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Influence of Mixed Sulfur/Peroxide Curing System on Properties of Thermoplastic Vulcanizates based on Natural Rubber/Polypropylene Blend

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Abstract

Influence of mixed sulfur/peroxide curing system on properties of thermoplastic vulcanizates (TPVs) based on natural rubber/polypropylene blends was studied. Even though the mixed sulfur/peroxide curing system did not much affect on the tensile strength, elongation at break and swelling behavior, it clearly influenced on tension set, gel content, morphology and rate of mass change during degradation of the TPVs. Changes in those values and behaviors of the TPVs were not only a consequence of vulcanization reaction generated by sulfur and peroxide but also a result of tendency of the PP to degrade in the presence of peroxy radicals. Blending the TPVs by using the mixed sulfur/peroxide system care has to be taken.

1. Introduction

Thermoplastic vulcanizates (TPVs) are materials that well known and make benefit in a broad industries due to their process and property. Not only the formulation that property of the TPV mainly relies, but it also depends on the crosslink density of elastomer phase. The latter is very important because fully vulcanization of the elastomer phase yields the TPVs with very fine elastomer particles distributed in the thermoplastic matrix and hence, increasing in service properties of the TPVs, such as modulus, strength, set property and etc. [1,2] Many researchers have done and investigated the effect of types of vulcanization on properties of the TPVs for example curing by sulfur, peroxide, phenolic resin. [3-10] Mixed sulfur/peroxide curing system is also studied and they found such great advantages of this system [11-14] However, non of the literature focuses on ratios between sulfur and peroxide yet and it is very interesting point to be consider especially in TPVs having polyolefins as thermoplastic matrix. As we know peroxide generates crosslinking in rubber molecules, however, in the presence of polyolefins peroxide can cause crosslinking also in polyethylene or make polypropylene degradation together with a decomposition of smelly by product. These reactions occur in the same time and they are competitive resulting in complicated properties. [8-10]

In this work, authors would like to investigate effect of various ratios of sulfur and peroxide in the mixed sulfur/peroxide curing system on properties (i.e., mechanical, thermal, morphological properties, gel content and swelling behavior) of TPVs and focus mainly on the TPVs based on NR/PP blend at fixed blend ratio of 60/40.

2. Experimental

2.1 Materials

NR (ribbed smoked sheet No.3, RSS3) was received from Khok-Pho Farmer Co-operation, Pattani, Thailand. PP used in this study was an injection-molding grade P700J with MFI of 12 g/10min at 230°C and specific gravity of 0.91, manufactured by the Thai Polypropylene Co., Ltd.,Rayong, Thailand. Naphthenic oil used as a processing aid was manufactured by Panjin Nynas North Bitumen Co., Ltd, China. Hydroxymethylol phenolic resin (HRJ-10518) used to prepare phenolic modified polypropylene (PhHRJ-PP) compatibilizer was manufactured by Schenectady International Icn, Freeport, USA. Stannous chloride ($SnCl_2.2H_2O$) used as a catalyst for preparation of the compatibilizer was manufactured by Ajax Finechem Ltd. (NSW, Australia). Dicumyl peroxide used as a vulcanizing agent was manufactured by Wuzhou International Co., Ltd., China. Trimethylolpropane trimethacrylate (TMPTMA) used as co-agent for peroxide cured system was manufactured by Nantong Litian Chemicals Co., Ltd., China. Zinc oxide and stearic acid used as an activator were manufactured by Global Chemical Co., Ltd., Samutprakarn, Thailand and by Imperial Chemical Co., Ltd., Pathumthani, Thailand, respectively. Sulfur used as a vulcanizing agent was manufactured by Ajax Chemical Co., Ltd., Samutprakarn, Thailand. MBTS used as an accelerator was manufactured by Flexsys (USA). Phenol type antioxidant, Wingstay® L was manufactured by Flexsys (USA). Xylene used as a solvent to extract the PP phase in the TPVs for morphological characterization and gel content determination was manufactured by Labscan Co., Ltd., Republic of Ireland.

2.2 Preparation of TPVs

The NR was firstly compounded with rubber chemicals using a two-roll mill at room temperature, with the formulation as shown in Table 1. The 60/40 NR/PP TPVs were then prepared via dynamic vulcanization during melt mixing using an internal mixer at 160°C. The PP was firstly pre-heated for 10 min in the mixing chamber without rotation. It was then melted for 2 min at a rotor speed of 60 rpm before PhHRJ-PP compatibilizer (at a loading level of 7 wt% of PP) was incorporated and continuously mixed for 1 min. After that, the NR compounds with different ratio of mixed sulfur/peroxide vulcanizing systems were added. Blending process was

continued for another 7 min to complete the dynamic vulcanization process.

Table 1. Chemical used for NR compounds

Chemicals	Quantities (phr)				
	9:1	7:3	5:5	3:7	1:9
RSS No.3	100	100	100	100	100
Stearic acid	2	2	2	2	2
ZnO	5	5	5	5	5
Wingstay L	1	1	1	1	1
Naphthanic oil	30	30	30	30	30
Sulfur	1.8	1.4	1	0.6	0.2
MBTS	0.9	0.7	0.5	0.3	0.1
DCP	0.1	0.3	0.5	0.7	0.9
TMPTMA	0.2	0.6	1	1.4	1.8

2.3 Mechanical testing

The dumbbell shaped specimens of the TPVs used for tensile testing were prepared by an injection molding machine. The tensile test was performed at 25±2°C at a crosshead speed of 500 mm/min according to ASTM D412 (2000). The instrument used was a Hounsfield Tensometer, model H10 KS manufactured by the Hounsfield Test Equipment Co., Ltd., UK.

2.4 Morphological studies

Morphological characterization was performed using a Leo scanning electron microscope; model JSM-5200, manufactured by Jeol Co., Ltd., Japan. The TPVs were cryogenically cracked in liquid nitrogen to avoid any possibility of phase deformation. The PP phase was later extracted by immersing the fractured surface in boiling xylene for 10 min. The samples were later dried in a vacuum oven at 40°C for 3 hrs. The dried surfaces were gold-coated before characterization by SEM.

2.5 Oil and chemical resistance

Oil and chemical resistance of the TPVs were tested according to ASTM D471 using ASTM oil No.3 and a mixture of benzene and toluene (50:50 v/v). The TPVs specimens in a rectangular form have dimensions of 10 x 10 x 2 mm were weighed and immersed in the test liquids at room temperature for 166 hrs. The test specimens were removed from the liquids and blotted with tissue paper to remove excess solvent from the surface before weight. The degree of swelling was calculated as follows:

$$\text{Degree of swelling (\%)} = \frac{W_2 - W_1}{W_1} x100$$

where W_1 and W_2 are weights of the specimen before and after immersing in the test liquid, respectively.

2.6 Gel content

1 g of the TPVs specimens were refluxed in 50 ml of xylene at 110-120°C for 3 hrs. The samples were later moved out from the hot xylene and dried at 40°C for 36 hrs. They were then cooled to ambient temperature before weight. Their final weights were taken to determine the gel content according to the following equation:

$$\text{Percent of gel content (\%)} = \frac{W_2}{W_1} x100$$

where W_1 and W_2 are original and final weights of the specimen, respectively.

2.7 Thermogravimetric analysis

Derivative thermogravimetry was carried out by using a Perkin-Elmer TGA7, manufactured by Perkin Elmer Co., Ltd., USA. The samples were scanned from room temperature to 800°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere. Result was then captured by a ConpuGraph acquisition system.

3. Result and discussion

Effect of the mixed sulfur/peroxide curing system on mechanical properties (i.e., tensile strength, elongation at break and tension set) and gel content of the 60/40 NR/PP TPVs are investigated. It is seen that all various ratios of the mixed curing system exhibited more or less the same values of both tensile strength and elongation at break as summarized in Table 2. They also exhibited similar trend of stress-strain curves (Fig. 1) of thermoplastic material with very high initial modulus and defined yield point. However, in consideration of area under the stress-strain curve which refers to toughness of material, TPVs which were crosslinked with peroxide dominant system (i.e., 3:7 and 1:9) showed lower toughness than TPVs cured with sulfur dominant system. This might be attributed to synergistic effect of vulcanizing chemicals especially by peroxide. Even though chemical bond of C-C generated by peroxide is stronger bond energy than C-S_x-C bond of sulfur curative and does provide higher toughness of the TPVs, peroxide also causes degradation of polypropylene molecules in the same time through the well known mechanism of β-scission. [8-10] These were competitive and be a reason of a bit lower of toughness in the peroxide dominance cured TPVs.

Various ratios of the mixed sulfur/peroxide curing system played an effect on tension set property of the TPVs. Increasing the ratios of peroxide to dominate, the TPVs with better tension set property achieved. This was due to most of crosslink bonds in the TPVs were the C-C bond which gave higher bond energy than C-S_x-C and yielded better set property of molecules after taking force out.

Table 2. Mechanical properties and gel content of the TPVs with various ratios of mixed sulfur/peroxide curing system.

Properties	Sulfur/peroxide ratios				
	9:1	7:3	5:5	3:7	1:9
T.S. (MPa)	9.31	9.44	9.70	9.21	9.36
E.B. (%)	250	245	264	249	236
Tension set (%)	55	56	55	51	51
Gel content (%)	45.6	49.2	50.2	52.8	46.0

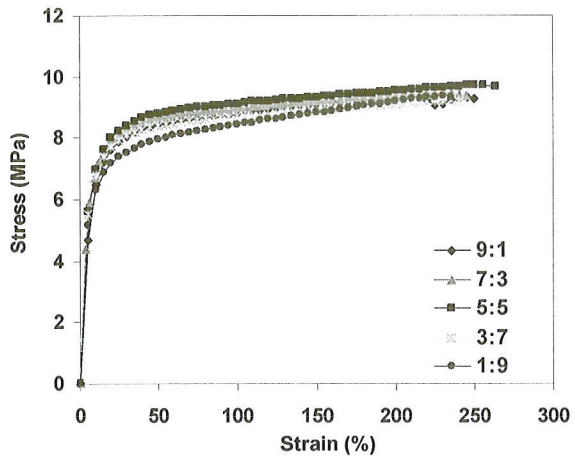

Fig.1 Stress-strain curves of the TPVs with various ratios of mixed sulfur/peroxide curing system.

Gel content of insoluble phase in the TPVs was indirectly measured by reflux the test specimens in hot xylene for several hours and the data obtained are given in Table 2. Actually, the gel content of the TPVs can be used to imply to the interfacial reaction between the phases and the crosslink density of the elastomer phase. As in this study we fixed equal amount of PhHRJ-PP compatibilizer at 7% wt by wt of PP, the gel content then be straightforwardly to result of influence of curing system. The gel content of the TPVs increased with increasing ratios of peroxide to dominate and reached the highest value at a ratio of 3:7. These phenomena could be explained by the effect of the vulcanization. As described before, types of chemical bonds occurred in the TPVs combined among C-C, C-S-C, C-S-S-C, and C-S_x-C ($2<X<8$) linkages generated from those two curatives. Further blend by changing ratios of the mixed system from the sulfur dominance (i.e., 9:1) to the peroxide dominance (i.e., 1:9), the crosslink bonds then altered from a rich side of low crosslink bond energy and long crosslink bridges given by sulfur cure to be a rich side of high crosslink bond energy, more stable and short crosslink bridged occurred by peroxide instead. Hence, the increasing trend of the gel content was observed. Continually increasing ratio of the mixed sulfur/peroxide curing system from 3:7 to 1:9, however, an in-turn result of the gel content was obtained. This is because of some of peroxy radicals tended to end up in the PP phase and did degradation of the PP molecules.

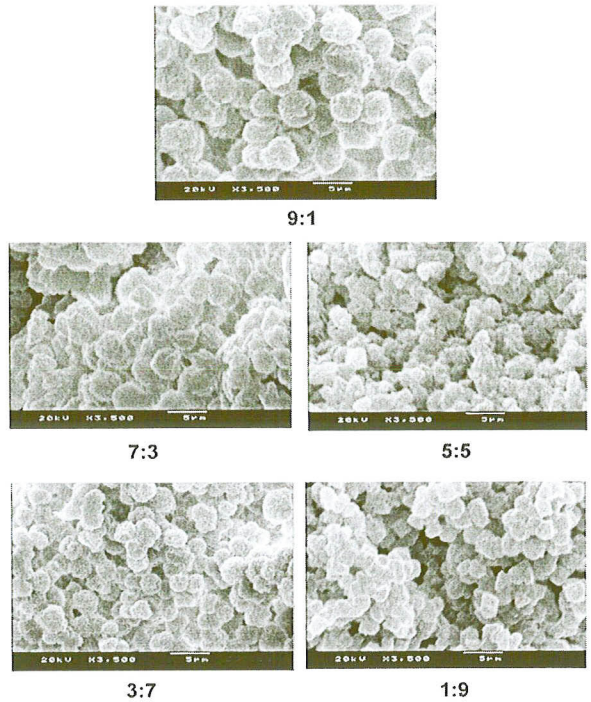

Fig.2 SEM micrograph of the TPVs with various ratios of mixed sulfur/peroxide curing system.

Fig.2 shows the SEM micrograph of the TPVs. The hot xylene-etched fracture surfaces after extraction of the PP phase were measured. For all TPVs, two-phase morphology was clearly observed which micron size spherical domains of the dispersed vulcanized NR phase in the PP matrix. However, it has been seen that ratios of the mixed vulcanization system played a sharp effect on the elastomer particles size. The TPVs cured with sulfur dominance exhibited the largest elastomer particles dispersing in the PP matrix. Increasing proportion of peroxide the elastomer particles size decreased. The TPVs showed the smallest particles size at the ratio of the mixed sulfur/peroxide curing system of 1:9. These were attributed to the strength of chemical bond generated by peroxy radicals will make the elastomer more stiff than sulfur system did. Under high shear force of mixing, the peroxide vulcanized elastomer then easily broke down into smaller size. Even the TPVs with formulation of 1:9 presented the smallest elastomer particles size the mechanical properties did not exhibit the best. This was due to the degradation of PP matrix can be occurred in the presence of peroxide as described before.

Degree of swelling of the TPVs in ASTM oil No.3 and a mixture of benzene and toluene (50:50 v/v) are shown in Fig. 3. There was very less influence of the ratio of the mixed sulfur/peroxide curing system on the degree of swelling of the TPVs. They all showed the same values of the degree of swelling and can not interpret in term of chemical bond and crosslink density.

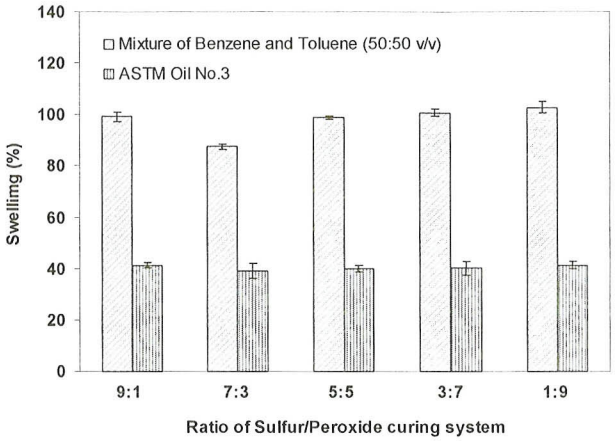

Fig.3 Degree of swelling of the TPVs with various ratios of mixed sulfur/peroxide curing system.

DTA thermograms of the TPVs with formulation of 9:1, 5:5, and 1:9 are shown in Fig. 4. All TPVs exhibited two transition steps of the NR and the PP phases with similar initial weight loss temperatures according to they have designed for the fixed blend component and blend proportion (i.e., 60/40 NR/PP). In comparison among derivative weight losses of those three selected TPVs, however, there was an effect of the ratios of mixed sulfur/peroxide curing system on rate of mass change. The first and the second transition steps responded to the degradation of the PP phase and the NR phase in the TPVs which showed maximum degradation temperature of approximately 390°C and 470°C, respectively. It was found that the TPVs cured with peroxide dominance, 1:9 exhibited the highest rate of the PP degradation (i.e., 10 % weight/min). Whiles the TPVs cured with sulfur dominance like 9:1 showed the lowest rate. These attributed to types of chemical bond, crosslink density and PP degradation which formed and competed in the rubber and plastic phases during mixing. It must balance among them when prepare the TPVs with the mixed sulfur/peroxide curing system in order to get the TPVs with desirable properties.

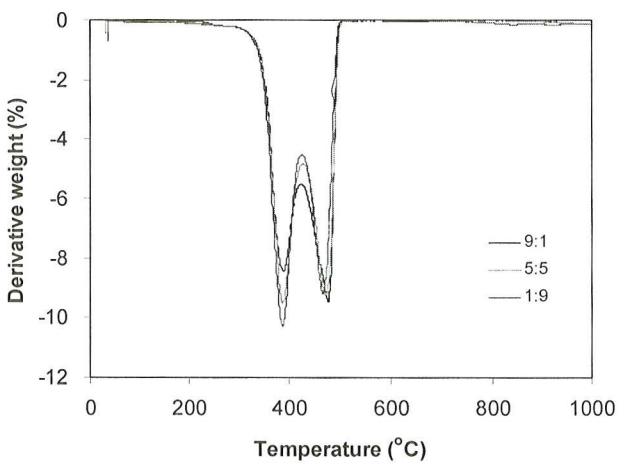

Fig. 4 DTA thermograms of the TPVs with various ratios of mixed sulfur/peroxide curing system.

4. Conclusions

The dynamically cured 60/40 NR/PP TPVs with various ratios of mixed sulfur/peroxide curing system were prepared and later investigated their mechanical, thermal, morphological properties, gel content and swelling behavior. Even though the mixed sulfur/peroxide curing system did not much affect on the tensile strength, elongation at break and swelling behavior, it clearly influenced on tension set, gel content, morphology and rate of mass change during degradation of the TPVs. Changes in those values and behaviors of the TPVs were not only a consequence of vulcanization reaction generated by sulfur and peroxide but also a result of tendency of the PP to degrade in the presence of peroxy radicals. Blending the TPVs by using the mixed sulfur/peroxide system care has to be taken.

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