wt % at 0.1 wt % DCP concentration is given in Figure 4. The percent grafting and homopolymer increased with an increase in NVP concentration. Maximum grafting of 4.2 wt % was obtained at 10 wt % NVP concentration. The percent grafting obtained in the single screw extruder was less compared to the Brabender Plasticorder, which is a closed batch reactor, and the reaction was kept for longer residence time. Song et al. obtained a higher degree of grafting in a batch mixer than extruder.³³ MFI values increased from 3.5 to 12 at 1 wt % NVP, then decreased to 5 at 10 wt % NVP. At lower NVP concentration, the availability of free radicals generated from initiator are more compared to radicals

TABLE I
Graft Copolymerization of NVP onto PP in Single Screw Extruder: Effect of Percent Grafting on Mechanical Properties and Paint Adhesion

Polymer ^a	Mechanical properties ^b				Paint adhesion ^c		
	G (%)	IS (kg cm/cm)	TS (kg/cm ²)	TM (kg/cm ²)	EP	PU	P ₁
PP	0	10.4	209	7858	F	F	F
PP-g-NVP ₁	0.6	6.7	217	9525	F	P	F
PP-g-NVP ₃	3.7	7.1	145	7000	F	1B	F
PP-g-NVP ₄	4.2	7.3	147	8869	F	F	F

^a Graft copolymers (PP-g-NVP₁₋₄) synthesized in the single screw extruder.

^b G: grafting; IS: impact strength; TS: tensile strength; TM: tensile modulus.

^c EP: with epoxy primer; PU: with polyurethane primer; P₁: without any primer; F: fail; P: pass. Paint adhesion: 1B = 35–65%.

TABLE II
Graft Copolymerization of NVP onto PP in Single Screw Extruder: Effect of Addition of PP-g-NVP₃ with PP on Mechanical Properties and Paint Adhesion^a

Polymer	Mechanical properties					Paint adhesion			
	Additivition		MFI (g/10 min)	IS (kg cm/cm)	TS (kg/cm ²)	TM (kg/cm ²)	EP	PU	P ₁
	PP	PP-g-NVP ₃							
PP	100	0	3.2	10.4	209	7858	F	F	F
NVP2.5	97.5	2.5	4.0	9.1	237	11087	F	F	F
NVP5	95	5	4.6	9.5	224	11050	F	P	F
NVP10	90	10	4.7	12.2	226	10936	2B	P	F
NVP15	85	15	4.8	10.1	225	10492	F	2B	F
NVP20	80	20	5.0	10.6	225	10446	F	F	F
NVP30	70	30	5.6	9.4	223	10346	OB	P	1B

^a PP-g-NVP₃: graft copolymer. Paint adhesion: OB: >65%; 1B, 35–65%; 2B: 15–35%.

^b For other abbreviations, see Table I.

generated from NVP, and there will be more scission than grafting, leading to increase in MFI values. As the NVP concentration increased, there will be more NVP free radicals, which react with available free radicals of PP, leading to more graft copolymer formation, which in turn decreases MFI values. At lower monomer concentration, scission reaction dominates over grafting, and at higher monomer concentration graft copolymerization reaction dominates. Homopolymer formation was observed along with graft copolymer.

Effect of grafting on mechanical properties

The effect of grafting on the mechanical properties is given in Table I. The IS decreased initially due to peroxide-induced scission of PP backbone, then it increased slightly with an increase in grafting—but it is always less than PP. The tensile strength and tensile modulus increased up to a percent grafting of 0.6 wt %, and then decreased. Incorporation of NVP onto the PP backbone as a graft copolymer (PP-g-NVP) at low percentages may create orderly rearrangement, which in turn increases tensile properties. Similar observations were found in PMMA-g-coir³⁴ and PAN-g-chemically modified sisal fibers at low concentrations.³⁵ At higher grafting there was no significant increase in mechanical properties.

Additivition of PP-g-NVP₃

The graft copolymer, PP-g-NVP₃, obtained by reaction of NVP with PP with a percent grafting of 3.7 wt %, was chosen as an additive (0–30 wt %) with PP. The effect of additivity on MFI and mechanical properties are given in Table II. MFI values increased by the addition of PP-g-NVP₃ due to the plasticizing effect of PP-g-NVP, which is present both as a homopolymer and a graft copolymer. There is an increase in impact strength, tensile strength, and tensile modulus by the addition of PP-g-NVP. Maximum impact strength of

12.2 kg cm/cm, was obtained at 10 wt %, tensile strength, and tensile modulus of 237 and 11087 kg/cm² were obtained at 2.5 wt %. This shows that at lower concentrations of PP-g-NVP, as explained earlier, contributes to tensile strength and modulus, and higher concentration improves impact strength. Addition of functionalized polyolefins with acid³⁰ and oxazoline,³² to PP improves mechanical properties because they form an very effective interface between nonpolar PP and polar compounds.³

Paint adhesion

The effect of grafting and the addition PP-g-NVP₃ to PP on paint adhesion were studied with and without epoxy and polyurethane primers, and their results are given in Tables I and II. Graft copolymer (PP-g-NVP) showed good paint adhesion and passed the test at 0.6

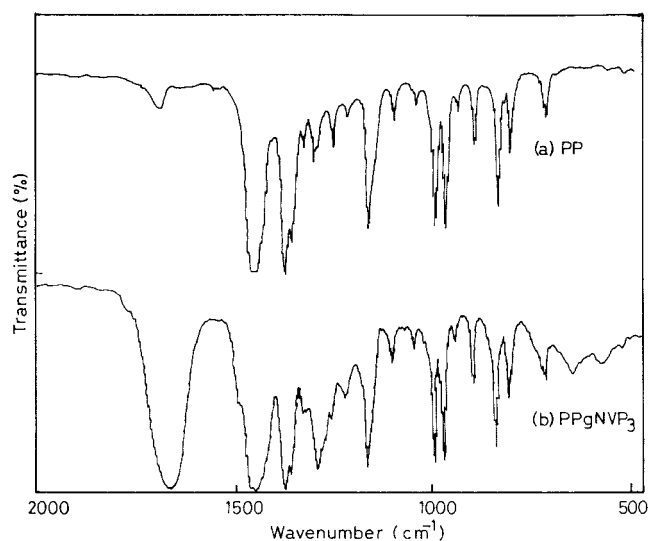


Figure 5 IR spectra of (a) PP and (b) graft copolymer (PP-g-NVP₃).

TABLE III
Graft Copolymerization of NVP onto PP in Single Screw Extruder: Effect of Percent Grafting on Thermal Properties^a

Polymer	Grafting (%)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	IDT (°C)	T_{50} (°C)	FDT (°C)
PP	0	165	68	115	76	271	368	453
PP-g-NVP ₁	0.6	164	74	125	70	296	453	486
PP-g-NVP ₃	3.7	165	48	130	73	300	442	486
PP-g-NVP ₄	4.2	165	64	128	76	242	393	476

^a Graft copolymers PP-g-NVP₁₋₄ were synthesized in the single screw extruder.

wt % grafting when it was used alone using polyurethane (PU) primer. Addition of PP to PP-g-NVP₃ increased paint adhesion and passed the test at 5–10 wt % with PU primer, as given in Table II. At higher additive concentration of 30 wt %, the paint adhesion was >65% with an epoxy primer. Thermoplastic polyolefins functionalized with other functional groups like anhydride and acid are directly paintable^{36,37} and improve paint adhesion.³⁸

Characterization of PP-g-NVP graft copolymers

IR spectroscopy

The graft copolymers (PP-g-NVP) were characterized by IR spectroscopy and their IR spectra of films are given in Figure 5. The IR spectra have not showed any strong carbonyl absorption when PP was melt mixed with/without DCP for 5 min [Fig. 5(a)]. The IR spectrum of PP-g-NVP graft copolymer [Fig. 5(b)] showed strong carbonyl absorption at 1680–1660 cm⁻¹ due to incorporation of NVP onto PP, thus confirming the formation of PP-g-NVP graft copolymer. Two more strong absorptions at 1285 and 1422 cm⁻¹ were seen in PP-g-NVP spectra. All these absorptions matches with the absorptions of polyvinylpyrrolidone reported in literature.^{31,39}

Differential scanning calorimetry

The graft copolymers (PP-g-NVP) synthesized earlier in the single screw extruder by reacting NVP with PP using DCP initiator were purified and their thermograms containing different percentages of grafting, viz. 0.6% (PPgNVP₁), 3.7% (PPgNVP₃), and 4.2 % (PPgNVP₄) were recorded. The results given in Table III show the effect of variation of grafting on the crystallization (T_c) and melting (T_m) temperatures. The thermograms showed sharp exo- and endotherms during cooling and heating, respectively. There was not much change in melting temperature of 164–165°C (T_m). PP crystallizes at 115°C, but the crystallization temperature was shifted to higher temperature of 125°C when 0.6 wt % NVP was grafted onto PP. As the percent grafting increased, T_c also increased from 125 to 130°C at 3.7 wt % grafting. DSC cooling curves of PP and graft copolymers containing a grafting of 0.6 wt % and 3.7 wt % are given in Figure 6. Maximum crystallization temperature of 130°C was obtained with a percent grafting of 3.7 wt %, with a shift in T_c of 15°C. The shift in T_c was due to poly(NVP) containing a carbonyl group acting as a nucleating agent, which in turn shifted the crystallization temperature. Graft copolymers contain carbonyl groups such as acid, anhydride,^{7,12,40} and acetal⁴¹ groups in the graft

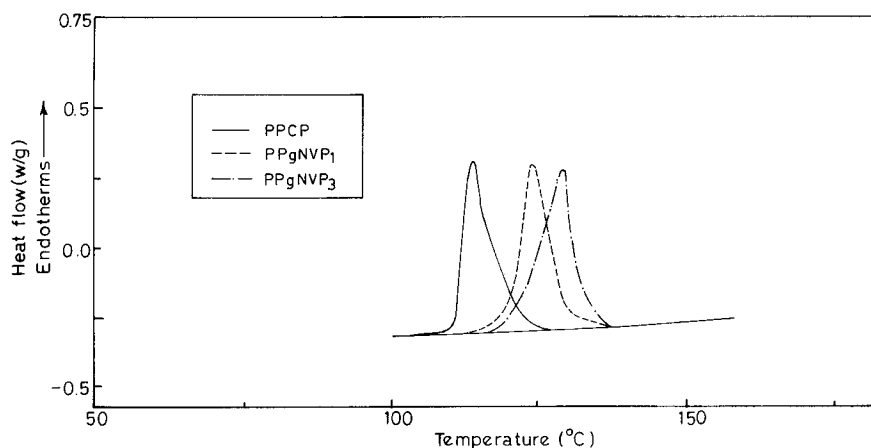


Figure 6 DSC cooling curves of PP (-) and graft copolymers: PP-g-NVP₁ (---), and PP-g-NVP₃ (- · - · -).

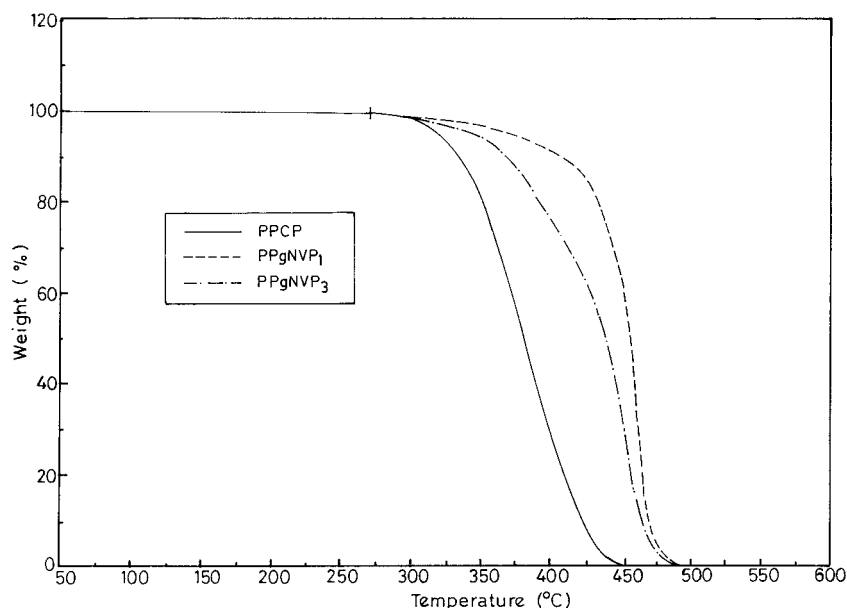


Figure 7 TGA thermograms of PP (-) and graft copolymers: PP-g-NVP₁ (- - -) and PP-g-NVP₃ (- · · · ·).

copolymers of PP-enhanced nucleation. These nucleating agents increase the crystallization rate, and decrease the product cycle times, resulting in cost savings per product unit⁴¹ because the product requires shorter cooling rates.⁴²

Thermogravimetric analysis

The IDT, (T_{50}), and (FDT) of PP, and PP-g-NVP₁ to PP-g-NVP₄ are given in Table III. The IDT, T_{50} , and FDT of the graft copolymers are higher than the PP, indicating the improvement in thermal stability by the incorporation of polyvinylpyrrolidone. TGA thermograms of PP and graft copolymers containing a percent grafting of 0.6 and 3.7 wt % are given in Figure 7. In the graft copolymer PP-g-NVP₁ containing 0.6 wt % grafting, the IDT, T_{50} and FDT shifted to higher temperatures of 296, 453, and 486°C from 271, 368, and 453°C of PP, respectively. A shift of 25, 85, and 33°C was obtained. Above this grafting there was not much shift in these temperatures. This indicated that the thermal stability of PP increased by the incorporation of polyvinylpyrrolidone. The thermal stability of PP was also increased by the incorporation of butyl acrylate in PP-g-butyl acrylate graft copolymers.⁴³

CONCLUSIONS

PP-g-NVP copolymers were synthesized and characterized, and their conditions were optimized, in the Brabender Plasticorder and the single screw extruder. The percent grafting increased with an increase in monomer and initiator concentration. DCP gave higher grafting due to more grafting reaction time. The graft copolymer PP-g-NVP enhanced the crystal-

lization temperature by 15°C compared to PP. The thermal stability increased as indicated by the increase in thermal decomposition temperatures. These temperatures were higher at the lower grafting level than at the higher due to incorporation of polyvinylpyrrolidone in small quantities and the orderly rearrangement in PP-g-NVP. Addition of PP-g-NVP with PP improved the mechanical properties. The paint adhesion to PP increased when PP-g-NVP was added along with an epoxy and polyurethane primers, whereas without these primers there was no paint adhesion. This is IPCL Communication No. 351.

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