Segregation Effect of Radiation Induced Crosslinking of HDPE: Morphology Change

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Scanning Electronic Microscopy has been used to study morphology of pure gel; sol-gel blend and sol-gel segregation samples of radiation induced crosslinking of HDPE. The results show that the morphology of segregation sample is the same as that of pure gel and different from that of sol-gel blend. This kind of morphology change proves that the sol-gel blend have occurred a liquid---solid phase segregation in the melting state. The liquid phase (sol) will naturally immersed in the network of the gel.

Introduction

The main effect of high-energy radiation on polyethylene is the formation of cross-linking between different chain. As a result, part of the homopolymer changes from the soluble fraction (sol) to the insoluble fraction (gel), and then the properties of polymer such as thermodynamics or mechanical properties change largely. In the past several decades, a number of papers concerning those have been published. However, in this literature, studies dealing with properties of pure gel seem to be cared to little.

Interested in the multiple melting peaks observed by Hikmet (1) from crosslinked polyethylene and by Zhong (2) from crosslinked PTFE, a series work have been done by our group recently.

As we have suggested in the first two paper in this series[3,4], crystallization process of sol—gel coexistence system involves at least a two—step process: sol fraction will crystal earlier than gel fraction. This is the reason why the multiple melting peaks appear after the sol—gel coexistence system annealed at high temperature for a long time.

The aim of present work is to study the morphology change of such sample in order to get more information.

Experimental:

Samples used in this experiment is DAQING-HDPE 5000S(density is 0.954g/cm^{-3}). The polymer was first placed between two sheet plates and heated at 150℃ until it was molten. Then press at 8.5MPa was applied for 10mins.

Sheet was cooled down to room temperature and sealed in glass tubes under vacuum. Irradiation was performed using 90000Ci Co-60 with radiation dose of 200kGy. Before extraction, samples were placed in air for two weeks, which will avoid post radiation effect.

The pure gel fraction was got by extraction of soluble fraction with xylene at 135℃. The samples were immersed in hot xylene for periods of 24 h. Then, the samples were dried in a vacuum oven at 60℃to a constant weight. The extraction was considered complete after two consecutive period of extraction. The solvent was changed to a fresh solvent between each consecutive extraction.

Segregation samples were got by such heat treatment sequence as follow: Initial sample →Irradiate→ Melted quench → Anneal→ cool to room temperature.

All the samples were dealed with convenient method before SEM examined them.

Results and Discussion

The electron micrograph of Figure a and b shows the fracture surface of initial HDPE. These pictures show the surface to consist of sheaflike structure. After irradiated 200kGy, crosslinking will make the surfaces of initial HDPE change largely, and if no heat treatment, the sheaflike structure disappeared from the surfaces of sol—gel coexistence samples (see figure c and d). Porous structure appears on the surface of pure gel, and the black portion is a hole where the sol fraction had been extracted off. From the figure c—f, we can confirm that sol—rich region and gel—

rich region are involved in the sol—gel coexistence system. Because the reaction induced by high—energy radiation is a random process, so the sol fraction and the gel fraction mix to each other in the boundaries between two phases, if no appropriate heat treatment, which cause the surface of sol—gel coexistence system change from sheaflike (fig. a and b) to totally uniform texture (fig. c and d).

It has been shown in our preview work that the annealing temperature using in this experiment is higher than the melting point of pure gel, and lower than the melting point of pure sol (see table 1-1). So at annealing

Table 1: Fusing enthalpy and melting point of HDPE under different radiation dose

Dose (kGy)	sol		Sol-gel		gel	
200	ΔH (J/g)	Tm (°C)	ΔH (J/g)	Tm (° C)	ΔH (J/g)	Tm (° C)
	206.33	129.84	173.19	126.59	151.7	123.17
400	162.56	128.61	155.73	124.98	152.5	121.6
1000	189.21	128.97	157.84	123.24	141.33	120.22

condition, gel—rich region and boundaries between two phases have been in molten state. We can image that if sol and gel are miscibile each other, then, after annealing, the morphology of sol—gel coexistence samples will not change; on the other hand, if sol and gel are immiscibile, because of different mobility between sol and gel, then the sol involved in the boundary and in gel—rich region will move to the sol—rich region,

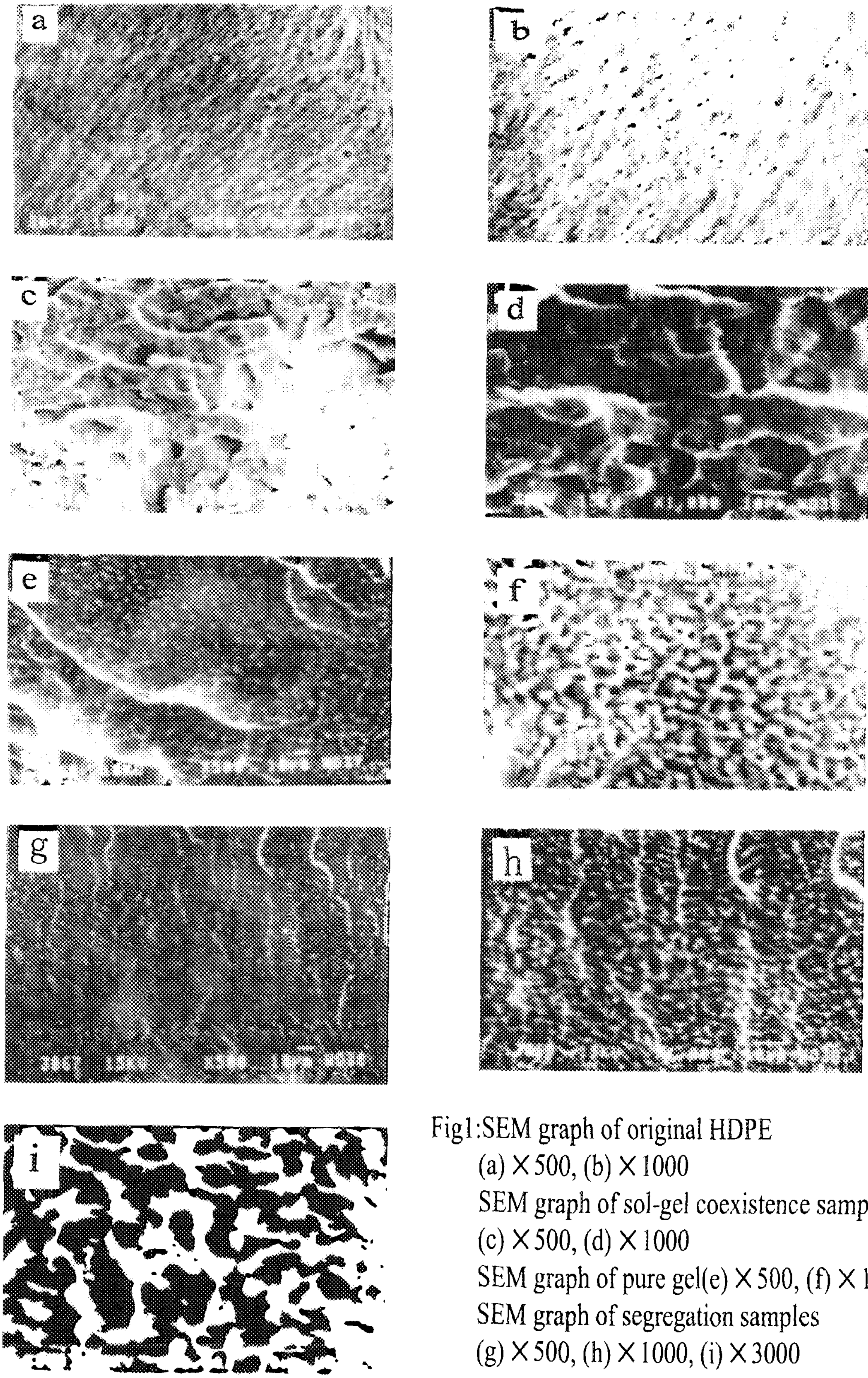

Fig1:SEM graph of original HDPE
(a) ×500, (b) ×1000
SEM graph of sol-gel coexistence samples
(c) ×500, (d) ×1000
SEM graph of pure gel(e) ×500, (f) ×1000
SEM graph of segregation samples
(g) ×500, (h) ×1000, (i) ×3000

which will result in the morphology of sol—gel coexistence samples change.

Porous fracture surfaces of annealing sol—gel coexistence samples are shown in figure g-I. Comparing with morphologies of pure gel, the black portion is the sol-rich phase. Similar porous morphology may suggest that some sol fraction have move from gel-rich phase and boundaries to the sol-rich phase, which indicates that the sol and gel are immiscibile. It is clearly that, in melting, instead of remixing, the segregation sol microdroplets coalesce themselves, and this kind of microseparation is solidified during quench crystallization.

In summary, as the multiple melting peaks (see fig.2), similar morphology between pure gel and sol—gel annealing samples indicates that sol-gel phase segregation really occur. Because these segregation resulting from the formation of crossliking between different chain, we suggest that this kind of phase segregation may be a common phenomenon in sol-gel coexistence samples.

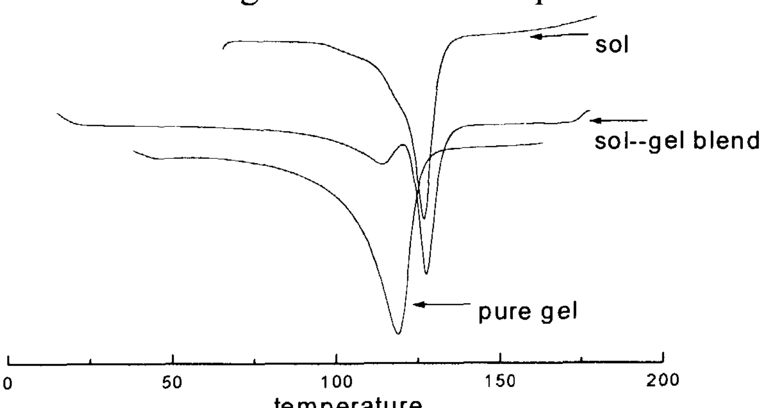

fig.2 the dsc trace of segregation sample, pure gel and pure sol at the same radiation dose

Reference

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