

Styrene을 그래프트시킨 Ethylene-Vinyl Acetate 共重合體

I. 放射線 그래프트 共重合

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Styrene-Grafted Ethylene-Vinyl Acetate Copolymer (I) Radiation Grafting

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요약 : Styrene-EVA 혼합물을 공기 존재하에서 放射線 조사시켜 그래프트重合시켰다. 放射線源은 Co^{60} 을 이용하였고 15-20°C에서 조사율은 5.04×10^4 mrad/hr로 고정시켰으며 생성된 그래프트重合體는 조사량, 혼합물의 조성 및 혼합물상을 변수로하여 그래프트율 (% graft)을 측정하였다.

그래프트重合 결과 EVA의 主鎖와 아세테이트基 α -위치의 탄소에 생성된 라디칼은 styrene monomer에 대해 비슷한 반응성을 나타내고 조사율은 중합속도에는 영향을 미치지 않고 단지 初期 誘導期間에만 영향을 나타낸다. 그래프트율은 EVA-styrene 혼합물 농도와 相에는 거의 영향을 받지 않는데 이 현상은 粘粗相의 반응혼합물 內에 溶장되어 있는 生成鎖가 반응에 미치는 영향이 단량체의 擴散作用이 反應에 미치는 영향보다 크기 때문인 것으로 해석된다.

이상의 事實들로 보건대 EVA-Styrene 계의 그래프트重合은 PE-Styrene계의 그것과 速度論적으로 비슷하다고 하겠다.

Abstract: Poly(styrene-g-EVA) were prepared by irradiation of EVA-styrene mixture in air atmosphere. The mixtures (the solution of ELVAX 40 in styrene and the swollen ELVAX 250 in styrene) were irradiated in the cobalt 60 source at 15-20°C with an average dose rate of 5.04×10^4 mrad./hr. The grafted EVA were characterized in terms of % graft, with the dose, concentration and mixture phase as reaction variables.

The results of grafting reactions indicated that the reactivity of the radicals formed at backbone and pendant acetate group (α -position) of EVA exhibited the similar reactivities toward monomer styrene. The dose rate doesn't affect on the polymerization rate but only on the initial induction lag of grafting reactions. The dependence of % graft on concentration and mixture phase is negligible, and these phenomena are believed to be due to the fact that the occluded growing chains in viscous matrix attribute to the reaction more than the diffusion variable does on irradiation reactions. It appears that the grafting reaction kinetics of EVA-styrene system is similar to that of linear PE-styrene system's.

INTRODUCTION

The free radicals or peroxides formed on the polymer backbone by irradiation can be used to initiate the polymerization which leads to graft copolymer formation. There are essentially four methods for producing such graft copolymers.¹⁻³

1) Simultaneous irradiation method:

A. Polymer irradiated while immersed in monomer.

B. Polymer irradiated while swollen or dissolved in monomer.

2) Pre-irradiation method:

A. Irradiation of dry polymer, in vacuo, followed by addition of monomer.

B. Irradiation of dry polymer, in air, followed by addition of monomer.

Simultaneous irradiation was adopted in the present study and the polymer-monomer mixture was irradiated directly.

The advantage of this technique is its simplicity, but disadvantages are that it is difficult to avoid the simultaneous formation of homopolymer and the danger of radiation damage of the exposed preformed polymer.

The grafting efficiency of various methods depend on the relative G-values for the radical formation of the polymers and monomers. For example, if the ratio $G(\text{monomer radicals})/G(\text{polymer radicals})$ is large, the homopolymer

produced may make isolation of pure graft copolymer difficult; in any case, the efficiency of graft copolymerization would be low. G-values for several vinyl polymerizations have been reported^{4,5,6} and summarized in Table 1. From

Table 1 Approximate G-values of Monomers and Polymers¹

Substance	G-Value (number of radicals produced per 100 e. v. absorbed)
Monomers	
Styrene	0.69
Acrylonitrile	5-5.6
Methyl methacrylate	5.5-11.5
Vinyl acetate	9.6-12
Vinyl chloride	10
Polymers	
Polystyrene	1.5-3
Polyisoprene	2-4
Polyethylene	6-8
Polymethyl methacrylate	6-12
Polyvinyl acetate	6-12
Polyvinyl alcohol	10
Cellulose	10
Polyvinyl chloride	10-15

Table 1 it is evident that the G-value for radical formation of monomer styrene should be much lower than those for PE and PVAc, leading to a low ratio of homopolymer to graft copolymer formed. Hence one can deduce that, to the ethylene-vinyl acetate copolymer, EVA,

the same principle can be well applied. If it is assumed that the irradiation susceptibility of a polymer is not sufficiently different from that of its monomer, the calculated G-values from monomers may be extended to the polymers. However the true G-values are only obtainable from the particular polymer-monomer system irradiated, so that energy transfer effects among the components are taken into consideration; for this reason, the utility of estimated G-values in graft synthesis is questionable. Apparently, the graft copolymerization by mutual simultaneous irradiation technique is not a simple function of the relative susceptibility to radical formation of polymer and monomer.

As for EVA-styrene system, graft copolymerization are yet to be studied, but many have been reported for PE-styrene and PVAc-styrene systems.⁷⁻¹⁹

In the present study, styrene-grafted EVA (poly (styrene-g-EVA)) were prepared by irradiation of γ -ray and the % grafts along with the experimental variables such as dose, concentration and the mixture phase were determined and the results are compared with those of PE-styrene irradiation graft copolymerization.

EXPERIMENTAL

Materials

Two kinds of EVA were used as polymer materials to be grafted. ELVAX-40 and ELVAX-250 were obtained from E. I. du Pont de Nemours and Co. ELVAX-40 is a high molecular weight copolymer which is soluble in styrene at room temperature. ELVAX-250 has lower content of vinyl acetate than ELVAX-40 and is not soluble but highly swollen in styrene at room temperature. Some important properties of ELVAX-40 and ELVAX-250 are listed in Table

2.

Table 2. Properties of ELVAX-40 and ELVAX-250^{20,21}

Properties	ELVAX-40	ELVAX-250
Vinyl acetate content, wt. %	39-42	28
Melt index, g/10 min.	45-70	25
Density, g/cc. at 23 °C	0.965	0.951
Refractive index, N_D^{25}	1.476	1.485

Styrene monomer, reagent grade, was obtained from Wako Chem. Co.

Procedure

Styrene was washed several times with 10% NaOH aqueous solution and then with distilled water until no alkalinity appears to litmus paper. The washed styrene was dried over molecular sieve for 24 hrs., and then distilled at 50-60°C under reduced pressure with passing dry N₂ gas. The purified monomer placed in a vial was frozen in a dry ice-acetone bath after filled with dry N₂ gas; The vial was then stored at -50°C until a few hours before irradiation.

EVA was purified by soaking in methyl alcohol for 24 hrs., then dried in a vacuum oven for 24 hrs. and finally deaerated at room temperature under 10⁻⁴ mmHg for 24 hrs.

Certain amount of EVA was added into the vial which already contains styrene monomer. The polymer-monomer mixture in the vial was set to become completely dissolved or equilibrium-swollen state. The vials were then irradiated by cobalt-60 source at 15-20°C with an average dose rate of 5.04 × 10⁴ mrad/hr. The source, 10,000 Ci, of the Korean Atomic Research Institute was used in the present experiment.

The percent graft of grafted EVA samples were determined by weight difference: The EVA was first weighted before placing in the vials. After irradiation, the vials were allowed

to stand for 24 hrs. at room temperature before working up. The grafted ELVAX-250 were poured into methyl ethyl ketone and the grafted ELVAX-40 into methanol respectively and set with intermittent shaking for 48 hrs. to complete the precipitation. The precipitates were then filtered and placed in a vacuum oven at 45°C for 24 hrs. to expel the solvents and monomer which may be occluded in the polymer matrix. The dried precipitates were weighed and this value was taken as the final weight. For reference a sample of EVA was also immersed in styrene and subjected to the same condition of irradiation reaction, i. e., time and temperature, but without irradiation. This sample was also precipitated and dried in

the same manner to the irradiated samples. The percent loss in weight was taken as a correction factor to be added to the final weight of the grafted sample so that the difference between this corrected final weight and the initial weight represents the weight of the styrene grafted. The per cent graft is obtained by dividing the weight of styrene grafted $\times 100$ by the original weight of EVA.

RESULTS

As previously pointed out, there are essentially five variables to be considered in irradiation grafting reactions, i. e., dose, type of EVA used, polymer solubility in monomer, tempera-

Table 3. Grafting Data of ELVAX-250 and ELVAX-40*

Sample Code	EVA used	Conc., % $100 \times (\text{EVA}) / (\text{styrene})$	Dose, mrad	% graft, $100 \times$ $(\text{styrene}) / (\text{EVA})$
A-1	ELVAX-250	1.25	0.5	2.50
A-2		1.25	1.0	17.34
A-3		1.25	1.5	53.11
A-4		1.25	2.0	84.20
A-5		1.25	3.0	89.45
A-6		1.25	4.0	92.02
B-1	ELVAX-40**	10	0.5	4.05
B-2		10	1.0	30.80
B-3		10	1.5	71.30
B-4		10	2.0	108.10
B-5		10	3.0	109.20
B-6		10	4.0	110.90
C-1	ELVAX-40**	2	4.0	110.80
C-2		6	4.0	109.80
C-3		10	4.0	110.90
C-4		14	4.0	114.80
C-5		18	4.0	116.00
C-6		22	4.0	119.10

* : Dose rate..... 5.04×10^4 rad/hr.

Irradiation temperature..... 15-20°C.

** : % graft = $100 \times (\text{weight of styrene grafted and styrene homopolymer}) / (\text{weight of ELVAX-40})$

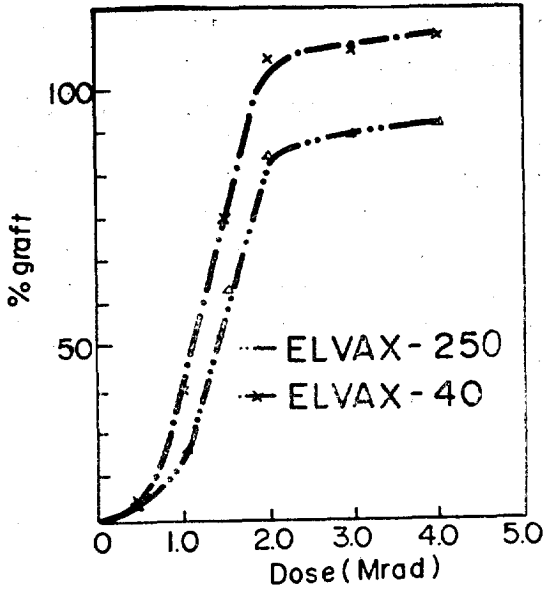


Fig. 1 Grafting of ELVAX-250 and ELVAX-40 at 15-20°C
Average dose rate = 5.04×10^4 rads./hr.
$$\% \text{ graft} = \left(\frac{\text{wt. of styrene grafted}}{\text{wt. of EVA}} \right) \times 100$$

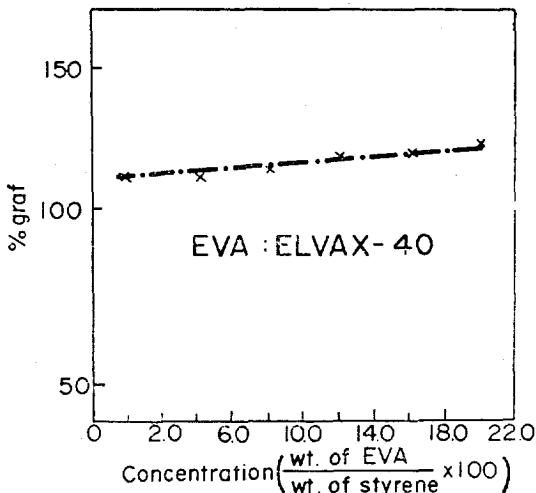


Fig. 2 Grafting of ELVAX-40 in Various concentration at 15-20°C
Average dose rate = 5.04×10^4 rads/hr.
Total dose = 4.0 Mrad

$$\% \text{ graft} = \left(\frac{\text{wt. of styrene grafted} \& \text{ styrene homopolymer}}{\text{wt. of ELVAX-40}} \right)$$

	Specification	phase in styrene	dose rate	commercial name
PE ⁹⁾	linear PE	film 1.5 MIL	2.28×10^5 rad./hr.	Marlex-50
	branched PE	film 20 MIL		Alathon-10
EVA	28% VAc 40% VAc	Swollen dissolved	5.04×10^4 rad./hr.	ELVAX-250 ELVAX-40

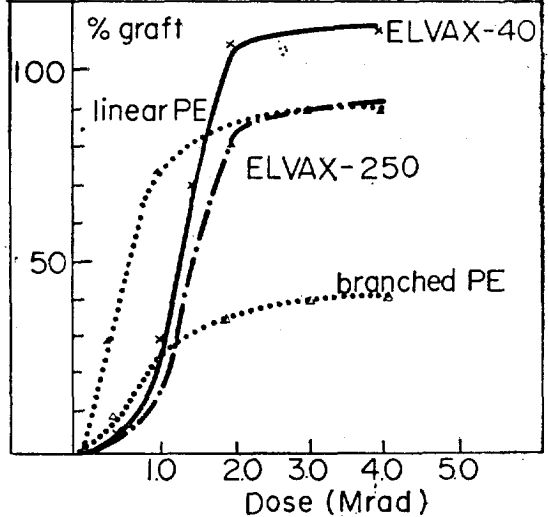


Fig. 3 Grafting of PE & EVA at 15-20°C

ture and dose rate. In this study, however, only the former three variables were studied with keeping the temperature and dose rate constant.

The grafting data of ELVAX 250-styrene and ELVAX 40-styrene system are represented in Table 3, Figures 1 and 3. As shown in Table 3, three series of experiments (A, B, C series) were conducted. The objective of A-series experiment is to get the true % graft of EVA-styrene system by irradiation and to compare them with those of polyethylene-styrene system. In this case, ELVAX-250 is not soluble but highly swollen in styrene.

The grafting data of polyethylene-styrene system by irradiation have been reported by many workers⁷⁻¹⁹ and shown in Figure 3 for the purpose of comparison with those of EVA-styrene system.

ELVAX-40 which is soluble in styrene is considered to be of more interest for the graft

copolymerization with styrene; ELVAX 40-styrene system can be grafted by bulk, suspension and emulsion polymerization methods.

In calculating the grafting data of ELVAX-40, since no appropriate solvent-nonsolvent pair to separate styrene homopolymer from grafted EVA was available, the % graft were taken as the percent of (weight of styrene grafted and styrene homopolymer)/(weight of ELVAX-40). From A- and B-series experiments, one can deduce the true grafting data of ELVAX 40-styrene system and how much the styrene homopolymer is formed during irradiation.

Table 3 and Figure 2 also indicate how the concentration will affect the grafting data of ELVAX 40-styrene system.

DISCUSSION

To understand the mechanism and kinetics of the reactions occurring in the grafting process, it is necessary to describe quantitatively the rates of various competing reactions which take place in such a polymer-monomer system. These processes are essentially the rate of initiation of free radicals, the rate of exposure of frozen-in free radicals, the rates of propagation, transfer and termination of the growing grafted chains. But the transfer reactions can be neglected due to the relatively low transfer rate constant of styrene radical with straight chain hydrocarbon, polyvinylacetate or polystyrene at room temperature.²²

As indicated above, it is practically infeasible to quantitatively describe these processes at the present time. However it is still possible to reach qualitative conclusions from the grafting data. First of all, it is quite clear that the degree of grafting should increase with dose, as noted before and shown in Figure 1. The shape of those curves, however, are influenced

by many factors as mentioned in INTRODUCTION, making the mechanism of grafting a very complex, unsteady-state process. Therefore, it will be proper to consider the general free radical polymerization first, before discussing the specific trends shown by the data.

In a free radical polymerization system of any homogeneous phase, it is generally assumed that the rate of polymerization may be represented by:

$$V_p = k_p[M][M\cdot]$$

Where V_p is the rate of polymerization or propagation, k_p is the propagation rate constant, $[M\cdot]$ the local concentration of free radicals, and $[M]$ the local monomer concentration. It is, of course, assumed that $[M\cdot]$ becomes essentially constant particularly in early stage of the reaction; steady state condition. In this steady state condition, the above equation is assumed to be averaged throughout the system and it will then represent the macroscopic rate of polymerization.

Although these assumptions are reasonable for a homogeneous system as that of ELVAX 40-styrene, it may not be applicable to a heterogeneous system as that of ELVAX 250-styrene. However, if the above equation is assumed to represent the overall rate of grafting and for the qualitative discussion of the present grafting systems, it is worth being applied as a reference equation.

$[M]$ generally varies due to the diffusion rate in the reacting system: The greater the diffusion rate becomes, the bigger $[M]$. The driving force of diffusion may be caused by the so-called "normal driving force for diffusion" and or the osmotic pressure. It is apparent that the diffusion rate in homogeneous ELVAX 40-styrene system would be greater than that of heterogeneous ELVAX 250-styrene's. As such, V_p of the former system would be higher than that

of the latter one. The experimental result, however, revealed that there was no noticeable difference in V_p between the two systems with the exception of initial step of reaction, as being evidenced by Fig. 1. On the other hand, homopolymerization in the bulk phase would increase the viscosity and decrease the monomer concentration, and thus the driving force for normal diffusion as well as diffusion accelerated by the osmotic pressure would be decreased. $[M]$ may also decrease due to crosslinking of the EVA matrix by grafted side chains, decreasing the equilibrium swelling value of the polymer. Such crosslinking may be occurring only where there are sufficient chain mobilities for the termination to occur by mutual combination. Furthermore, the presence of occluded chains (as well as frozen-in free radicals) may contribute to the lower degree of chain termination.

$[M\cdot]$ may increase due to occlusion of growing chains in the viscous polymer matrix, leading also to a decrease in the termination rate due to a decrease in the termination rate constant (k_t). This is similar to the well-known "gel effect" noted in bulk polymerizations and in polymerization occurring in precipitation media, and has been postulated to occur in heterogeneous graft polymerizations at low or room temperatures²³. This effect would become more important at the low temperatures.

As shown in Figure 3, the pronounced effects noted were the sharp increase of % graft up to the dose of 2 mrad. Hence, 2 mrad may be called as the critical dose in these experiments. This phenomenon indicates that the equation, $V_p = k_p [M][M\cdot]$, holds up to the dose of 2 mrad.

The leveling-off phenomenon may be due to a relative decrease in either $[M]$ or $[M\cdot]$ or in both, such that the net effect is an overall decrease in rate.

From the above discussion, $[M\cdot]$ should increase due to the occlusion of growing chains, and therefore $[M]$ should decrease as dose or time of the irradiation increase. The decrease in $[M]$ may be due to the inability of the diffusion rate to keep pace with the rate of polymerization in the EVA.

In Figure 1, it is observed that the shape of one curve is similar to that of another but the % graft is somewhat deviated from each other due to the inclusion of styrene homopolymer formed during irradiation. From Fig. 3, it is also observed that the shape of linear PE-styrene system is very similar to that of EVA-styrene's. This rather unexpected result indicates that the grafting reaction rate (or V_p) of linear PE-styrene system is little different from that of EVA-styrene's, and thus illustrates that the reactivity of the radicals formed on backbone and pendant acetate group (α -position) of EVA is almost identically reactive toward styrene, which also means that the experimental result is somewhat consistent with the proposed G-value ratio of PE-styrene and PVAc-styrene system in Table 1.

The initial lag of % graft between EVA and PE in Figure 3 is thought to be caused by the difference in dose rate and difference in mixture phase.

The dependence of % graft on concentration, as shown in Figure 2, is somewhat on the contrary to expectation. This phenomenon is believed to be due to the fact that the occlusion of growing chains in viscous matrix affects little more than the diffusion variable does on the irradiation-induced grafting reactions.

CONCLUSION

Following observations and conclusions were obtained from the irradiation-induced grafting

experiments of EVA-styrene system:

- 1) The critical dose is 2 mrad : the % graft increases sharply up to this point but levels off from that on.
- 2) The dependence of % graft on concentration and mixture phase (solution or swollen phase) is negligible. This result is believed to be due to the fact that the occlusion of growing chains in viscous matrix affects more on the grafting reactions than the diffusion variables do.
- 3) The reactivity of the radicals formed on both of the backbone and the pendant acetate group (α -position) is almost equal toward styrene.
- 4) The irradiation-induced grafting reaction of EVA-styrene system is very similar to that of linear PE-styrene's.

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