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EFFECT OF CROSSLINKING AGENTS ON MORPHOLOGY AND MECHANICAL PROPERTIES OF ETHYLENE PROPYLENE DIENE MONOMER / POLY VINYL CHLORIDE COMPOSITES

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ABSTRACT

The effects of cross-linking systems on the morphology and mechanical properties of EPDM/PVC composites were studied. Three cross-linking systems, sulphur, dicumyl peroxide and a mixture consisting of sulphur and peroxide were used for vulcanization. DCP vulcanized system possesses higher torque than sulphur cross-linked ones. Composite with 7.5 phr PVC samples prepared exhibited optimum mechanical properties. The amount of cross-linking agent is also found to affect the mechanical properties. The morphology has been studied for complementing the observations related to the above mentioned characteristics.

Key words: Polymer composites, Mechanical properties, Effect of vulcanizing system.

INTRODUCTION

Polymer blends and composites are being used extensively for the development of a wide spectrum of products. Unfortunately, the demands for many applications need a set of properties that most of single polymers cannot fulfill. Mixing of properly selected polymers has been a widely accepted technique to develop high performance matrices to meet the demands for new materials. Raw rubber, either polar or non polar, has poor physico-mechanical properties. To improve these properties, some ingredients such as accelerators, activators, antioxidants, softeners and white and black fillers were added to the rubber vulcanizates. The addition of fillers to polymers is a fast and cheap method to modify the properties of the base materials. In this way, strength, stiffness, electrical and thermal conductivity, hardness and dimensional stability, among other properties can be tailored to the required values[1]. Several studies have been reported on the mechanical and morphological properties of polymeric systems[2]. Stelescu[3] investigated the mechanical properties of EPDM/PVC blends with special reference to the crosslink agents and found that the properties depend upon the vulcanizing system used. Rattanasupa et al.[4] investigated the influence of vulcanization system on the mechanical properties of $CaCO_3$ filled vulcanizates and discovered that the mechanical properties increased with sulphur concentration.

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The objective of the present work is to investigate the effect of different cross-linking systems on the morphology and mechanical properties of EPDM/PVC composites, with special reference to the amount of sulphur.

EXPERIMENTAL

Materials

Ethylene propylene diene monomer (EPDM) with an E/P ratio of 62/32 and a diene content of 3.92% (Herdilla Unimers, New Mumbai) and Poly vinyl chloride (PVC) (SigmaAldrich) were used. The additives such as sulphur, zinc oxide, stearic acid, and mercapto benzothiazyl disulphide (MBTS) used were of commercial grade. The mixing of EPDM with PVC in different ratios was done on a two roll mixing mill (150 x 300 mm), with a nip gap of 1.3 mm and a friction ratio 1 : 1.4. The roll mill was provided with a metal tray under the roll collect dropping from the mill. First the process was mastication. This was done to break the long chain of bonds in rubber matrix. The rubber becomes a perfectly homogeneous mass, capable of being made into sheets after the addition of chemicals. The process involves passing rubber 3-4 times with a nip gap of 4 mm, 2 mm and 1mm successively. The EPDM was masticated for two minutes and PVC powder then added. After 4 minutes, other ingredients were added in the following order: zinc oxide, stearic acid, MBTS and sulphur. The processing time after the addition of each component added was about 2 minutes.The compounded composites were compression moulded at 170^{o}C for optimum cure time using a hydraulic press having electrically heated plates, under a load of 5 MPa to get the tensile sheets (mould dimension : 150 x 150 x 2 mm^3).

Investigation of mechanical properties

The test specimens were punched out from the moulded sheets using a die. Tensile strength tests of composite samples were conducted on computerized Universal Testing Machine (Tinius Olsen H10KS USA). The tensile strength and elongation at break were calculated using the equation,

Tensile strength = Load failure / Cross sectional area

Elongation at break = Displacement at failure / Effective gauge length x 100

Morphological studies

The samples for Field Emission Scanning Electron Microscopy (FESEM) were prepared by cryogenically fracturing them in liquid nitrogen. They were sputter coated with gold and morphology examination were performed on a scanning electron microscope (JEOL-JS IN-T330-A-SEM; ISS Group, Whittington, Manchester, U.K).

RESULTS AND DISCUSSION

Cure characteristics from Rheometric data

The curing behaviour of the composites was studied by a Monsanto rheometer (R-100) at a cure temperature of 170^{o}C. The initial decrease in torque is due to the softening of the matrix. Torque then increases due to the formation of C-C cross-links between the macromolecular chains and thereby exerting greater resistance to the rotation of Brabender mixing rotors. The leveling off is an indication of the completion of the curing process. The maximum torque (M_H) is a measure of crosslink density and the stiffness of the matrix. Fig. 1 shows the rheograph of 100/5 EPDM /PVC composite vulcanized by three cross-linking systems. Cure characteristics of 100/5 EPDM/PVC composites cured by different cross-linking systems are given in Table 1.

Table 1: Cure characteristics of 100/5 EPDM/PVC composites cured by different crosslinking systems

Sample	M_{90} (dNM)	T_{90} (min)	T_2 (min)	M_2 (dNM)	M_H (dNM)	M_H-M_2
Sulphur cured	3.2783	28.5	8.4	0.752	3.6425	2.8505
DCP cured	5.484	12.8	5.484	0.6445	6.0933	5.4488
Mixed	5.528	24	1.2333	0.7812	6.1422	5.3610

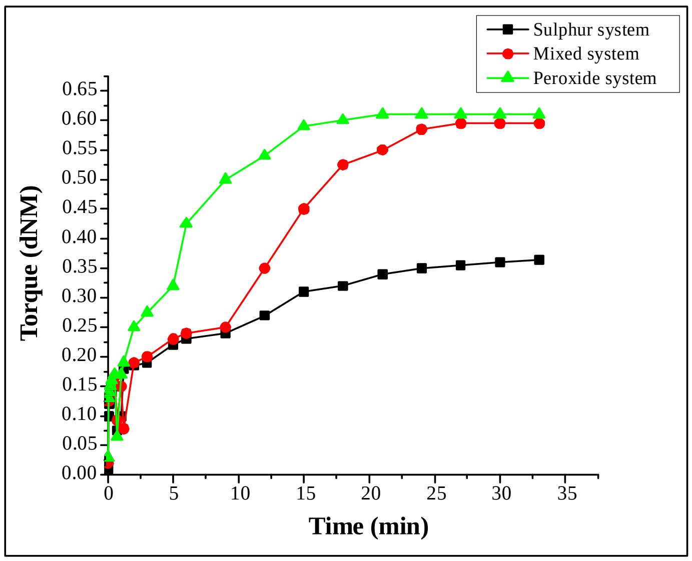


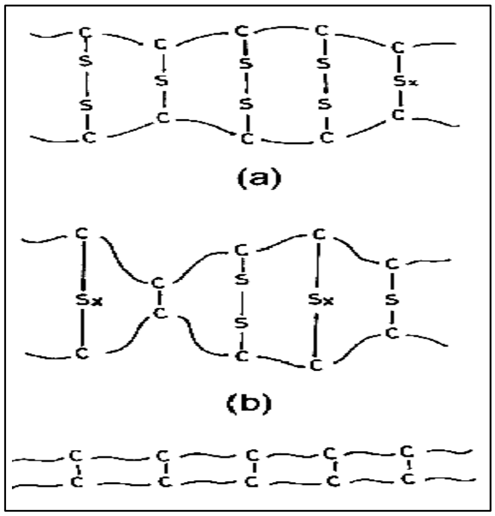
Fig. 1: Rheograph of different cross linked 100/5 EPDM/PVC composites

The M_H-M_2 values are higher in composites vulcanized with peroxide than those vulcanized with sulphur. The stable and rigid C-C cross-links introduced by the free radical mechanism in peroxide vulcanization contribute significantly to the high M_H-M_2 values[5].

The sulphur cured system exhibited the longest cure time. The increase in cure time for sulphur can be attributed to the low efficiency of EPDM when vulcanized with sulphur system, since EPDM rubber has low diene content[6]. The chemical reaction consisting in the addition of sulphur to the double bonds of the rubber molecules are always involved in the vulcanization of rubber with sulphur, which constantly forms the three dimensional networks. For peroxide curing, the free radical produced by peroxide is the driving force for peroxide cross-linking, which is much faster than sulphur cure. The effect of cross-linking system on mechanical properties of EPDM/PVC composites are given in Table 2. Among the different vulcanizing systems, the sulphur system shows the highest tensile strength when compared to peroxide system due to the flexible polysulphidic linkage. The young's modulus is higher for DCP cured samples than sulphur cured composites. Also, the DCP cured system showed lower elongation at break compared to sulphur cured system due to the rigid C-C crosslinks between the macromolecular chains in the DCP system. The nature of different networks formed by crosslinking using sulphur, peroxide and mixed systems is given in Fig. 2. The mono, di and polysulphidic linkages in sulphur system impart high chain flexibility to the polymer network. In the DCP system, only rigid C-C linkages are present and in mixed system, all these mono, di, polysulphidic and C-C linkages are present.

Table 2: Effect of crosslinking system on mechanical properties of EPDM/PVC composites

Sample	Young's modulus (MPa)		Tensile srenght (MPa)		Elongation at break (%)	
EPDM/PVC	**Sulphur**	**DCP**	**Sulphur**	**DCP**	**Sulphur**	**DCP**
100/2.5	2.11	2.24	1.45	1.14	420	117
100/5	2.44	2.49	1.4	1.15	402.77	88
100/7.5	2.86	2.36	1.48	1.4	400.17	194
100/10	3.11	2.21	1.20	1.04	211.21	54



(c)

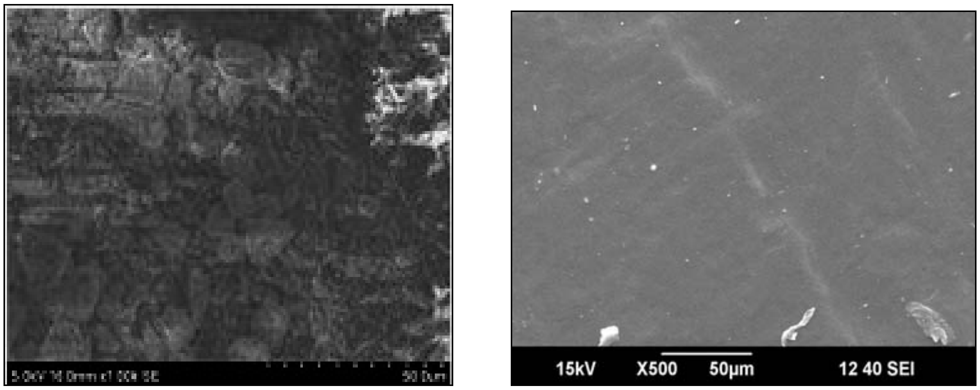
Fig. 2: Schematic representation of different networks formed : (a) Sulphur system, (b) Mixed system and (c) DCP system

Table 3 shows the effect of concentration of sulphur on mechanical properties of sulphur cured EPDM/PVC composites. It can be seen that tensile strength increases with increase in sulphur concentration, in all the samples. Result for tear strength also exhibits a similar trend. The introduction of crosslinks into the elastomer phase is responsible for enhancement of these properties. The crosslink density increases with increase in sulphur concentration. This means that the number of the individual macromolecular chains increases, albeit they become shorter, stiffer and require more energy to cause failure[7]. The incorporation of sulphur also increases the Young's modulus. It can be seen that the elongation at break value, Eb, increases with sulphur concentration.

Table 4: Effect of concentration of sulphur on mechanical properties of EPDM/PVC composites

Composite	Tensile strenght (MPa)		Young'modulus (MPa)	
EPDM/PVC	**S = 2 phr**	**S = 3 phr**	**S = 2 phr**	**S = 3 phr**
100/2.5	1.13	1.45	1.78	2.11
100/5	1.19	1.4	1.94	2.44
100/7.5	1.25	1.48	1.96	2.86
100/10	0.88	1.20	1.46	3.11

Figure 3 shows Scanning Electron Micrographs of 100/10 EPDM/PVC composites cross-linked with sulphur and peroxide. Figure clearly shows the PVC domains that distributed in the EPDM matrix. Here, due to the improvement in filler dispersion, the DCP cured composite displays significantly finer morphology[8]. The domain size of the dispersed phase was found to decrease when going from sulphur to DCP system [9].



(a) **(b)**

Fig. 3: Scanning electron micrographs of 100/10 EPDM/PVC composites; (a) Sulphur cured and (b) Peroxide cured

REFERENCES

1. H. Salmah, C. M. Ruzai di and A. G. Supri, J. Phys. Sci., **20(1)**, 99 (2009).
2. Nina Vranjes and Vesna Rek, Macromolecular Symposia, **258**, 90 (2007).
3. Maria-Daniela Stelescu, Macromolecular Symposia, **263(1)**, 70 (2008).
4. Bussaya Rattanasupa, Wirunya Keawwattana and Kasetsart, J. Nat. Sci., **41**, 239 (2007).
5. C. K. Radhakrisnan, M. Padmini, A. Sujith and G. Unnikrishnan, Progress in Rubber, Plastics and Recycling Technology, **23(2)**, 83 (2007).
6. W. Arayapranee and G. L. Rempel, Int. J. Mater. Struct. Reliability, **5(1)**, 1 (2007).
7. H. Ismail and Salmah M. Nasir, Polymer Testing, **20**, 819 (2001).
8. R. Asalatha, M. G. Kumaran and Sabu Thomas, European Polymer J., **35**, 253 (1999).
9. M. Padmini, C. K. Radhakrishnan, A. Sujith, G. Unnikrishnan and E. Purushothaman, J. Appl. Polym. Sci., **101**, 2884 (2006).