

Analysis of Low-Density Polyethylene-g-Poly(vinyl chloride) Copolymers Formed in Poly(vinyl chloride)/Low-Density Polyethylene Melt Blends with Gel Permeation Chromatography and Solid-State ^{13}C -NMR

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ABSTRACT: Gel permeation chromatography (GPC) and solid-state ^{13}C -NMR techniques were used to analyze the structural changes of poly(vinyl chloride) (PVC) in blends of a low-density polyethylene (LDPE) and PVC during melt blending. The GPC results showed that the weight-average molecular weight (M_w) of PVC increased with LDPE content up to 13.0 wt % and then decreased at a LDPE content of 16.7 wt %, whereas the number-average molecular weight remained unchanged for all of LDPE contents used. The ^{13}C -

NMR results suggest that the increase in M_w was associated with the formation of a LDPE-g-PVC structure, resulting from a PVC and LDPE macroradical cross-recombination reaction during melt blending. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3167–3172, 2004

Key words: poly(vinyl chloride) (PVC); NMR; degradation; blends; processing

INTRODUCTION

When processing poly(vinyl chloride) (PVC) at high temperatures, special care has to be taken because of thermal degradation, which includes the dehydrochlorination, chain scission, and crosslinking of macromolecules. These reactions cause the evolution of free hydrogen chloride (HCl), the discoloration of the PVC products, and also chemical and physical changes. It is accepted that the dehydrochlorination process results in the formation of long, conjugated double bonds or polyene sequences, causing a color change in PVC compounds. When exposed to oxygen, carbonyl groups in the PVC compound can be formed because of the oxidation reaction. The polyene formation then leads to crosslinking, chain scission, and aromatic pyrolysates.¹ It has been reported² that the degradation of PVC by the chain scission reaction usually results in a decrease in weight-average molecular weight (M_w) with a possible increase in number-average molecular weight (M_n), whereas the degradation by the crosslinking of macromolecules results in

an increase in M_w with a decrease in M_n . Starnes³ conducted a comprehensive review of the thermal degradation of PVC and indicated that the precise nature of PVC degradation in polymer blend systems has not been fully understood for a number of reasons, including the miscibility of the blends, the polarity of the medium, PVC aggregation, HCl solubility and diffusion rate, and the interaction of PVC with intermediates that are derived from the degradation of the other polymer.

The degradation of PVC that incorporates polyethylene (PE) remains of interest because in packaging and bottle applications, PVC articles are likely to be contaminated by polyolefins, such as PE and polypropylene. Minsker⁴ proposed a mechanism for the thermal degradation of PVC/PE blends through the effects of blending methods and PE content on the thermal stability of the blends. He found that the dehydrochlorination process was dependent on the blending method. In elastic-deformation mode, the addition of PE to PVC accelerated the formation of HCl because the PE was occluded by PVC or vice versa, depending on the amount of each component. In certain cases, these two polymers became compatible at the molecular level, which resulted in an increased rate of the dehydrochlorination of PVC. This effect was found when PVC/PE blends were annealed at temperatures above the melting point of PE. However, the mechanism of this accelerated degradation

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reaction has not been confirmed by any well-known chemical facts. In solution blends, the rate of PVC degradation was dependent on the basicities of the solvents. The more basic the solvent was, the faster the rate of degradation was.^{5,6} A study by Arnold and Maund⁷ suggested that the addition of 0.2% of PE would accelerate the PVC degradation because of an increase in PE free radicals under thermal degradation, which would then deplete the stabilizers in the PVC compound. Pospisil et al.⁸ studied the thermal degradations of various polymer blend systems. They found that for PVC/low-density polyethylene (LDPE) blends, the amounts of PVC that were grafted onto LDPE increased with PVC content under process temperatures above 180°C.

More recent work by Sombatsompop et al.⁹ examined the structural changes in PVC in melt blends of LDPE and PVC with differential scanning calorimetry, thermogravimetric analysis, Fourier transform infrared spectroscopy, and color index measurements. The preliminary results suggested that the addition of LDPE to PVC could lead to the formation of LDPE-*g*-PVC copolymers, but no physical evidence at the molecular level has yet been offered to confirm the formation of such grafted copolymers.⁹ In this article, we report some physical evidence at the molecular level from gel permeation chromatography (GPC) and solid-state ¹³C-NMR techniques to reveal the changed chemical structures of PVC in LDPE/PVC blends during melt blending.

EXPERIMENTAL

Raw materials

Two thermoplastics were used: (1) PVC (B0504BLA), supplied in granule form by Thai Plastics and Chemicals, Co., Ltd. (Bangkok, Thailand) and composed of 1.2 pph calcium stearate, 1.2 pph tetrabasic lead sulfate, 0.1 pph PE wax, and 4.0 pph CaCO₃, and (2) LDPE, supplied in granule form by Thai Polyethylene Co., Ltd. (Bangkok, Thailand), with a melt flow rate of 5 g/10 min (2.16-kg load at a 190°C test temperature), whose procedure was ASTM D 3364 (1990).

Melt-blending process

PVC was melt-blended with various contents of LDPE with a twin-screw extruder (Haake Polylab-Rheomex CTW 100P, Bersdorff, Germany). The concentration of LDPE in PVC was varied from 0.0 to 16.7 wt % (i.e., corresponding to LDPE contents of 0–20 g/100 g of PVC). The temperature setting profiles on the extruder were 140, 150, and 160°C from hopper to die zones. A screw rotating speed of 100 rpm and a three-strand die (with each strand 3 mm in diameter) were used. The extrudates we pro-

duced were passed through a water bath before they went into the pelletization unit to produce polymer blend granules. For consistency and comparison purposes, all of the pure polymers underwent the same blending process before further use, with the blending consisting of five extrusions.⁹ The resulting blends were conditioned at 21°C and 50% relative humidity before they were characterized.

Blend characterizations

GPC

M_w and M_n values of PVC for the resulting blends obtained from various test conditions were determined with a GPC Waters-150CV (Polymer Laboratories Ltd., Massachusetts) (the gel permeation chromatograph was calibrated with narrow-molecular-weight polystyrene). Tetrahydrofuran (THF) was used both as a solvent and an eluent. The molecular weight and molecular number of the PVC were the main interests in this work.

Solid-state ¹³C-NMR

The solid-state cross-polarity/magic-angle spinning ¹³C-NMR spectra of the PVC/LDPE blends and the neat polymers were recorded on a Bruker AVANCE 300 system, operating at 75.4 MHz (Rheinstetten, Germany). A zirconia rotor 7 mm in diameter was used to acquire the spectra at a spinning rate of 4 kHz. The recycle delay and contact times used were 2 s and 1 ms, respectively. All of the spectra were accumulated with 2000 scans.

RESULTS AND DISCUSSION

M_w and M_n values for PVC in PVC/LDPE blends

As stated in the Introduction, it has been reported that the degradation of PVC by a chain-scission reaction most likely leads to a decrease in M_w with an increase in M_n , whereas degradation by crosslinking is indicated by an increase in M_w with a decrease in M_n .² A deviation of these behaviors was observed when we examined the structural changes of PVC in the PVC/LDPE blends used in this study. Figure 1 shows the variations of the M_w and M_n values for PVC at different LDPE concentrations. M_w of PVC increased with LDPE content up to 13.0 wt % and then decreased at a LDPE content of 16.7 wt %. Surprisingly, M_n remained unchanged at all of the LDPE contents. In this article, we postulate that the increase in M_w could have been caused by a cross-recombination of PVC and LDPE macroradicals generated during melt blending as a result of thermal and shearing effects. This, then, resulted in the formation of a LDPE-*g*-PVC copolymeric structure in the blends. The decrease in M_w at an

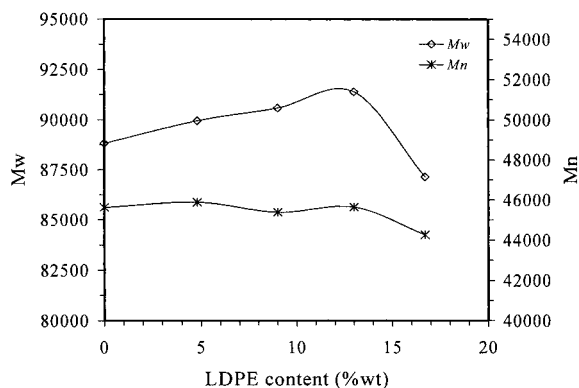


Figure 1 Variations in M_w and M_n values of PVC blended with different LDPE contents.

excess LDPE content (16.7 wt % LDPE) was probably due to the formation of the copolymer when the LDPE and PVC macroradicals reached a maximum (with no more LDPE macroradicals combining with PVC macroradicals), simultaneously accompanied by PVC molecular degradation.⁷

Formation of the LDPE-g-PVC structure in the PVC/LDPE blend

The formation of the LDPE-g-PVC structure that occurred during melt blending was confirmed through ^{13}C -NMR results, as shown in Figure 2, which illustrates the chemical shifts of the samples of PVC melt blended with different LDPE concentrations. The results were compared with those for neat PVC and LDPE samples. For a single polymer system, the chemical shifts of the neat PVC sample [Fig. 2(a)] exhibited two peaks at 57.3 ppm ($-\text{CHCl}-$) and 46.2 ppm ($-\text{CH}_2-$), whereas the neat LDPE sample [Fig. 2(b)] peaked at 32.5 ppm ($-\text{CH}_2-$ in the main chain) and 14.6 ppm ($-\text{CH}_3$ at a branch chain).¹⁰

In a PVC/LDPE blend system, because the two polymers are not compatible because of different polarities, one would then expect to find their chemical shifts at the same positions observed in neat polymers. The results in Figure 2(c-f) indicate that apart from the chemical shifts of neat PVC and LDPE, there were two additional peaks at chemical shifts around 26 and 22 ppm, and the characteristics of all peaks changed with LDPE content. It can be observed that the positions of all of the peaks changed with LDPE content. This was expected because the environment in the molecular structure of the PVC changed as the grafting process progressed. The change in the molecular structure could affect the homogeneity of the magnetic field during the NMR test, thus different positions of the peaks were possible.¹¹ As proposed earlier, the melt blending of LDPE into PVC resulted in the formation of LDPE-g-PVC copolymers because of a macroradical

cross-recombination, as was also observed by the increase in M_w . In this study, the NMR peaks at about 26 and 22 ppm were thought to suggest a structural chemical change in the PVC. To verify this, a blend sample of PVC and LDPE (16.7 wt %) was prepared via a blend of the PVC and LDPE solutions, which were prepared by the dissolution of PVC and LDPE with THF and *p*-xylene, respectively, which were precipitated in methanol and run on a ^{13}C -NMR spectrometer. The results are given in Figure 3. There were no peaks at chemical shifts of about 26 and 22 ppm, as found in the PVC and LDPE melt blending, because these two polymers were not compatible in the solution blend. The difference in the NMR results from the melt and solution blends involved thermal and shearing effects, which produced such PVC and LDPE macroradicals and also promoted the compatibility of these two polymers;⁴ that is, the graft structure was not found in the solution blend.

In this study, we propose that the LDPE-g-PVC structure occurred as a result of recombinations of PVC and LDPE macroradicals generated by degradations of PVC and LDPE molecules during melt blending in the extruder. The copolymer probably occurred in two different forms, as shown in Figure 4: PVC grafted with short-chain LDPE (*s*-LDPE-g-PVC) and PVC grafted with long-chain LDPE (*l*-LDPE-g-PVC). In this particular case, the LDPE-g-PVC structure was probably derived from *s*-LDPE-g-PVC [Fig. 4(a)]. This can be explained in conjunction with the solubility change of the PVC component in THF. A solubility test was carried out as an independent experiment to qualitatively observe the solubility of PVC with and without LDPE in THF for 6 h [the blend sample contained a small amount of LDPE (4.8 wt %)] and to also ensure that the production of the proposed grafted structure was not caused by a recombination of the PVC molecules themselves. During the experiment, naked-eye observation indicated that the neat PVC sample was totally soluble, whereas the PVC/LDPE blend sample was partially soluble in THF, even though only a small amount of LDPE was added. This meant that the polarity of the PVC considerably decreased with the addition of LDPE. If a recombination of the PVC molecules themselves had occurred, the polarity of PVC-g-PVC would have been similar to that of PVC alone. Therefore, from the solubility test, we strongly believe that the obtained LDPE-g-PVC structure occurred as a result of the recombination of short-chain LDPE and PVC molecules, which showed soluble characteristics in THF, where the molecular weights were determined by GPC. The insoluble part of the blend samples probably represented the *l*-LDPE-g-PVC structure [Fig. 4(b)].

To verify the LDPE-g-PVC structure in such blends, all of the NMR peaks in Figure 2 were given peak numbers, and the results were interpreted in associa-

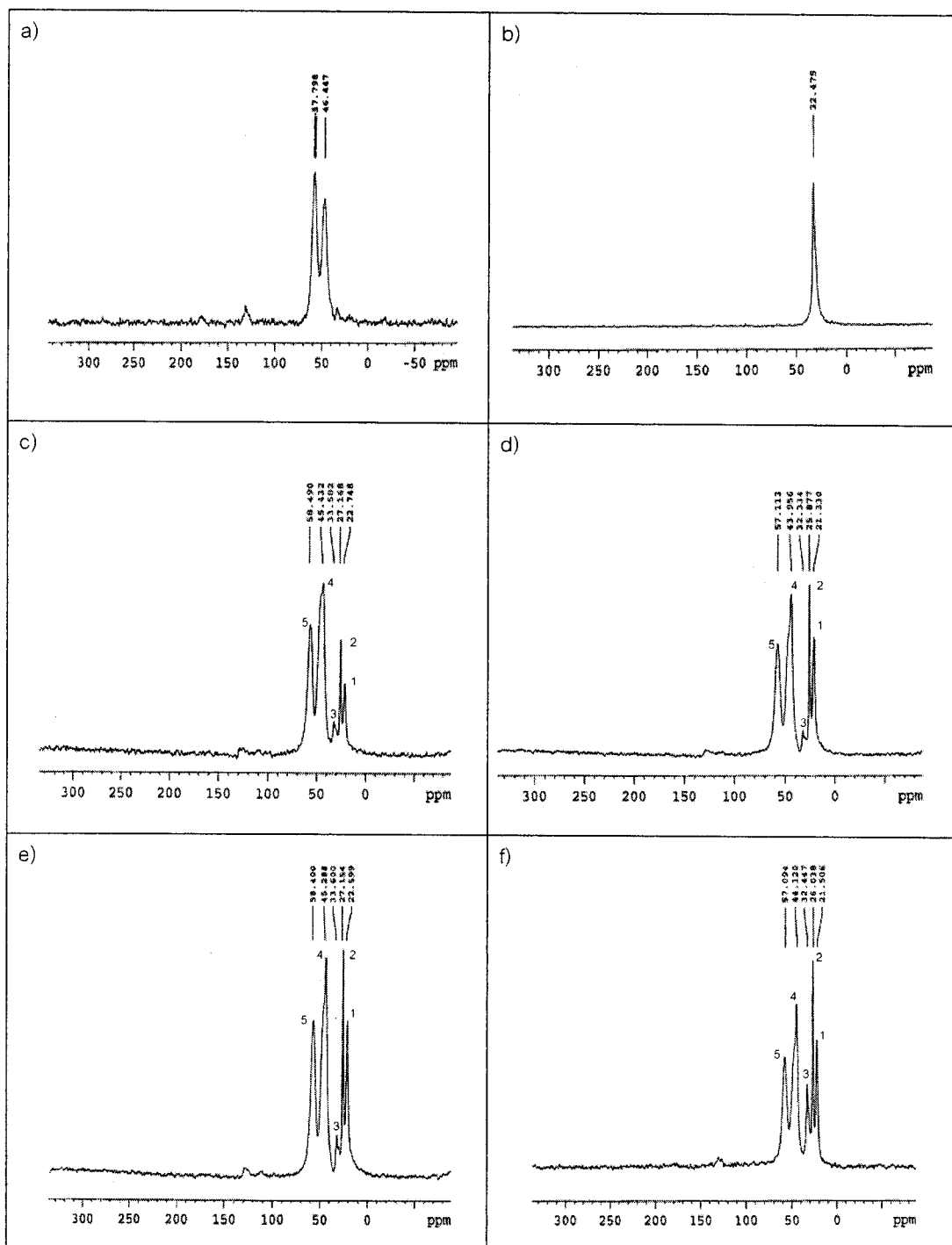


Figure 2 ^{13}C -NMR spectra and peak assignments for PVC, LDPE, and PVC/LDPE blends under melt blending: (a) neat PVC, (b) neat LDPE, and PVC with (c) 4.8, (d) 9.0, (e) 13.0, and (f) 16.7 wt % LDPE.

tion with the *s*-LDPE-*g*-PVC structure, as presented in Figure 5:

1. Peak 1 (~22 ppm) and Peak 2 (~26 ppm) were probably linked with carbon atoms at LDPE molecules (B_1 , B_2 , or B_3), which acted as a branch chain to the PVC main chain.

2. Peak 3 (~32 ppm) was referred to as the LDPE part, which was a combination of $-\text{CH}_2-$ in neat LDPE and the LDPE-*g*-PVC structure in the blends. The peak exhibited two characteristics, a sharp peak and a shoulder peak. As the LDPE concentration was increased, the peak tended to form a shoulder up to a LDPE content of 13.0 wt

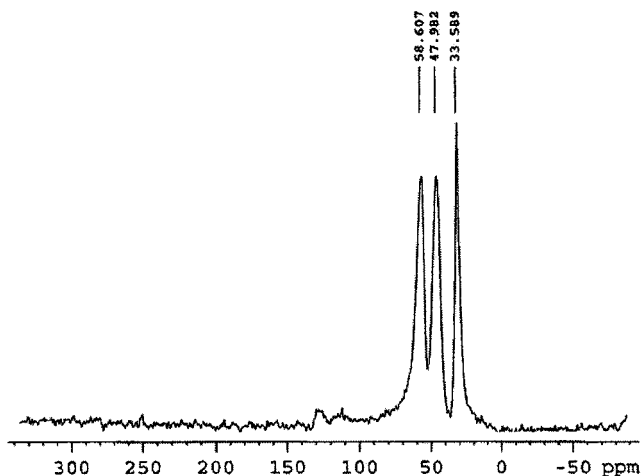


Figure 3 ^{13}C -NMR spectra for the PVC/LDPE (16.7 wt %) blend by solution blending.

% before it became a single peak at a LDPE content of 16.7 wt %, which was similar to the behavior observed for neat LDPE. The shoulder peak was associated with the changing environment of LDPE molecules resulting from the LDPE-g-PVC structure. In the blend with 16.7 wt % LDPE (an excess LDPE loading), the sharp peak occurred because no more of the LDPE-g-PVC structure could be formed; this was also indicated by a decrease in M_w , as shown in Figure 1.

- As stated earlier, Peak 4, at a chemical shift of around 45 ppm, represented $-\text{C}^*\text{H}_2\text{CHCl}-$ in neat PVC. In the LDPE/PVC blends, the characteristic of the peak changed with the LDPE content. The peak seemed to deviate from that found in neat PVC as the LDPE content was increased, tending to show a shoulder because of the different

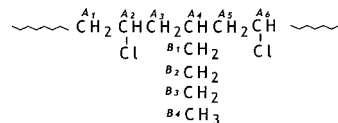


Figure 5 Code assignment for carbon atoms in s-LDPE-g-PVC copolymers.

polarities of CH_2 at the A_1 and A_3 positions as a result of the formation of the LDPE-g-PVC structure (this was supported by Kumar and Yang¹²). Interestingly, Peak 4 values at LDPE contents from 13.0 to 16.7 wt % [Fig. 2(e-f)] were very similar. This was expected because there was no more grafting of LDPE and PVC, as stated earlier.

- Peak 5, at a chemical shift of about 57 ppm, illustrated $-\text{CHCl}-$ (at positions A_2 and A_6) in neat PVC. In the LDPE/PVC blends, there was no change in the peak characteristics with LDPE content. This was not surprising because its environment was unaffected by the formation of the LDPE-g-PVC structure. Peak 5 was $-\text{CHCl}-$, which did not participate in the macroradical formation of the LDPE-g-PVC structure (Fig. 4).

CONCLUSIONS

The structural changes of PVC in PVC/LDPE blends were studied with GPC and solid-state ^{13}C -NMR techniques. The results indicate that M_w of PVC increased with a LDPE content up to 13.0 wt % and then started to decrease until a LDPE content of 16.7 wt % was reached; M_n remained unchanged at all of the LDPE contents used. The increase in M_w was associated with the formation of the LDPE-g-PVC structure, whereas the decrease in M_w was due to the formation of a

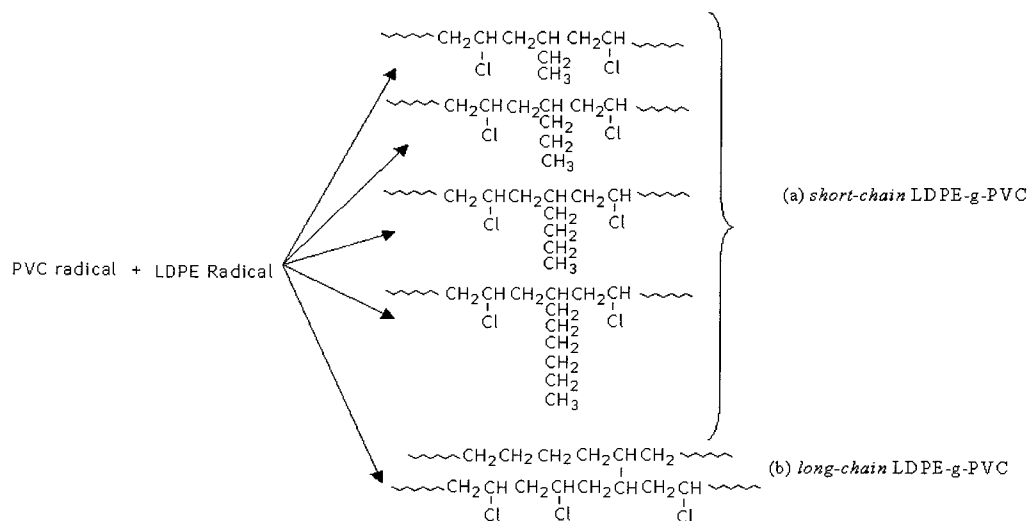


Figure 4 Possible LDPE-g-PVC structures in the PVC/LDPE blends: (a) s-LDPE-g-PVC and (b) l-LDPE-g-PVC.

maximum amount of the LDPE-g-PVC structure, accompanied by a degradation of the PVC molecules. LDPE-g-PVC copolymers occurred as a result of a cross-recombination reaction between PVC and short-chain LDPE radicals during melt blending. Molecular compatibility between PVC and LDPE was found in the melt-blending method as a result of thermal and shearing effects during processing.

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