Melt Grafting of *n*-Butyl Methacrylate onto Poly(vinyl chloride): Synthesis and Characterization*

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ABSTRACT: The graft copolymerization of *n*-butyl methacrylate monomer onto compounded poly(vinyl chloride) was carried out by melt-mixing process in a Brabender plasticorder (BPCR) using a free-radical initiator. The reaction conditions such as initiator and monomer concentration, shear rate (rpm), residence time, and temperature were optimized in the mixing head of BPCR attached to a torque rheometer. The graft copolymers were Soxhlet extracted with cyclohexane and were characterized by intrinsic viscosity, FTIR, and ^{13}C-NMR spectroscopy. A maximum of 14% grafting was obtained. The graft copolymer showed significant improvement in processibility and both thermal and mechanical properties. Scale-up studies of the optimized recipe were carried out in a single-screw extruder for commercial trials/evaluation. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2442–2449, 2004

Key words: graft copolymers; monomer; initiator; mixing; poly(vinyl chloride) (PVC)

INTRODUCTION

Poly(vinyl chloride) (PVC) is a well-known versatile commodity thermoplastic, whose production and consumption worldwide is second to other plastics.[1] It has various fields of applications for both rigid (unplasticized) and flexible (plasticized) products. However, PVC has some inherent drawbacks, such as poor thermal stability, processibility, impact strength, weatherability, and low-temperature brittleness. These drawbacks are mainly attributed to the presence of labile chlorine atoms in the backbone of the PVC chain, which start to liberate HCl at the glass-transition temperature (T_g).[2] To improve many of these deficiencies virgin PVC is usually modified by various techniques. The physical route of modification by selective compounding with different additives is well known,[3] although the chemical route of modification by graft copolymerization with a second monomer is relatively new.[4–7] The graft copolymerization can be carried out in two ways: solution polymerization process or melt processing during mixing/extrusion process. Many authors have reported the solution polymerization route of modification of PVC with a monomer in a suitable solvent, to improve the thermal stability, processibility, or impact strength of PVC.[8–14] However,

this method has inherent drawbacks, such as requiring a large quantity of solvent and its removal after the reaction, and remains in the realm of academic interest, although it is not commercially feasible.

On the other hand, the melt grafting process of PVC with a monomer has potential from the commercial perspective. In the open literature, various type of monomers and methods have been used to modify PVC for various type of applications,[15–21] although the free-radical grafting of *n*-butyl methacrylate (BMA) monomer onto PVC during melt processing is very scanty. There are no reported data of the grafting reaction of PVC by this route. In this article, we report the synthesis of BMA-grafted PVC, in the mixing head attached to a Brabender torque rheometer, and characterization of the product.

EXPERIMENTAL

Materials

PVC (67 ER 092 grade, K = 67 value; IPCL, Baroda, India), octyl tin maleate (OTM, Ala Chemicals, Bombay, India), calcium stearate (Fluka, Bombay, India), stearic acid (S. D. Fine Chemicals, Bombay, India), stabilized *n*-butyl methacrylate (BMA; GSFC, Polymer Unit, Baroda, India), and dicumyl peroxide (Fluka, Germany) were all used as received.

Synthesis method

PVC resin was compounded with the following additives in a sigma mixer attached to a Brabender plasticorder (PLV-151, Brabender OHG, Germany) at 88°C,

60 rpm for 10 min [(in phr): PVC, 100; OTM, 1.5; calcium stearate, 1.5; stearic acid, 0.5].

The above compounded PVC (C-PVC) was used for the melt-grafting reaction in the Brabender mixing head (capacity 30 mL) at 170°C, 50 rpm, for 9 min of mixing. Initially the desired amount of C-PVC (31 g) was charged into the preheated mixing head under a load of 5 kg and melt mixed for 4 min. Afterward, a calculated amount of initiator dissolved in a known amount of BMA monomer was fed into the C-PVC melt and mixed for an additional 5 min. During the mixing operation, the torque–time variation curve was recorded. Identical instrumental settings were maintained in all the experiments.

The melt-mixed lump material was collected quantitatively, cut into small chips, and weighed. The chips were ground into a coarse powder ($\sim$ 1 mm) in the cryogenic grinder (Microjet 10J, New York).

Characterization

Characterization of the graft copolymers was carried out by the following analytical techniques.

Gravimetric analysis (Soxhlet extraction)

The melt-mixed lumps (homopolymer + graft copolymer) were removed quantitatively from the mixing head of the Brabender plasticorder and were cut into small pieces, while still in a hot condition. These were weighed on an analytical balance to determine the apparent increase in weight.

For Soxhlet extraction, a weighed amount of this material was taken and ground to a fine powder with the help of liquid nitrogen in a Microjet 10J Quartztech machine. The dried and preweighed powder was taken in cellulosic thimbles and extracted with the help of cyclohexane for 108 h to remove the homopolymer.[22] The thimbles containing graft copolymers, after extraction, were dried to a constant weight. Percentage of grafting, percentage of homopolymer formed, and percentage of grafting efficiency were calculated by the following equations[23]:

$$\text{Percentage of grafting} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

$$\text{Homopolymer formed (\%)} = \frac{W_b - W_g}{W_0} \times 100 \quad (2)$$

$$\text{Grafting efficiency (\%)} = \frac{W_g - W_0}{W_b - W_0} \times 100 \quad (3)$$

where W_0 is the initial weight of C-PVC (g), $W_b = W_0$ + increase in weight after grafting = total weight of material, and $W_g = W_0$ + weight of grafted material.

Intrinsic viscosity [η]

The dilute solution viscosities of virgin PVC resin, C-PVC (melt mixed), BMA-g-PVC (without initiator), and BMA-g-PVC (with initiator and unextracted) copolymers were measured as 0.2% (w/v) solution in tetrahydrofuran (THF) solvent using a Ubbelohde viscometer (Cannon–Ubbelohde, State College, PA) at 30°C.

FTIR spectroscopy

Thin films (0.025 mm thick) of both extracted and unextracted samples were prepared from THF solution (2% w/v) casting method and dried, after which IR spectra were recorded on a PE 1600 FTIR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT).

^{13}C-NMR spectroscopy

^{13}C-NMR spectra were recorded in deuterated THF solution on PVC, BMA-g-PVC (with initiator and extracted), and BMA monomer samples on a JNM-FX 100 FT NMR spectrometer (JEOL, Tokyo, Japan) at 50°C using HMDS as an internal reference standard.

Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) traces were recorded on a Dupont-9900 thermal analyzer (Dupont, Boston, MA) in N_2 atmosphere in the range of room temperature to 600 and 150°C, respectively, at a heating rate of 10°C/min.

Torque–time analysis

The torque generated was recorded versus time under identical conditions during melt mixing. The energy requirement to process and the torque index (%) (i.e., thermomechanical stability) were calculated using the following equations[24]:

$$\text{Energy requirement } (W) = 2\pi n \int_{t_1}^{t_2} M \, dt, \text{ (kJ/h)} \quad (4)$$

where n is the rotor speed (min^{-1}), M is the mixing torque (N m), t_1 is the initial time (min), and t_2 is the final time (min).

$$\text{Torque index (\%)} = (M_{10}/M_1) \times 100 \quad (5)$$

where M_{10} is the torque at the 10th min of mixing and M_1 is the torque at the 1st min of mixing.

TABLE I
Results on Variation of Monomer Concentration

Sample	C-PVC taken (g)	BMA taken (wt %)	DCP taken (wt %)	Total weight after grafting (g)	Remarks
1	31.0	0.00	0.10	31.09	Blackish yellow
2	31.0	5.78	0.10	32.56	Opaque
3	31.0	11.56	0.10	34.07	Opaque
4	31.0	14.45	0.10	34.82	Translucent
5	31.0	17.35	0.10	35.79	Transparent
6	31.0	20.23	0.10	36.55	Hazy oily
7	31.0	23.12	0.10	—	Oily, monomer smell
8	31.0	17.35	0.00	35.27	Monomer smell

TABLE II
Results on Variation of Initiator Concentration

Sample	C-PVC taken (g)	BMA concentration (wt %)	DCP concentration (wt %)	Total weight after grafting (homo + copolymer) (g)	Remarks
1	31.0	17.35	0.00	35.27	Oily, monomer smell
2	31.0	17.35	0.10	35.79	Transparent
3	31.0	17.35	0.25	35.20	Translucent
4	31.0	17.35	0.50	34.27	Opaque
5	31.0	17.35	1.00	34.36	Opaque

RESULTS AND DISCUSSION

The conditions for melt grafting of BMA onto C-PVC are optimized in the mixing head of a Brabender torque rheometer by varying the monomer and the initiator concentrations.

Effects of monomer concentration

Results on the effect of monomer concentration on the formation of copolymer (homo +graft) are presented in Table I. The total weight (i.e., homo + graft) is increased with the increase of monomer concentration at a fixed initiator concentration of 0.1 wt %. At 17.35 wt % of monomer concentration, the grafted material is transparent and there is no smell of unreacted monomer. Beyond 17.35 wt % monomer concentration the grafted material was hazy and emitted an unreacted monomer smell. Thus at this optimum concentration (17.35 wt % BMA) was chosen for further grafting studies.

Effect of initiator concentration

Results on the effect of varying initiator concentration at fixed monomer concentration (17.35 wt %) are shown in Table II. Here the total weight of the grafted copolymer formed was increased and was highest at 0.1 wt % of initiator concentration and then decreased.

It may be observed from Table II that the maximum weight (homo + copolymer) was obtained in sample 2; thus this was considered to be the optimum concentration of initiator and monomer for the grafting of BMA monomer onto C-PVC in the melt.

Characterization

Results of the percentage grafting, grafting efficiency, and homopolymer formation, estimated by Soxhlet extraction with cyclohexane followed by standard gravimetric methods [eqs. (1)–(3)], are shown in Table III.

The results shown in Table III clearly indicate that the percentage grafting is highest for sample 2 (13.8%). Therefore, this was considered to be an optimum monomer and initiator concentration for the grafting reaction.

Intrinsic viscosity studies

The dilute solution viscosities of PVC resin, C-PVC (melt mixed), BMA-g-PVC (melt grafted, without initiator), and BMA-g-PVC (grafted with initiator and

TABLE III
Results on Soxhlet Extraction

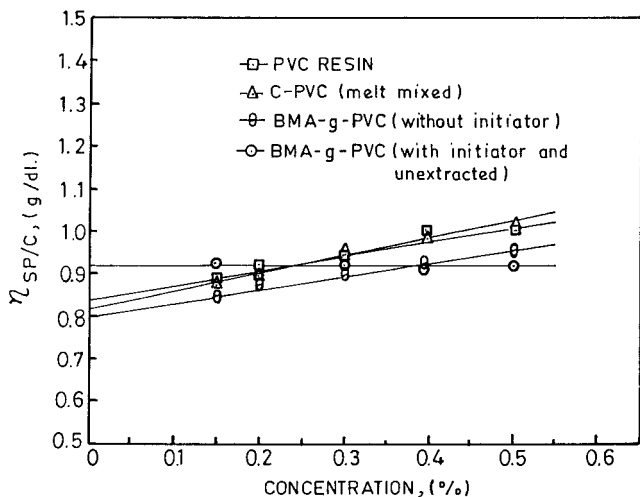| Sample (Ref. Table II)	Grafting (%)	Grafting efficiency (%)	Homopolymer formed (%)
1	12.7	82.3	2.1
2	13.8	89.2	1.7
3	10.4	81.5	2.4
4	10.5	84.5	1.9
5	11.0	85.0	1.7

Figure 1 Dilute solution viscosity of the grafted material in THF solution.

unextracted) copolymers are presented in Figure 1. It is observed from Figure 1 that intrinsic viscosity [η] of BMA-g-PVC (with initiator) is higher (0.92 dL/g) than that of the other samples, indicative of high molecular weight. These results show that BMA-g-PVC copolymer has been formed and has a higher molecular weight than that of the base resin (PVC).

FTIR studies

The IR spectra of PVC resin, C-PVC (melt mixed), BMA-g-PVC (melt grafted, without initiator), and BMA-g-PVC (grafted with initiator and extracted) copolymers are presented in Figure 2. The IR spectra of PVC resin and C-PVC melt mixed showed distinct absorption bands at 1425, 1325, and 2906 cm^{-1}, which may be attributed to $-CH_2-$ vibration and asymmetrical vibration of the $-CH_2-$ group, and absorption at 1067 cm^{-1} may be attributed to $-C-C-$ bond. The IR spectrum of BMA-g-PVC (extracted) showed a strong absorption band at 1720 cm^{-1} (Fig. 2), attributed to the carbonyl group ($>C=O$) of ester linkage of grafted poly(butyl methacrylate). No such peak was observed in PVC or C-PVC (melt mixed), which showed a distinct evidence of grafting. However, the appearance of a small peak of weak intensity at 1720 cm^{-1} of the C-PVC (melt mixed) sample may be attributed to carbonyl group of stearic acid, which was added to PVC during compounding in a small quantity. An absorption band attributed to the ester linkage also appeared at 1720 cm^{-1} in the BMA-g-PVC (melt grafted, without initiator) sample, although its intensity was smaller (film thickness was same) than that of BMA-g-PVC (with initiator and extracted) copolymer. This observation further confirmed that BMA was grafted onto PVC in the melt to form a BMA-g-PVC copolymer.

^{13}C-NMR studies

The ^{13}C-NMR spectra of PVC-resin, BMA monomer, and BMA-g-PVC (grafted with initiator and extracted) copolymer samples are presented in Figure 3. The NMR spectrum of BMA monomer shows the presence of carbonyl carbon of the ester group at δ 166.4 and 176.44 in the Soxhlet-extracted graft copolymer of BMA-g-PVC, along with methylene, methanic, and methyl carbons at δ 46.68, 29.21, and 21.83, respectively. In the BMA-g-PVC (extracted) a prominent peak appears at δ 14.0 attributed to the methylene
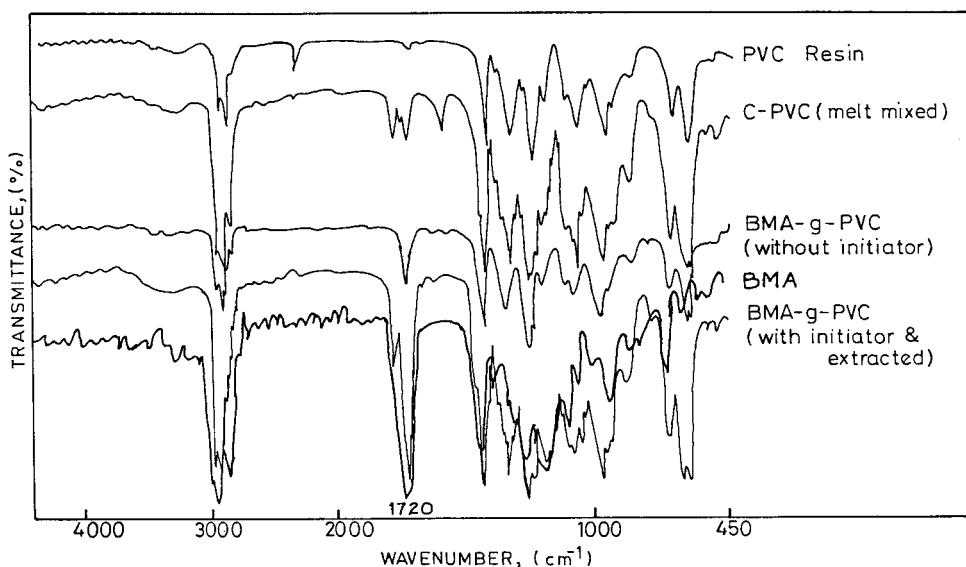

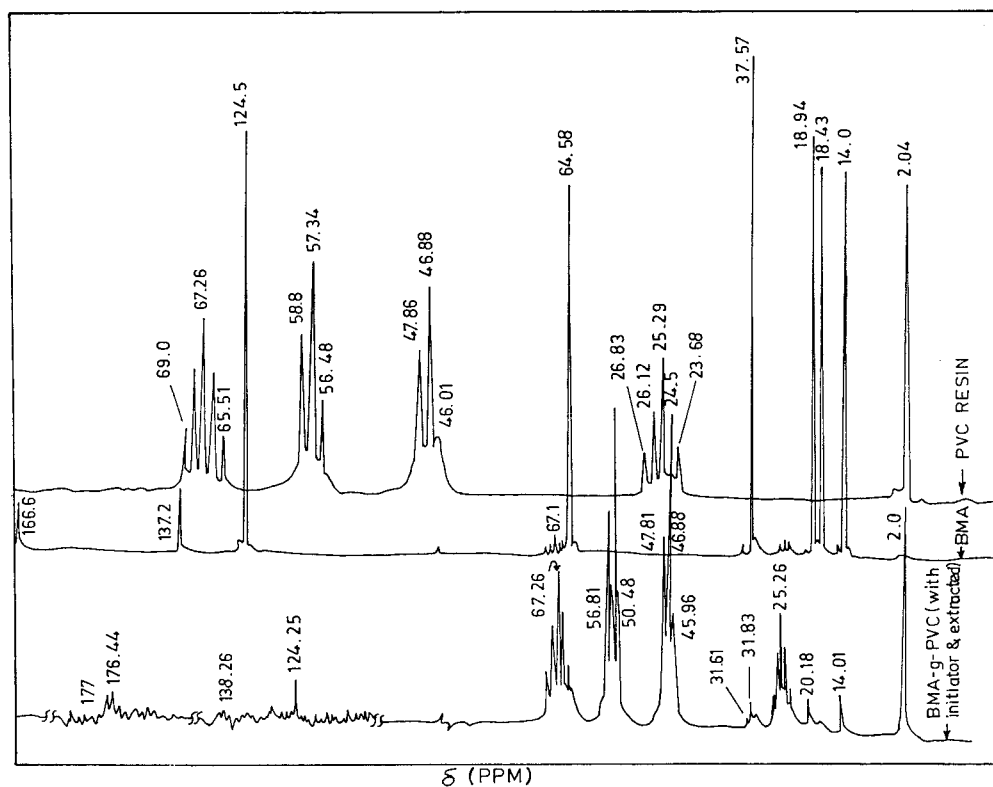**Figure 2** FTIR spectroscopy of the grafted materials.

Figure 3 ^{13}C-NMR spectroscopy of the grafted materials.

group, whereas virgin PVC does not show any signal at δ 14.0, 166.4, and at 176.44. Thus ^{13}C-NMR studies also indicate the grafting of BMA monomer onto PVC, complementary to IR studies.

Thermal analysis (TGA and DSC studies)

The TGA and DSC traces of C-PVC (melt mixed), BMA-*g*-PVC (grafted without initiator), and BMA-*g*-
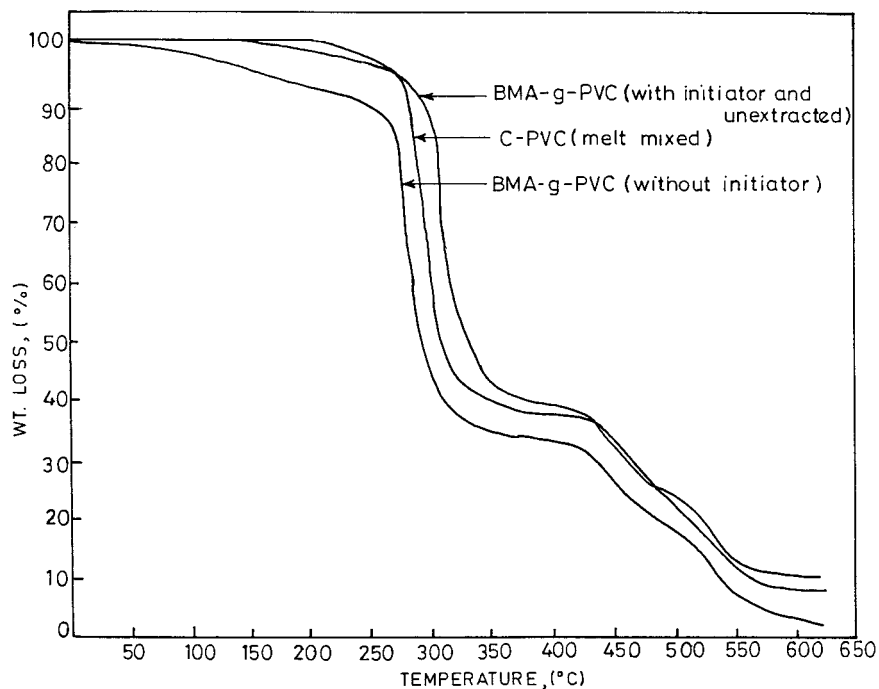

Figure 4 TGA thermograms in N$_2$ atmosphere of the grafted materials.
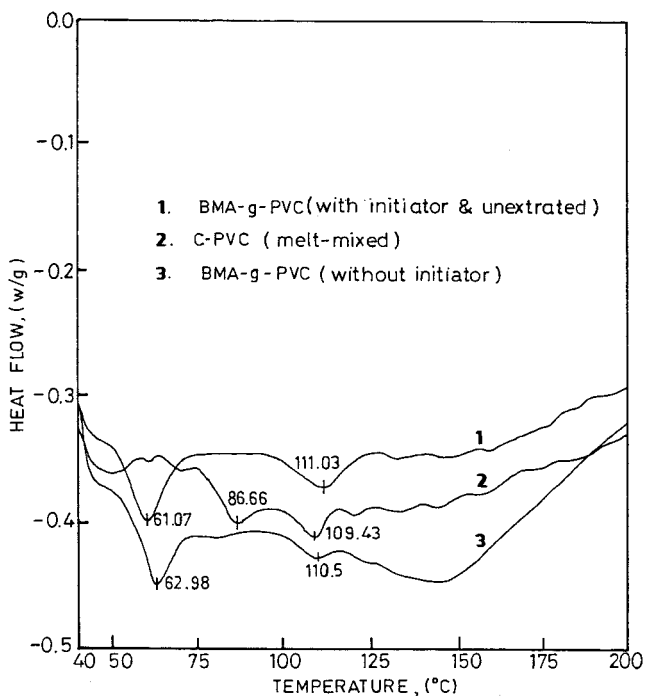
Figure 5 DSC thermograms in N_2 atmosphere of the grafted materials.

PVC (grafted with initiator and unextracted) in N_2 atmosphere are shown in Figures 4 and 5, respectively. From the TGA traces (Fig. 4) some other parameters, such as integral procedural decomposition temperature (IPDT), initial decomposition temperature (IDT), final decomposition temperature (FDT), temperature at 50% weight loss, and percentage residue, were also calculated based on Doyel's method[25] and are presented in Table IV.

The IPDT value of BMA-*g*-PVC (with initiator) is higher by 27°C than that of C-PVC (melt mixed).This shows that grafting of BMA onto PVC enhances the thermal stability and consequently reduces the thermal degradation during processing.

From the thermogravimetric traces (Fig. 4) it was determined that thermal degradation occurs in two steps. In the first step, the weight loss begins at about 260–290°C followed by a rapid weight loss up to 350°C. Then from 350 to 425°C there is no appreciable weight loss, indicating that some kind of crosslinking stabilization reaction occurred. In the second step, there is rapid

weight loss around 425–550°C, which may be attributable to degradation/chain scission of the copolymer.

The heating cycles of DSC traces of three samples are shown in Figure 5. In the case of the C-PVC (melt mixed) sample, a broad endothermic peak about 87°C is observed, attributed to the glass-transition temperature of PVC. This peak shifted to a lower temperature ($\sim$ 60°C) in the case of grafted samples. This phenomenon may be the result of internal plasticization on graft copolymerization. The second endothermic peak ($\sim$ 110°C, in all three samples) may be attributed to the additive added to PVC for compounding.

Mixing torque–time analysis

The resultant data on melt-mixing torque–time analysis [based on eqs. (4) and (5)] on the samples (cf. Table II) are given in Table V.

Table V shows that the torque generated during melt mixing of C-PVC with BMA monomer is less than that of C-PVC and is also takes less energy to process. This indicates that BMA monomer plasticizes the C-PVC by the method of graft copolymerization and enhances its ease of processibility. However, the torque index shows that the thermomechanical stability is poorer at a given time and temperature than that of the C-PVC. This may be attributable to the shearing effect of the rotor; the material thus behaves in a shear-sensitive manner and can be processed at lower shear rate and lower temperature than can C-PVC.

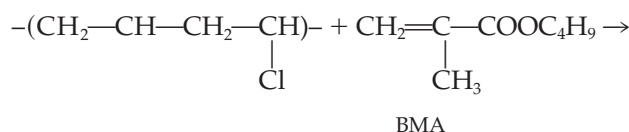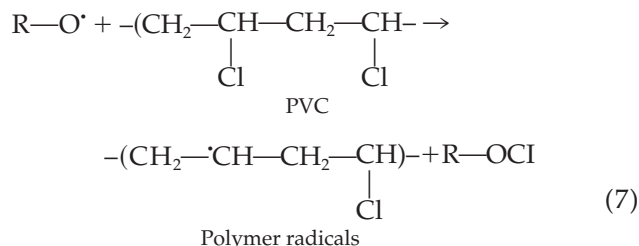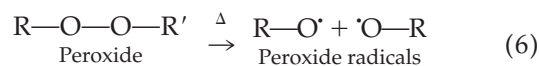The plausible free-radical grafting reaction mechanism may be represented as follows:

$$R-O-O-R' \xrightarrow{\Delta} R-O^{\bullet} + {}^{\bullet}O-R \qquad (6)$$
$$\text{Peroxide} \qquad\qquad \text{Peroxide radicals}$$

$$R-O^{\bullet} + -(CH_2-CH-CH_2-CH- \rightarrow$$
$$\qquad\qquad\qquad | \qquad\qquad |$$
$$\qquad\qquad\qquad Cl \qquad\qquad Cl$$
$$\qquad\qquad\qquad\qquad PVC$$

$$-(CH_2-{}^{\bullet}CH-CH_2-CH)-+R-OCI$$
$$\qquad\qquad\qquad\qquad | \qquad\qquad\qquad (7)$$
$$\qquad\qquad\qquad\qquad Cl$$
$$\qquad\qquad \text{Polymer radicals}$$

$$-(CH_2-CH-CH_2-CH)- + CH_2{=}C-COOC_4H_9 \rightarrow$$
$$\qquad\qquad | \qquad\qquad\qquad\qquad |$$
$$\qquad\qquad Cl \qquad\qquad\qquad\qquad CH_3$$
$$\qquad\qquad\qquad\qquad BMA$$

TABLE 4
Results on Thermogravimetric Analysis

| Sample description	IPDT (°C)	IDT (°C)	FDT (°C)	Temperature at 50% weight loss (°C)	Residue at 600°C (%)
C-PVC (melt mixed)	437	275	560	306	8.0
BMA-*g*-PVC					
without initiator	422	270	555	287	4.0
with initiator	464	285	585	330	10.0

TABLE V
Results on Torque–Time Analysis

Sample	Equilibrium torque (N m)	Energy requirement to process (kJ/h)	Torque index (%)
1	11.3	28.9	121.1
2	14.2	37.2	152.5
3	13.7	35.0	114.3
4	15.7	40.4	123.1
5	14.7	38.0	130.4
C-PVC	17.9	47.7	192.1

$$-CH_2-CH-CH_2-CH\sim$$
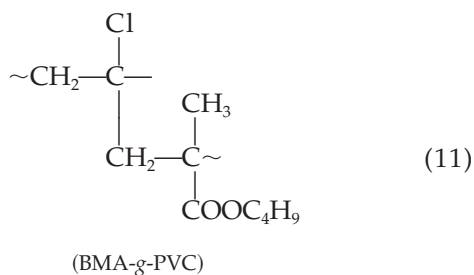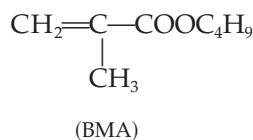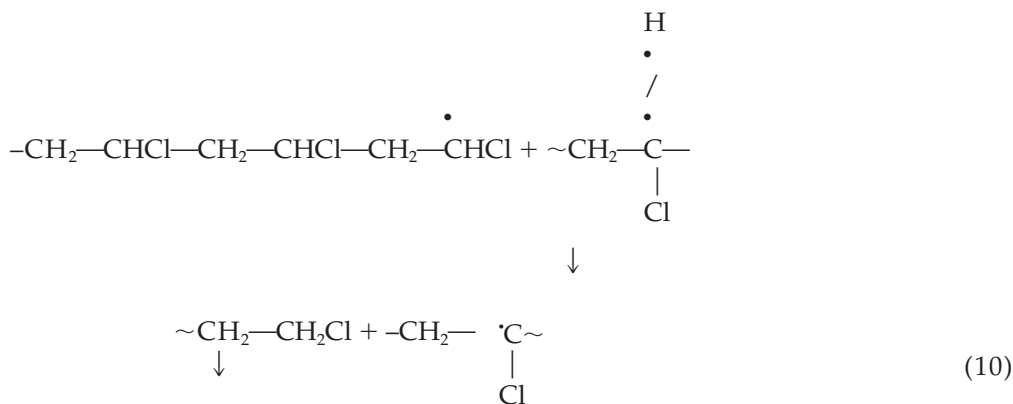with Cl, CH₃, CH₂—C~, COOC₄H₉ substituents (8)

(BMA-g-PVC)
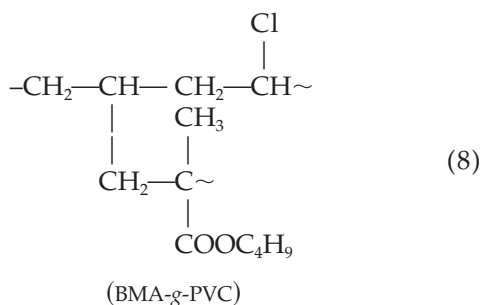
The thermal grafting reaction mechanism may be explained as follows. Termination is responsible for many different end-group structures as well as certain irregular groups formed within PVC molecules that have been terminated by coupling. When polymeriza-

tion of two growing radical chains is terminated by coupling, the resultant polymer molecule has an initiator fragment at each end.

$$R-[-CH_2-CH_2-]_n-CH_2-\overset{H}{\underset{Cl}{C}}{}^\bullet + {}^\bullet CH_2-CH_2-R'$$

(9)
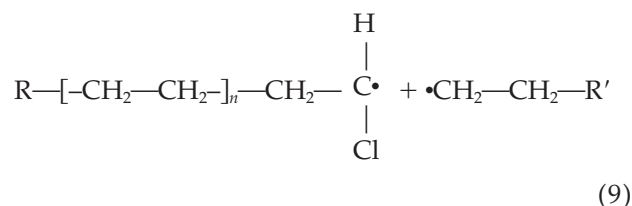
Apart from the preceding reaction, PVC has weak links that initiate the polymerization, by transfer to a dead polymer or by backbiting reactions.

$$-CH_2-CHCl-CH_2-CHCl-CH_2-CHCl + \sim CH_2-\overset{H/{}^\bullet}{\underset{Cl}{C}}-$$

$$\downarrow$$

$$\sim CH_2-CH_2Cl + -CH_2-\overset{}{\underset{Cl}{{}^\bullet C}}\sim$$

(10)

$$CH_2=C-COOC_4H_9$$
with CH₃ substituent

(BMA)

$$\sim CH_2-\overset{Cl}{\underset{}{C}}-$$
with CH₃, CH₂—C~, COOC₄H₉ substituents (11)

(BMA-g-PVC)

These initiator fragments left over in PVC molecules and weak links may assist the thermally induced graft copolymerization reactions.

CONCLUSIONS

It is concluded from the foregoing results that BMA can be successfully grafted onto PVC in the melt during processing using DCP as a free-radical initiator.

- A maximum of 14% grafting with a grafting efficiency of 90% was obtained.
- FTIR and ^{13}C-NMR studies showed distinct evidence of grafting.

- DSC and TGA studies indicated enhancement in thermal stability upon graft copolymerization.
- The grafted PVC shows ease of processibility, which may be attributed to the fact that BMA helps to promote early fusion of PVC grains to reduce the melt viscosity.

Scale-up studies and related mechanical properties will be reported in a separate communication.

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