

## **TENSILE PROPERTIES AND MORPHOLOGY OF DYNAMICALLY VULCANIZED ENR-50/EVA BLENDS: DIFFERENT VULCANIZATION SYSTEM**

Z. MOHAMAD<sup>1</sup>, H. ISMAIL<sup>2</sup>, R. CHANTARA THEVY<sup>3</sup>

### **ABSTRACT**

Blends of epoxidized natural rubber (ENR-50) and ethylene vinyl acetate (EVA), with varying proportion of the components, were dynamically vulcanized using different cross-linking systems, namely, sulfur and dicumyl peroxide (DCP). The blends were prepared by melt mixing in Haake Rheometer. The effect of curing systems on the tensile properties and morphology were investigated. The results revealed that, dynamic vulcanization are capable to improve tensile properties of ENR-50/EVA blends by producing a finer and homogenous dispersed phase of ENR-50 in EVA matrix. Dispersed phase is in a form of crosslink rubber particles (ENR-50) which have the ability to improve tensile properties of the blend. Overall morphology showed that, crosslink phase will become a dispersed phase at all blend ratios.

**Key Words :** Epoxidized natural rubber, EVA blend, dynamic vulcanization, ENR-50/EVA blend, TPE

### **1.0 INTRODUCTION**

A thermoplastic elastomer (TPE) is a blend of rubber and thermoplastic polymer. It is a rubbery material with properties and functional performance similar to those of conventional vulcanized rubber at ambient temperature, yet it can be processed in a molten condition as a thermoplastic polymer at elevated temperature. Thermoplastic vulcanizate (TPV) or dynamic vulcanizate is a special class of TPEs, where the rubber phase is vulcanized by a suitable crosslinking agent during its mixing step with a thermoplastic polymer. Dynamic vulcanization was first described by Gessler [1] in 1962 and then developed by Fisher [2], and Coran et al. [3,4]. Dynamic vulcanization is a route to new TPEs which give properties as good as or even in some cases better than, those of elastomeric block copolymers.

Epoxidised natural rubber, ENR is a chemically modified natural rubber. The epoxidation of NR to produce ENR involves the random introduction of epoxide groups onto the double bond of the NR polymer chain. ENR poses excellent properties like oil resistance, gas impermeability, good wet grip and high damping characteristics [5]. The oil resistance of ENR-50 is due to the polarity of the epoxide group. However the market and applications for ENR found to be limited. Thus attempts are being made to diversify the usage and application of this rubber especially in advanced engineering field. As mention above, blending with other polymer is the easiest and the cheapest way to tailor the properties of

---

<sup>1</sup>Polymer Engineering Department, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.

<sup>2</sup>Division of Polymer, School of Materials and Mineral Resources Eng., Universiti Teknologi Malaysia, 14300 Seri Ampangan Seberang Perai Selatan, Pulau Pinang, Malaysia

<sup>3</sup>Malaysia Institute for Nuclear Technology Research (MINT), BAngi, 4300, Kajang, Malaysia  
Correspondence to : Zurina Mohamad (zurina@fkkksa.utm.my)

ENR and at the same time reduce the material cost. Furthermore, the present of oxirane group in ENR found to be effective in causing specific interaction with a second polymer [6].

Ethylene vinyl acetate copolymers (EVA) are randomly structured polymers which offer excellence ozone resistance, weather resistance and excellence mechanical properties [7]. 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 [8]. EVA is chosen to be blended with ENR-50 due to its excellence properties and halogen free thermoplastic. This paper deals with the dynamic vulcanization of ENR-50/EVA blends of different compositions. The tensile properties and morphology of the blend have been investigated.

## **2.0 EXPERIMENTAL**

### **2.1 Materials**

Epoxidised natural rubber, ENR 50 with 50 mol % epoxidation (grade EPOXYPRENE 50) used in this study was obtained from Kumpulan Guthrie Sdn. Bhd., Malaysia with specific gravity value of 1.03. Ethylene vinyl acetate (Grade H2020) having 15% vinyl acetate content with MFI value of 1.5g/10min and density of 0.93g/cm<sup>3</sup> was purchased from The Polyolefin Company, Singapore. DCP (Dicumyl peroxide), sulfur, zinc oxide, stearic acid, IPPD (N-Phenyl-1-N-Isopropyl-para-Phenylene diamine), CBS (N-Cyclohexyl-2-Benzothiazole sulfenamide) was supply by Bayer Co. Ltd. (Malaysia).

### **2.2 Mixing Procedure**

The ENR-50/EVA blends were prepared by melt-mixing the ENR-50 and EVA in a Haake Rheomix Polydrive R 600/610 at temperature 120°C and rotor speed at 50 rpm. The blend ratios of ENR-50/EVA used in this studies are 0/100, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0 (wt %). The compounding formulation for dynamic vulcanization is given in Table 1. EVA was charged into the mixing chamber and allowed to melt for 2 minutes. Then ENR-50 was added to the molten EVA and the mixing was continued for a further 4 minutes. For dynamic vulcanization samples using DCP and sulfur, curatives were added at 4<sup>th</sup> and 5<sup>th</sup> minutes respectively. After that the mixing was continue for another two minutes and three minutes for dynamically vulcanized samples. A torque versus time curve was plotted for each composition during mixing process in order to monitor processing condition. The samples were then compression molded at 120°C for 5 minutes for unvulcanized samples, 150°C for 5 minutes for sulfur cure samples and 180°C for 7 minutes for DCP cure samples. After that the samples was cooled for 2 minutes to produce one and two millimeter thick sheets.

### **2.3 Tensile Properties**

The tensile properties were measured with a Tensometric tensometer M 500 according to ASTM D 412 at 50 mm/min crosshead speed. The molded samples of one millimeter thick were cut into standard test pieces using a Wallace die cutter.

## TENSILE PROPERTIES AND MORPHOLOGY

**Table 1** Formulations for dynamic vulcanization

| Components (wt %)       | Formulation             | Formulation                |
|-------------------------|-------------------------|----------------------------|
| ENR-50                  | 20, 40, 50, 60, 80, 100 | 0, 20, 40, 50, 60, 80, 100 |
| EVA                     | 80, 60, 50, 40, 20, 0   | 100, 80, 60, 50, 40, 20, 0 |
| <b>Curatives (phr)*</b> |                         |                            |
| Zinc oxide              | 5                       | -                          |
| Stearic acid            | 2                       | -                          |
| IPPD                    | 2                       | -                          |
| CBS                     | 2                       | -                          |
| Sulfur                  | 1                       | -                          |
| DCP (php)*              | -                       | 2                          |

\*phr-part per hundred rubber  
php-part per hundred polymer

### 2.4 Morphology Study

Examination of the fractured surfaces was performed using a scanning electron microscope (SEM) model Leica Cambridge S-360. The samples were cryogenically fractured and the surface was treated with methyl ethyl ketone to selectively etch the ENR-50 phase. A samples were examined after first sputter coating with gold to avoid electrostatic charging and poor image resolution.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Scanning Electron Microscopic Studies

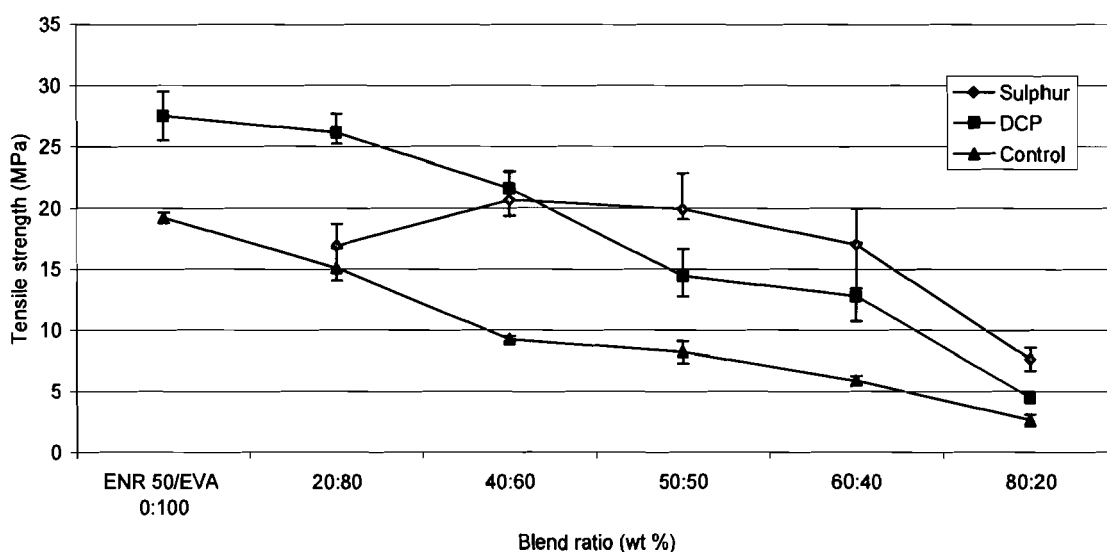
Scanning electron microscopy has been successfully used by several researchers to follow the failure mechanism in polymer blends.[9,10] The scanning electron micrographs of tensile fractured surfaces and cryogenic fractured surface of uncured, sulfur and peroxide cure ENR 50/EVA blends are shown in Figures 3 and 4.

The ENR-50/EVA blends with dynamic crosslinking shows brittle like fracture compared to uncured blend. Tensile fractured surfaces of sulfur crosslink systems illustrate ductile fractured behavior in EVA dominant blend (Figure 3D) and some matrix tearing occur in ENR-50 dominant blend (Figure 3F). This is evidence of increase in tensile strength and elongation at break in EVA dominant blends and impart the elasticity behavior in ENR 50 dominant blend.

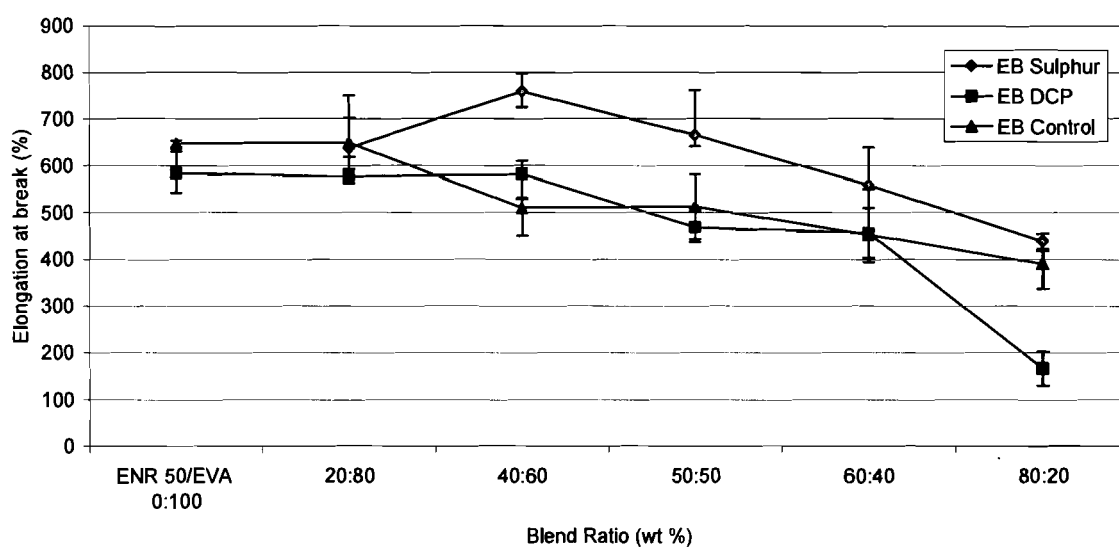
On the other hand, DCP crosslink systems exhibit a brittle type fractured surface (Figure 3G-3I) with some tear line especially in EVA dominant blend. This nature of failure supported the decrease in elongation at break compared to others blend and increase in tensile strength compared to unvulcanized blends. In ENR-50 dominant blend, DCP exhibit a smooth failure surface (Figure 3I), which is characteristic for rubbers.

SEM studies provide further evidence of phase compatibility, where blend with DCP produced a finer and smoother morphology compared to blend with sulfur and unvulcanized blends especially at higher rubber content (Figure 4D). In the DCP system, the distribution

fine and uniform and hence, the cross-linking is more effective in the DCP system compared to sulfur system. However, the effect of cross-linking is not so predominant on the properties of the DCP system due to the degradation of EVA phase in the presence of DCP. Cryogenic fractured surfaces revealed that (Figure 4C-4F) dynamic vulcanization improved the dispersion and distribution of non continuous phases compared to unvulcanized blend. Crosslink rubber phase (ENR-50) is a dispersed phase at all blend compositions compared to unvulcanized blend, where ENR-50 is a dispersed phase only at 40 wt % and below.

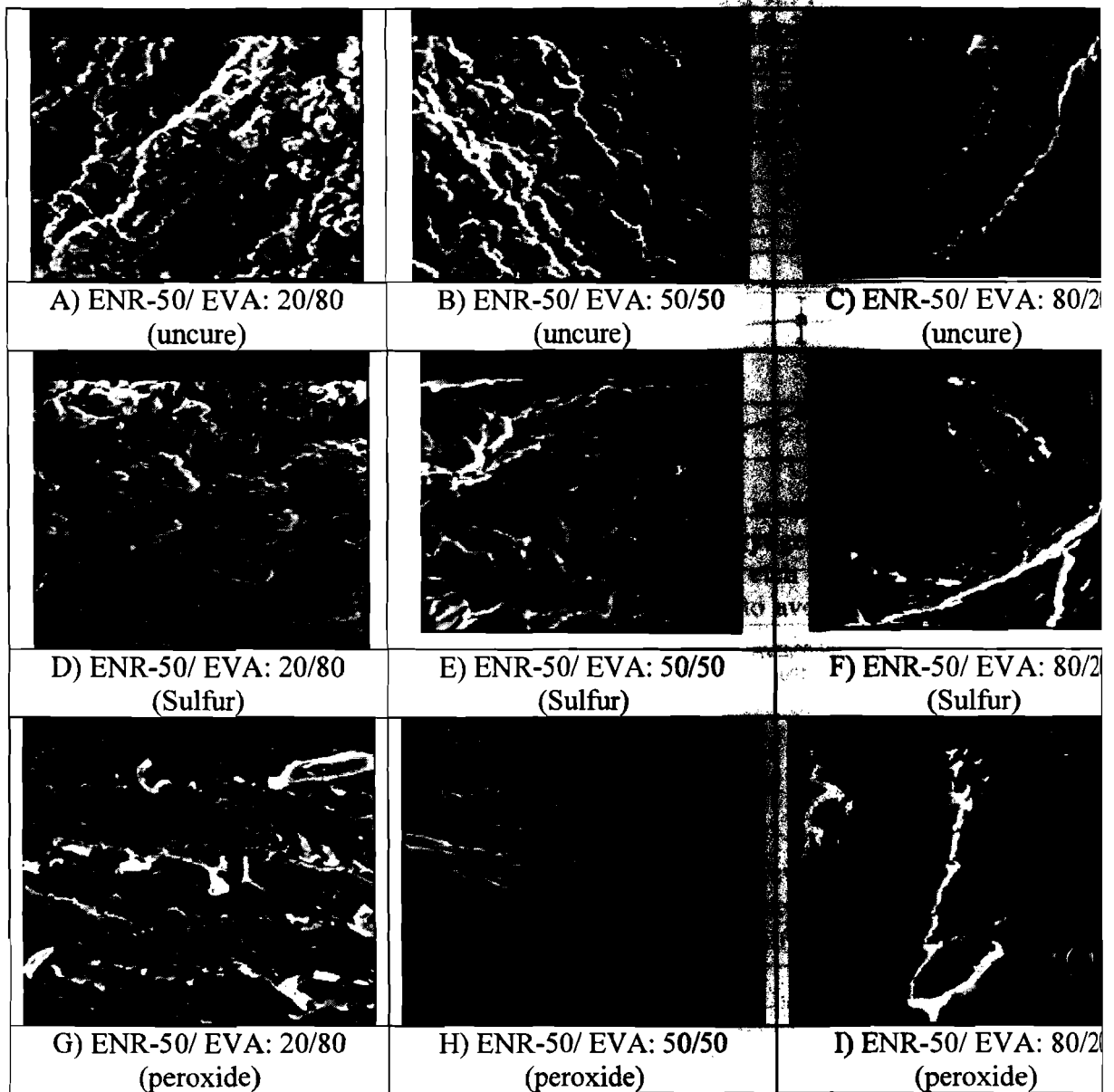


**Figure 1** The effect of dynamic vulcanization on the tensile strength for ENR-50/EVA blend at different blend ratios.

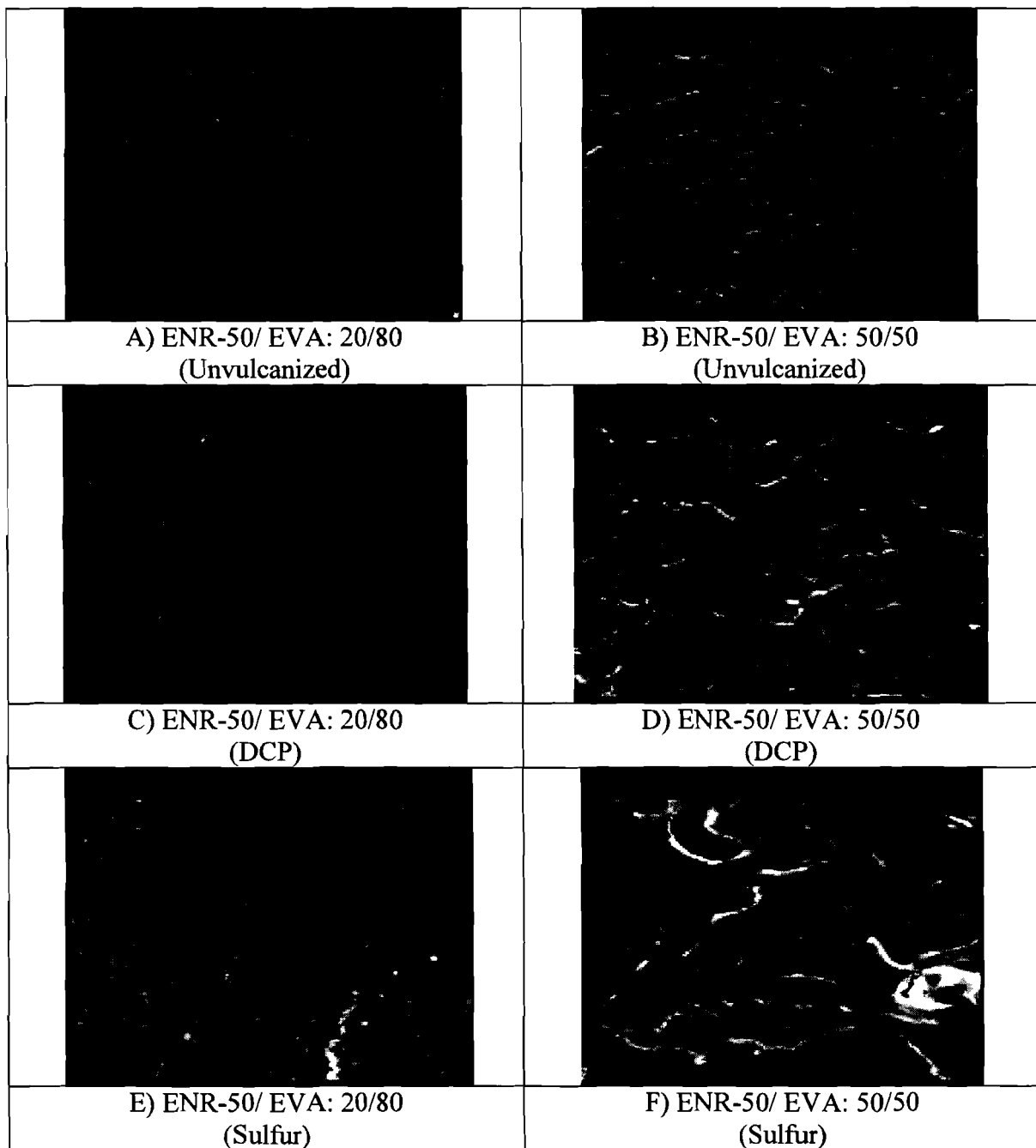


**Figure 2** The effect of dynamic vulcanization on the elongation at break for ENR-50/EVA blend at different blend ratios

## TENSILE PROPERTIES AND MORPHOLOGY



**Figure 3** SEM micrograph of tensile fractured surfaces for ENR-50/EVA blend with sulfur curing system at 500X.



**Figure 4** SEM micrograph of tensile fractured surfaces for ENR-50/EVA blend with and without curing system at 2000X.

## TENSILE PROPERTIES AND MORPHOLOGY

### 4.0 CONCLUSIONS

Sulfur curing systems enhanced the tensile properties due to **the existence** of crosslink rubber particles and imparts the elastomeric behaviour to the blend with ENR-50 dominant blend. Dynamic vulcanization of ENR-50/EVA blend has produced a better dispersion and distribution of crosslink rubber particles in the blend. **In general, dynamically vulcanized** ENR-50/EVA blends have improved the tensile properties and morphology of the blend. Blend ratio of 40/60 with sulfur curing system registered **the highest** tensile strength compared to others. Overall morphology showed that, **crosslink** phase will become dispersed phase at all blend ratios.

### ACKNOWLEDGEMENT

The author would like to express gratitude to Universiti Teknologi Malaysia for the financial support (scholarship) throughout this study.

### REFERENCES

- [1] Gessler, M. 1962. Process for preparing a vulcanized blend of crystalline polypropylene and chlorinated butyl rubber, U.S. Patent 3037954.
- [2] Fisher, K. 1973. Thermoplastic blend of partially cured monoolefin copolymer rubber and polyolefin plastic, U.S. Patent 3758643.
- [3] Coran, A. Y. and R. P. Patel. 1980. Rubber-thermoplastic compositions Part I. EPDM-polypropylene thermoplastic vulcanizates, *Rubber Chem Technol.* 53:141-150.
- [4] Coran, A. Y., R. P. Patel and D. Williams. 1982. Rubber-thermoplastic compositions Part V. selecting polymers for thermoplastic vulcanizates, *Rubber Chem Technol.* 55:116-136.
- [5] Gelling, I. R. 1991. Epoxidised Natural Rubber, *J. Nat. Rubb. Res.* 6: 184-205.
- [6] Kallitsis, J. K. and N. K. Kalfoglou. 1989. Compatibility of ENR with thermoplastic and thermosetting resins, *J. Appl. Polym. Sci.* 37: 453-465.
- [7] Doak, K. W. 1986. Ethylene polymer, in *Encyclopedia of polymer science and Engineering*. Vol. 6, Mark, H. F., N. M. Bikales, C. G. Overberger and G. Menges, Eds. New York: Wiley.
- [8] Shifeng, W., Z. Yong, Z. Yinxi, Z. Changming and L. Enjun. 2004. Crosslinking of polyvinyl chloride by electron beam irradiation in the presence of ethylene-vinyl acetate copolymer, *Journal of App. Polym. Sci.* 91: 1571-1575.
- [9] Varghese, H., S. S. Bhagawan and S. Thomas. 1999. Effect of blend ratio, crosslinking system and fillers on the morphology, curing behavior, mechanical properties and failure mode of acrylonitrile butadiene rubber and poly(ethylene-covinyl acetate) blends, *J. of App. Polym. Sci.*, 71:2335-2364.
- [10] Soares, B. G., F. F. Alves, M. G. Oliveira and A. C. F. Moreira. 2001. The compatibilization of SBR / EVA by mercapto-modified EVA, *European Polym. J.* 37: 1577-1585.