# 8. Polymers (2)

## 8.1 Enhanced Interfacial Radiation-induced Reaction for Improving the Interfacial Adhesion of Incompatible Polymer Blend PP/BR

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Abstract γ-radiation induced interfacial changes of incompatible polymer isotactic polypropylene(PP) and cis1,4-polybutadiene(BR) blends containing polyfunctional monomer (PFM) triallyl isocyanurate(TAIC) were investigated. The results of the study are as following: PP is incompatible with BR; TAIC is hardly dissolved in both PP and BR; when blended with PP/BR, the concentration of TAIC in the interfacial region is higher than that in dispersion phase of BR or matrix of PP. The crosslinking and/or grafting of which TAIC occured under radiation in the interfacial region anchored the dispersed BR phase to PP matrix. The interaction between adjacent phases is changed from sole van der Waals force to co-action of both chemical bond and molecular forces. Crosslinking between adjacent phases links the dispersed phase with PP matrix, and grafting in the boundary regions increases the thickness of interface. These result in a good interfacial adhesion between dispersed phase and matrix.

### INTRODUCTION

The interfacial condition and adhesion between different polymer phases obviously dominate the properties of polymer blend at some extent. The key of successfully preparing polymer blend is controlling the morphology and phase structure, solving the question of interfacial tension and adhesion between two adjacent phases.

In regard to incompatible polymer blends, the interaction is weak and the stability of phase structure is poor, and the interfacial adhesion is poor too. There is a tendency of phase separation from matrix. The stress cannot be well distributed and transferred between phases. Therefore improving the interfacial adhesion become one of the most important factors for preparing excellent polymer blend. It have been reported that the morphology of polymer blend can be affected by high energy radiation. Besides that each internal phase is influenced, the interfaces of blend are also influenced. Crosslinking and grafting will occur between different polymer blend components in the interfacial region. The former improves the force of adhesion of dispersed phase and matrix, the later increases the thickness of interface. However, for an immiscible or incompatible blend system, the crosslinking and grafting reaction between different components only occur in the interfacial region. Radiation initiate interfacial reaction simultaneously, it also act on each internal phase to initiate various radiation reaction, such as crosslinking, grafting and degradation; and only achieving some certain dose, it produce significant effect on the interface, whereas it may have produced serious effect on the dispersed phase and matrix at the same time

(S.Thomas, et al, 1987), which is unexpected sometimes. It is well known that the behavior of polymer showing at radiation field can be changed by addition of polyfunctional monomer (PFM), to change radiation reaction mechanism and assure crosslinking or grafting reaction being predominate (G. Odian, et al, 1964). At present there is no report on studying enhancement crosslinking and grafting reaction in the interfacial region of incompatible polymer blend to improve interfacial adhesion, and this work is very important for stabilizing morphology of blend, preparing excellent polymer alloy by high energy radiation. Therefore we selected blend of polypropylene(PP) and cis1,4-polybutadiene(BR) as our studying system. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), differential scanning calorimeter (DSC), dynamic viscoelasticity techniques and gel measurement were used to study enhancement radiation induced interfacial reaction in this paper.

## EXPERIMENTAL SECTION

The polymers used in this work are PP1330 (Mn 16888, Mw 306639) and BR9000 (cis1,4-polybutadiene, Ni as catalyst). Triallyl isocyanurate (TAIC) is used as PFM. PP, BR and TAIC were mixed at two roll mixer and kneaded at 180 ℃. The milled samples were then press-molded 1mm thickness sheet. The Samples packed with PE film subsequent were subjected to γ radiation at room temperature. Dose rate was 10KGy/hr. The gel fraction was determined by solvent extraction, using xylene as solvent at boiling temperature for 48hrs. The morphology studies involved scanning electron microscopy of fracture surface produced at liquid nitrogen temperature. These surfaces were evaporated onto thin layer of gold. In addition, polymer blends were examined by transmission electron microscopy, the ultrathin sections were stained with $O_sO_4$. The thermal properties were carried out in DSC-7, with raising temperature rate 10 ℃/min. The properties of dynamic viscoelasticity of blends were measured on DDV-II-EA instrument, with raising temperature rate 3℃/min, temperature range -120℃ 200℃, frequency 3.5Hz.

## RESULTS AND DISCUSSION

PP is a crystalline polymer, BR is a non-crystalline amorphous polymer. In the blend system consisted with them, PP crystalline phase is incompatible with BR non-crystalline phase and their aggregated state is very different. There is no strong interaction between them, the compatibility of blend system may be predicted bad. Fig.1 is TEM microphotograph of PP/BR blend. Here the black parts are BR particles, the white parts are PP continuous phase. It shows that PP and BR cannot form uniform phase. Fig.2 is SEM microphotograph of PP/BR blend. On the fracture surface the morphology and phase structure are clearly visible. The cavities and holes shown in microphotograph are rubber droplets which have been drawn out. The cavities and holes are more and well distributed, their edge are smooth, no inter-drawing has been

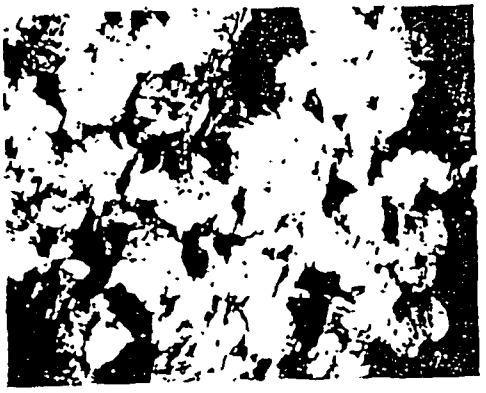

Fig.1 TEM microphotograph of PP/BR blend

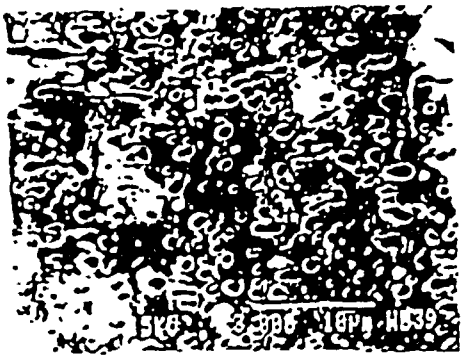

Fig.2 Morphology of PP/BR/TAIC (80/20/2)

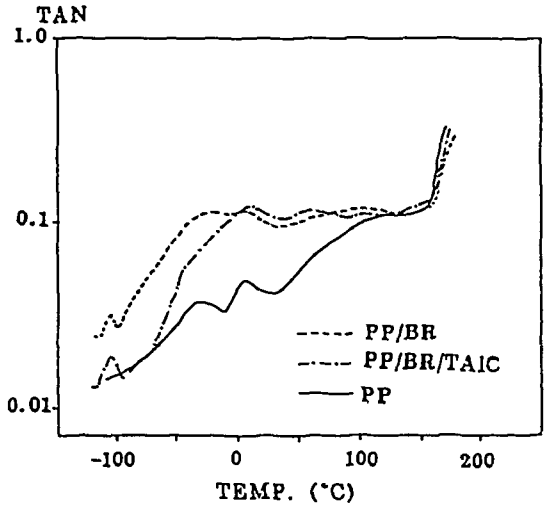


Fig.3 tg δ -T curves of PP/BR blend

Fig.4 Morphology of PP/BR/TAIC (80/20/2): at 90KGy

found. It indicates that the rubber particles which adhered loosely to PP matrix are easily drawn out of PP matrix when stress fracture happened. We further investigate the compatibility of PP/BR blend by using dynamic viscoelasticity data, as showing in Fig.3. The tg$\delta$-T curves of blend have three separate peaks, each of them is in correspondence to the tg$\delta$ peaks of PP and BR respectively. The Tg of PP in blend is basically in agreement with that in pure PP. These also illustrates the compatibility of PP/BR being bad.

We also study the compatibility of PFM TAIC blending with PP/BR system. We have found that TAIC would migrate, blooming (or"sweating") from the blends when blended with PP or BR. This demonstrates that the compatibility of TAIC with polymer PP or BR is poor. In addition, according to the solubility parameters, the compatibility of TAIC with polymer can be estimated. The $\delta$ of PP, BR and TAIC are 16.6, 17.8 and 22.0 respectively. There are larger differences between TAIC and PP or BR. TAIC has poor compatibility with them. According to Helfand and Tagami (1972), there is a lower density in incompatible blend interfacial region. So TAIC would migrate from dispersed phases and

matrix to the interface and surface when TAIC was blended with PP/BR, which induced higher concentration of TAIC in the interfacial region. So the crosslinking and grafting reaction would be enhanced in the incompatible interfacial regions when irradiated.

Fig.4 is SEM microphotograph of PP/BR/TAIC blend irradiated at 90KGy. The cavities and holes are dramatically less than that in Fig.2. The sum of BR particles being drawn out decrease, interface between BR phase and PP matrix is ambiguous (or"obscure"), BR phase and PP matrix are difficult to be distinguished. The case of one phase affected another can be seen in the fracture surface.

The changes of melting temperature of PP/BR/TAIC blend system irradiated at various dose are investigated, as showing in Fig.5. The main melting peak and sub-melting peak decrease 4.4K and 5.7K respectively when irradiated at 50KGy dose. At common case the damage of crystal by radiation is low at 50KGy dose. It shows that the PP crystalline phase is linked with amorphous BR phase by radiation induced interface reaction, which increases the interfacial adhesion and the interfacial thickness. Non-crystalline segments act on crystalline segments induced Tm decreasing.

Fig.6 is tg$\delta$ curves of PP/BR/TAIC blend irradiated at various dose. The peak of tg$\delta$ of BR move toward high temperature range with 40KGy dose irradiated, the original peaks of tg$\delta$ of PP move toward low temperature range, the gel of blend at this time is low, approximately 3 percent, the crosslinking degree is very limited, the adhesion between two phases is improved. At 90KGy dose, a new tg$\delta$ peak appear, the original peaks of tg$\delta$ of PP and BR disappear, the gel content of blend at this time is about 18 percent. PP and BR partly form crosslinking network. BR particles are anchored to PP matrix; the

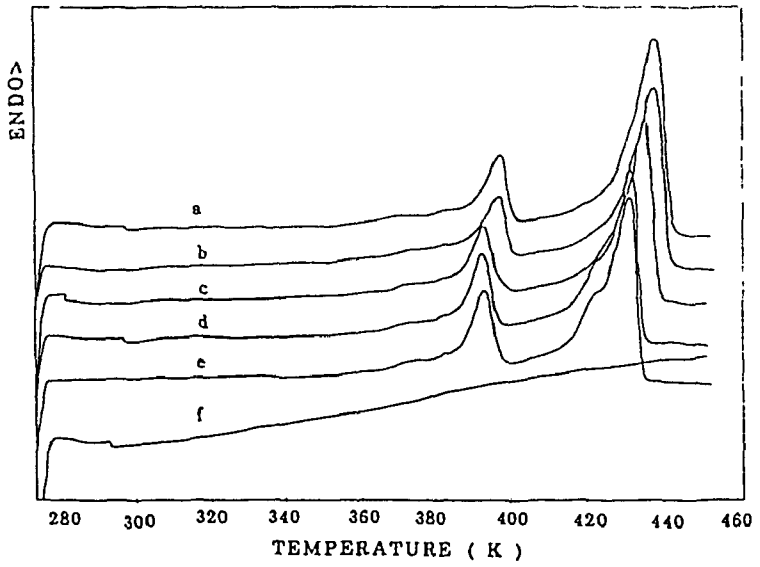


Fig.5 DSC curves of PP/BR blends a: PP b: PP/BR/TAIC, 0KGy
c: PP/BR/TAIC, 50KGy d: PP/BR/TAIC, 100KGy
e: PP/BR/TAIC, 150KGy f: BR

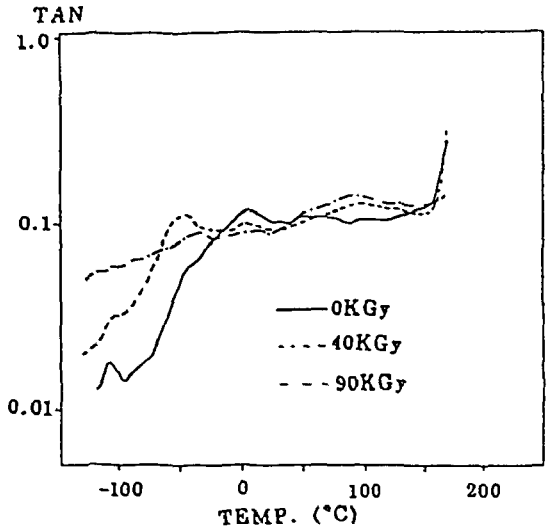


Fig.6 tg δ-T curves of PP/BR/TAIC blend: effect of radiation

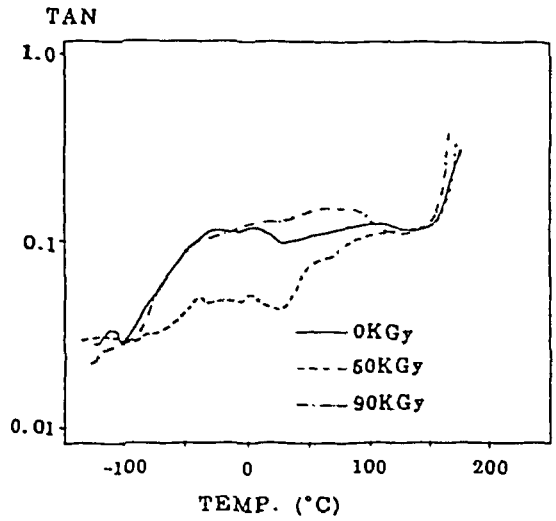


Fig.7 tg δ-T curves of PP/BR blend: effect of radiation

adjacent phases are linked by chemical bond and thick interface; the interfacial adhesion of blend is greatly improved. Nevertheless for PP/BR blend without TAIC, irradiation produce more effect on peak of tg δ of BR and less on PP tg δ peaks, as showing in Fig.7. It demonstrates that the radiation induced BR phase crosslinking but hardly affected on PP matrix, the degree of interface reaction is weakness.

## CONCLUSIONS

PP/BR is incompatible blend system. TAIC is also incompatible with PP and BR. The distributing concentration of TAIC in blend is higher in interfacial region than that in BR phase and PP matrix. Crosslinking and grafting which is produced by TAIC when irradiated link the adjacent phases and increase the thickness of interface in the interfacial regions. Enhancement radiation-induced interfacial reaction is available to improve the interfacial adhesion of incompatible polymer blend.

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