Crosslinking of Polyvinyl Chloride by Electron Beam Irradiation in the Presence of Ethylene–Vinyl Acetate Copolymer

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ABSTRACT: Electron beam (EB) irradiation of polyvinyl chloride (PVC) was carried out in the presence of three different ethylene–vinyl acetate copolymers (EVA). The mechanical properties of the original and irradiated blends were tested. The gel content measurement, chlorine loss upon electron irradiation, and gel permeation chromatograph (GPC) were used to characterize the effect of EVA on the irradiation behavior of PVC/EVA blends. The content and the chemical structure of EVA in the blends had considerable effects on the mechanical properties and gel content of the blends. The incorporation of EVA into PVC blend can increase the gel content and reduce chlorine loss of the blends. The GPC analysis of the soluble part in the irradiated PVC samples showed that the addition of EVA into the PVC blend lowered the polydispersity of molecular weight of PVC. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1571–1575, 2004

Key words: polyvinyl chloride; ethylene–vinyl acetate copolymer; irradiation crosslinking; chlorine loss

INTRODUCTION

When a polymer is exposed to high-energy irradiation, its composition and structure inevitably undergo some changes, which in turn lead to changes in physical and chemical properties of the polymer.[1] It is well known that the effects of high-energy irradiation on polymers are mainly degradation or crosslinking; the last effect leads to an improvement in thermal resistance and mechanical properties.[2]

Irradiation crosslinking can be used to improve the wear and creep resistance of polymer products. Moreover, their solvent resistance and thermal stability (thermal mechanical and dimensional characteristics) are also enhanced. The irradiated polymers can be used as extruded articles, like electrical wire and cable insulants, heat shrinkable tubes, etc.

Polyvinyl chloride (PVC) is a low-cost and weather-resistant polymer. The irradiation behavior of PVC has been investigated thoroughly.[3–6] PVC is known to be highly sensitive to high-energy irradiation. For PVC, its carbon–chloride bond is weaker than its carbon–carbon bond and carbon–hydrogen bond. Upon exposure to high-energy irradiation, some of the carbon–chloride bonds are broken, giving rise to organic radicals and chlorine radicals, which lead to the degradation or crosslinking of PVC. In the previous work, the irradiation behaviors of PVC/styrene–butadiene rubber (SBR), and PVC/nitrile–butadiene rubber (NBR) have been studied.[7,8] It was found that the incorporation of NBR into PVC decreased the chlorine loss of the PVC/NBR blends, and NBR lowered the degradation of PVC upon irradiation.

Ethylene–vinyl acetate (EVA) is one of the widely used polymers for cable insulants. It is also frequently used as a long-lasting-life plasticizer to improve the mechanical and processing properties of PVC.[9,10] The study on PVC/EVA blend has been reported in many literatures.[11–16] EVA is available as a plastic, thermoplastic elastomer, and rubber, depending on the vinyl acetate (VA) content in the copolymer. EVA containing 28% VA is a thermoplastic elastomer, and 50% VA is a rubber. The α-hydrogen atoms with respect to the vinyl acetate groups in EVA are sites sensitive to irradiation.[17] They can produce crosslinking sites in EVA and help increase crosslinking degree. So, the incorporation of EVA into PVC may be helpful for increasing the crosslinking and decreasing the degradation of PVC. Until now, such research has seldom been addressed in open literature.

The aim of this work is to improve the mechanical properties of PVC by means of electron beam irradiation crosslinking in the presence of EVA. The present article reports the study on the effect of irradiation dose, EVA content in the blends, and chemical structure on the mechanical properties. The effect of EVA on the gel content and the degradation of PVC blends were also studied.


EXPERIMENTAL

Materials

PVC (M_n=81,250) was produced by Shanghai Chloro-Alkali Co., Ltd.

EVA (VA%=28%, EVA28), EVA (VA%=50%, EVA50) were produced by Bayer Co., Ltd. Elvaloy-741 (VA%=24%, EVA741) was produced by Du Pont Co., Ltd. Its chemical composition was as follows: ethylene content 66%, vinyl acetate content 24%, and carbonyl content in the main chain 10%. The chemical structure was as follows:

$$-(CH_2-CH_2)_n(CH_2-CH-)_m\overset{O}{\overset{\|}{C}}-$$
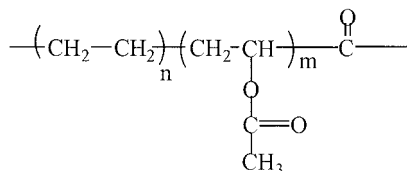
Trioctyl trimellitate (TOTM), trimethylpropane triacrylate (TMTPA), calcium carbonate, and thermal stabilizers were industry-grade products.

The basic recipe as follows: PVC, 100phr; TOTM 35phr; TMPTA 5phr; CaCO$_3$ 10phr, stabilizer 6phr.

Preparation of samples

TOTM, TMPTA, thermal stabilizers, calcium carbonate, EVA, and PVC were mixed in a high-speed (1200 rpm) mixer (produced by Factory of Beijing Plastics Machinery, China) at 60–70°C. The resulting powders were roll milled for 5 min to ensure adequate mixing and then compression molded to form a 1 mm sheets at 170°C, and cold pressed to sheet for test.

Electron beam irradiation

The PVC sheet samples were irradiated in the air using an electron beam (EB) accelerator (GJ-2 type, made by Shanghai Pioneer Electric Motor Co., Ltd.) The irradiation dose was 5 Mrad unless otherwise stated.

Mechanical properties test

The samples were cut into the dumbbell-shaped samples to test. The tensile strength and elongation at break of the PVC samples were measured according to Chinese Standard GB 8815-88 using an Instron 4465 tensile tester at a crosshead speed of 250 mm/min.

Chlorine-loss measurement

The specimens were fractured under cryogenic condition of liquid nitrogen, then the fractured surfaces of the specimens were coated with a thin layer of gold before measurement. The chlorine concentration in the irradiated PVC blend samples was measured with an energy-dispersive X-ray (EDX) analyzer (Hitachi S-520, made by Japan).

$$L = (1 - R_1/R_0)*100\% \qquad (1)$$

where L is the chlorine loss rate upon irradiation, R_1 is the ratio of chlorine to calcium in the irradiated samples, and R_0 is the ratio of chlorine to calcium in the original samples.

Gel content measurement

Gel content was measured by using a Soxhlet extraction apparatus. A selected blend sample was first extracted by ethyl ether for 48 h, and then extracted by tetrahydrofuran for 48 h,

$$Gel = (W_1/W_0)*100\% \qquad (2)$$

where "Gel" is the gel content of the crosslinked blend, W_0 is the initial weight of PVC in a blend, and W_1 is the weight of the insoluble portion of PVC in the blend.

Gel permeation chromatography (GPC) analysis

About 5 mg of irradiated sample was immersed into 2 g of tetrahydrofuran for two days; the unsolvable part was filtered using a nylon film and the solution (solvable part) was used for the molecular weight measurement. The measurement was performed on GPC (Perkin Elmer Series 200).

RESULTS AND DISCUSSION

Effect of irradiation dose on properties of PVC blends

It is well known that a high-irradiation dose will lead to serious degradation of PVC, but too low a dose
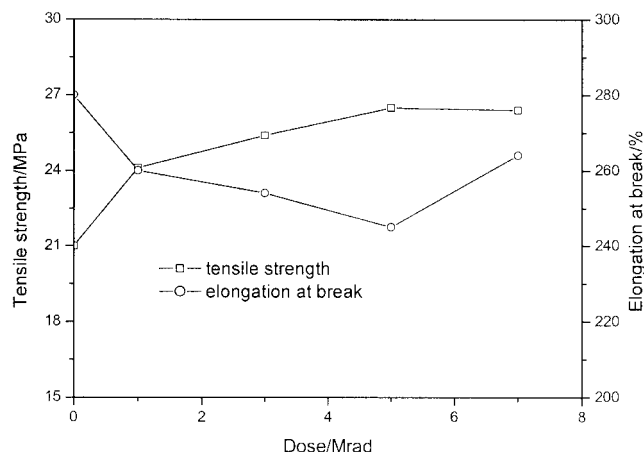

Figure 1 Effect of irradiation dose on the tensile strength and elongation at break of PVC blends.

TABLE I
Effect of Irradiation Dose on Gel Content of PVC Blends

Irradiation dose (Mrad)	1	3	5	7
Gel content (%)	42.3	56.2	65.5	72.3

cannot cause effective crosslinking. In order to find an optimum dose, the effect of irradiation dose on the mechanical properties of PVC blends is investigated.

The effect of irradiation dose on the tensile strength and elongation at break of PVC blends is shown in Figure 1. With increasing the irradiation dose, the tensile strength increases gradually and levels at about 5 Mrad, but the elongation at break decreases at first and then increases after 5 Mrad. The crosslinking bonds among PVC molecular increase with increasing irradiation dose, leading to an increase of tensile strength and a decline of elongation at break. When the irradiation dose is over 5 Mrad, the irradiation can effectively cause PVC crosslinking as well as degradation. The degradation of PVC may produce PVC molecules with low molecular weight, which plasticize the PVC blend and lead to the improvement of elongation at break above 5 Mrad dose.

The effect of irradiation dose on the gel content of PVC blends is shown in Table I. The gel content increases with increasing irradiation dose, and the increasing degree become small when the irradiation dose reaches 5 Mrad, which corresponds to the variation of mechanical properties with irradiation dose. So, the irradiation dose of 5 Mrad was used in the following experiments.

Effect of chemical structure and content of EVA on mechanical properties of PVC/EVA blends

Because the α-hydrogen atoms with respect to the vinyl acetate groups are sites sensitive to irradiation.
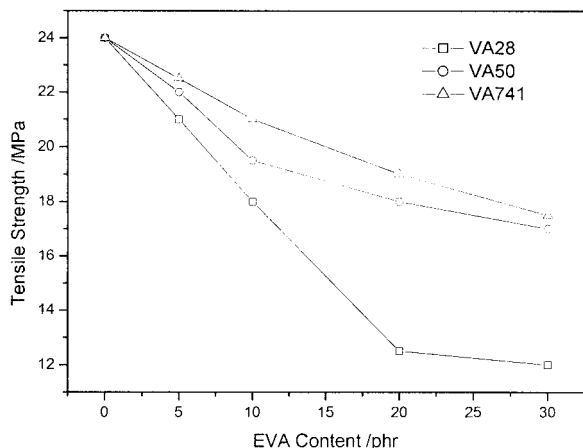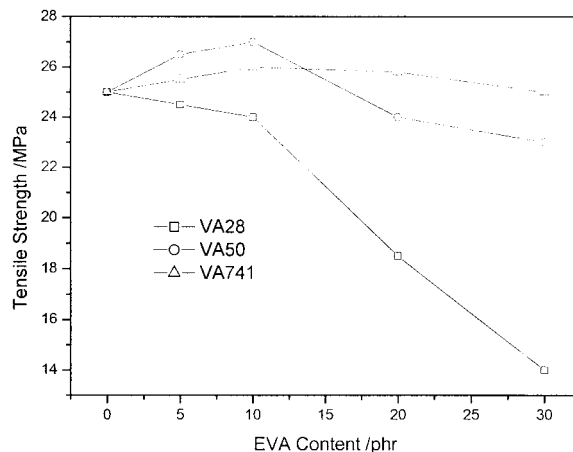

Figure 3 Effect of the EVA content on the tensile strength of irradiated PVC/EVA blends.

The incorporation of EVA into the PVC will influence the crosslinking of PVC blends. So, the chemical structure and content of EVA would influence the chemical and mechanical properties of PVC/EVA blends.

Figures 2 and 3 show the effects of three different types of EVA on the tensile strength of PVC blends before irradiation and after irradiation, respectively.

With increasing EVA content, the tensile strength of blends decrease. Among the three types of EVA, EVA28 leads to decrease of the tensile strength most significantly, while EVA741 has the smallest effect. Because of low glass transition and the temperature of EVA (T_gs for EVA28, EVA50, and EVA741 are -18, -9, and $-35°C$, respectively), the incorporation of EVA into PVC can plasticize PVC and reduce the interactions between PVC molecules, leading to the decrease of tensile strength.

The compatibility between PVC and EVA also influences on mechanical properties. The compatibility depends on the VA content in EVA. The higher VA
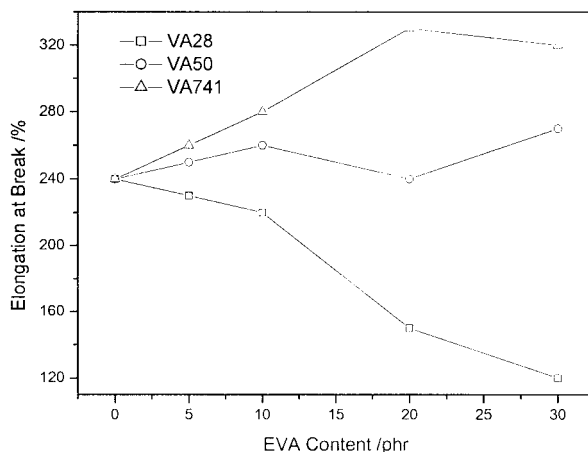

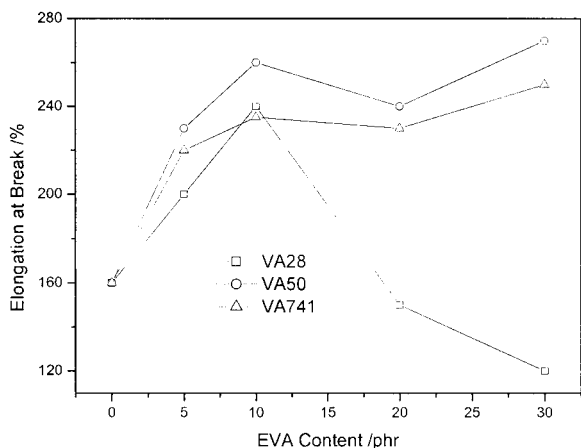**Figure 2** Effect of the EVA content on the tensile strength of PVC/EVA blends.

Figure 4 Effect of the EVA content on elongation at break of PVC/EVA blends.

Figure 5 Effect of EVA content on the elongation at break of irradiated PVC/EVA blends.

Figure 7 The chlorine-loss rate of PVC/EVA blends varies with EVA type (a) without EVA, (b) EVA28, (c) EVA50, and (d) EVA741.

content in EVA is, the more compatible the PVC/EVA blend is.[9] The PVC/EVA50 blends have higher tensile strength than PVC/EVA28 blends. Because there are carbonyl groups in the backbone of EVA741, which can greatly improve the compatibility between PVC and EVA, and the PVC/EVA741 blends have the highest tensile strength.

After the PVC/EVA blends were irradiated and crosslinked, the tensile strength became higher than the corresponding original samples. The tensile strength of PVC/EVA50 blends and PVC/EVA741 blends increases with increasing EVA content when it is less than 10 phr. When it is over 10 phr, the tensile strength decreases with increasing EVA content. It indicates that a small amount of EVA leads to an increase in the crosslinking degree, and the tensile strength increases therefore. When the EVA content excesses 10 phr, the plasticizing effect of EVA on PVC surpassed the crosslinking effect, and the tensile strength decreases. The tensile strength of the PVC/
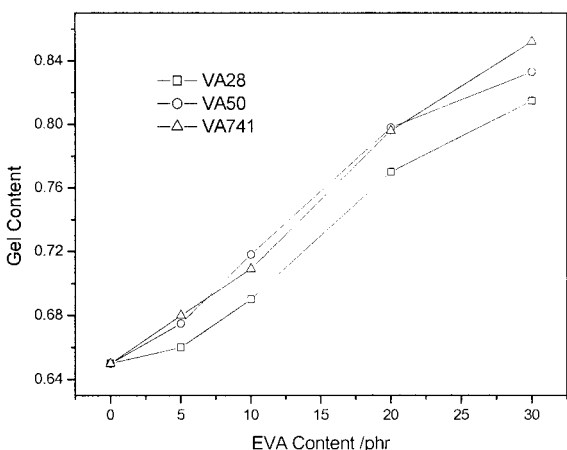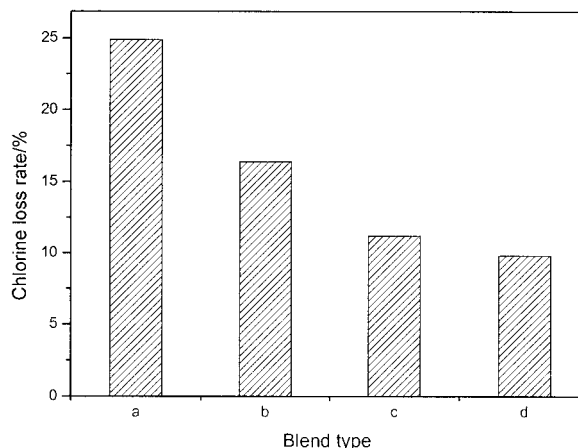
EVA28 blends decreases in the whole range with increasing EVA28 content. It may due to relative poor compatibility between PVC and EVA28, which lead to lower tensile strength.[9,10]

Figures 4 and 5 show the effect of EVA content on the elongation at break of PVC/EVA blends before and after irradiation, respectively. EVA741 and EVA50 lead to increasing in the elongation at break of the original blends, while EVA28 lead to a decrease. The elongation at break of the blends after irradiation is lower than the corresponding original blends, which should be caused by the crosslinking of the PVC/EVA blends. It is noticeable that the elongation at break of the irradiated PVC/EVA28 blend increases with increasing EVA28 content when the EVA28 content is less than 10 phr. It may be caused by the improvement of compatibility by irradiation.
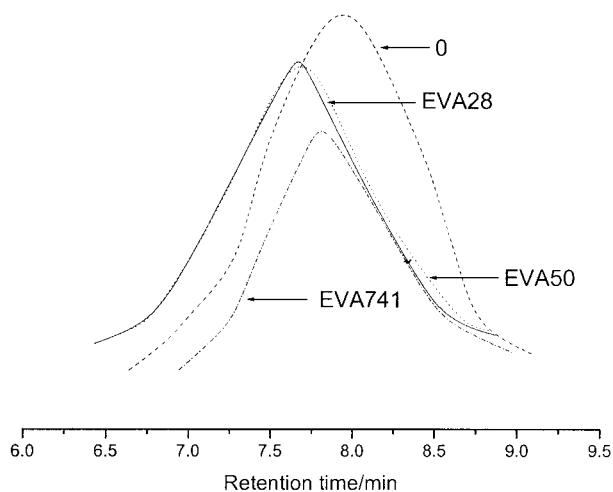

Figure 6 Effect of the EVA content on the gel content of PVC/EVA blends.

Figure 8 GPC analysis of soluble part in irradiated blends.

TABLE II
Comparison of GPC Analysis Results of Soluble Part in PVC Blends
After Irradiation Crosslinking

Sample	Retention time	Peak molecular weight	Weight average molecular weight	Number average molecular weight	M_w/M_n
0	7.936	49140	84670	33010	2.565
EVA28	7.676	89620	134700	57610	2.337
EVA50	7.676	89620	127400	58110	2.192
EVA741	7.813	65240	76630	41090	1.865

EVA content is 20 phr.

Effect of chemical structure and content of EVA on the gel content of PVC/EVA blends

The effect of EVA content on the gel content of PVC/EVA blends is shown in Figure 6. The gel content increases with increasing EVA content. The PVC/EVA741 and PVC/EVA50 blends have higher gel content than the corresponding PVC/EVA28 blends. Because PVC is prone to degradation upon high irradiation dose, while α-hydrogen atoms of carbonyl group in EVA will easily become a crosslinking site upon irradiation. It may graft onto PVC chains or self-crosslinking. The more crosslinking sites in the blend upon irradiation might increase the crosslinking degree. EVA741 has active hydrogen atoms beside carbonyl group in the main chains except α-hydrogen atoms in the side chain. It has more crosslinking sites, which makes the gel content increase fastest. The VA content of EVA50 is higher than that of EVA28, so the PVC/EVA50 blends have more crosslinking sites than the corresponding PVC/EVA28 blends, and the gel content of PVC/EVA50 blends is higher than PVC/EVA28 blends.

Chlorine-loss analysis

The chlorine-loss of different blends upon irradiation is shown in Figure 7. The addition of EVA into PVC decreases the chlorine loss of PVC. The chlorine loss of the irradiated PVC blend without EVA is 24.9%. When the EVA is added into PVC, the chlorine loss decreases. The amount of 20 phr EVA741, EVA50, and EVA28 makes the chlorine-loss decrease to 9.8, 12.7, and 16.4%, respectively. It indicates the good compatibility between EVA and PVC will lead less chlorine loss upon irradiation.

GPC analysis

The GPC analysis results of soluble part of irradiated blends are shown in Figure 8 and Table II. When the 20 phr EVA28, EVA50, or EVA741 was added into PVC blends, the retention time decreased. The polydispersity of molecular weight in soluble PVC became smaller than that of the blends without EVA. It further demonstrates that the EVA decrease the degradation of PVC upon irradiation.

CONCLUSIONS

Incorporation of EVA into the PVC has great influence on the mechanical properties and gel content of PVC/EVA blends upon irradiation. The more the VA groups in EVA, the better comprehensive mechanical properties of the PVC/EVA blends before and after irradiation have. The gel content of the blends increases with the increasing EVA content and active hydrogen atoms in EVA. The chlorine loss of PVC upon irradiation decreases with the addition of EVA into PVC blends. The incorporation of EVA into PVC also decreases the polydispersity of molecular weight in soluble PVC in the irradiated blends.

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