



Influence of Blend Mode of Extender Oil on the Properties of EPDM/PP-Based Thermoplastic Vulcanizates

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이피디엠/폴리프로필렌 열가소성 경화물에서 오일의 블렌드 방식이 경화물의 물성에 미치는 영향

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ABSTRACT : Influence of blend mode of extender oil on the properties of thermoplastic vulcanizates (TPVs), based on an ethylene-propylene-diene copolymer (EPDM) and a polypropylene (PP), was studied. The EPDM/PP TPVs were prepared in an open roll mill using two different modes in blending sequence of paraffinic oil and phenolic curative, *i.e.*, Oil-Cure and Cure-Oil modes. Degree of cross-linking by gel fraction and properties such as hardness, tensile strength, elongation at break, and melt flow rate were investigated as a function of extender oil content for the two modes. Little influence of the blend mode of extender oil on the degree of cross-linking and mechanical behaviors was observed. However, the use of Cure-Oil mode in the preparation of EPDM/PP TPVs resulted in a marked increase in the level of processability as reflected by melt flow index, as compared to the use of Oil-Cure mode.

요약 : 이피디엠/폴리프로필렌 열가소성 경화물을 오일의 배합 순서를 달리한 두 가지 방식(오일 블렌드 후 가교 방식과 가교 후 오일 블렌드 방식)으로 제조하여 가교도(겔분율), 경도, 인장강도, 신율, 용융흐름지수 등을 조사, 오일의 블렌드 방식이 열가소성 경화물의 물성에 미치는 영향을 알아보았다. 오일의 블렌드 방식에 따른 두 경화물의 가교도와 기계적 물성의 차는 크지 않았으나, 가공성에 있어서는 가교 후 오일 블렌드 방식으로 제조한 경화물의 용융흐름지수가 현저히 증가한 결과를 보였다.

Keywords : thermoplastic vulcanizates, EPDM, polypropylene, extender oil, blend mode

I. Introduction

Thermoplastic elastomers are polymer materials that combine the processing characteristics of thermoplastics with the elastic and mechanical properties of vulcanized rubbers. An important class of thermoplastic elastomers is thermoplastic vulcanizates (TPVs). TPVs are produced by dynamic vulcanization of blends containing a thermoplastic and an elastomer.¹⁻⁵ The effect of the dynamic vulcanization of elastomer/plastic blends is to produce compositions which have the improvements in permanent set, ultimate mechanical properties, hot oil resistance, melt strength, and thermoplastic fabricability. In addition, these materials are readily reground and recycled.⁶ With thermoset rubbers, neither reground nor recycle is possible without severe chemical modification of the

materials.

In many applications thermoplastic elastomers are able to replace thermoset rubbers because they offer equivalent or better performance, generally with a significant cost saving due to part fabrication cost differences.⁴ In order to replace the thermoset rubbers, TPVs should become more rubber-like in properties and so an increase in amounts of rubber is required. By increasing the rubber content, however, processing properties inherent in the TPVs may be lost. In such cases, incorporation of the processing or extender oil is required to improve processability of the TPVs.

Extender oils are compatible hydrocarbon oils employed in substantial quantities as a cost-reducing liquid filler in rubber industry. The oils can improve the resistance to oil swell, heat stability, hysteresis and permanent set as well as the economic benefit and the processing properties of the compositions. The effect of the oils on processability is complex since this will

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not only involve a reduction in compound viscosity but also extrudate smoothness, power consumption during compounding, and shaping and filler dispersion.

Elastomers are complex viscoelastic materials and their mechanical response behavior strongly depends on the loading procedure, loading history, time and temperature.^{7,8} While there has been considerable attention given to the loading procedure of curing agent in the polyolefin/EPDM blends,^{9–12} there has been little interest in mixing sequence of extender oil. In this study, we have prepared thermoplastic vulcanizates of EPDM and PP in a roll mill using two different modes in loading sequence of extender oil. The changes of cross-link density, and mechanical and processing properties of the TPVs prepared using the two modes were investigated and compared.

II. Experimental

1. Materials

Materials included in this work are listed in Table 1. The ethylene-propylene-diene copolymer (EPDM) with ethylidene norbornene as a termonomer and the polypropylene (PP) were commercially available grades. In the EPDM, 75 phr of oil was comprised in the base-polymer. The extender oil used was the same rubber-grade as paraffinic oil extended in the EPDM. The ingredients such as curatives and antioxidant were also used as received from the suppliers.

2. Preparation of TPVs

Compounding of the EPDM and PP with the extender oil and additives was carried out in an open roll mill (Kansai Roll, 8" Electric) at a temperature of 180 °C using two different modes. The extender oil loadings were selectively varied from 0 to 75 at 25 phr intervals, and the amounts of phenolic curative, zinc oxide, stearic acid were fixed with 5, 5, and 1 phr

based on the amount of base-polymer in the EPDM, respectively. Antioxidant was 0.2 phr of polypropylene weight.

The EPDM, PP, and additives except for the paraffinic oil and phenolic curative were preblended in the roll mill at 180 °C for 10 min. One mode was to mix the preblended EPDM/PP mixture with the oil for 10 min and then cure the EPDM in the oil-extended compound dynamically for another 10 min (Oil-Cure mode). The other mode was to dynamically cure the preblended mixture first and blend the dynamically cured compound with the oil afterward (Cure-Oil mode). Figure 1 shows a schematic diagram of the compounding procedure for the Oil-Cure and Cure-Oil modes.

3. Samples preparation

Samples from the appropriately compounded materials were prepared in a compression moulding machine (Nisshin Kagaku, HP-2000TS) under a pressure of 14.7 MPa and at a temperature of 200 °C for 10 min, then the sheets prepared were cut using a cutter (JIS No. 1). The test specimens were subsequently kept in an oven at 25 °C for 72 h.

4. Measurements

Mechanical tests were performed according to JIS K-6301 test method and five samples per formulation were tested. Tensile strength and elongation at break were measured on a tensile testing machine (Monsanto, Tensometer-10) with crosshead rate of 500 mm min⁻¹. Shore A hardness was determined using a durometer (Ueshima, HD-101N). The hardness was observed after 5 s of pressor foot contact. Mechanical properties of the TPV after hot-air aging were also measured. The aging study was carried out in an air-circulating oven at 135 °C for 168 h following the method described in ASTM D 573. Degree of cross-linking was described in terms of gel fraction. The gel fraction was determined by means of a typical extraction procedure of refluxing in boiling xylene for 3 h. The solution was subsequently filtered and the insolubles were combined and dried under vacuum at 140 °C to constant weight. The gel fraction was defined as the weight fraction of undissolved portion after making suitable corrections for the soluble and insoluble components.^{13,14} Processing property was evaluated as a melt flow index. The melt flow index was determined according to ASTM D 1238 using a melt flow tester (Toyoseiki, Melt Indexer) at 230 °C with a load of 10 kg.

III. Results and Discussion

1. Degree of cross-linking

Degree of cross-linking introduced during dynamic vulcan-

Table 1. Materials and Their Characteristics

Material	Characteristics	Grade
EPDM	Mooney viscosity ^a 63.0	KEP-980 ^b
	E/P= 70/30, ENB= 4.5% M _n = 1.2x10 ⁵	(Kumho Polychem)
PP	Melt flow index ^c 4.1	Y-130
	Density 0.90	(Honam Petrol. Chem.)
extender oil	d ₄ ¹⁵ = 0.893, VGC ^d = 0.817	EP-POIL
	Dynamic viscosity(40°C) 160	(Mobil Korea)
curing agent	Brominated phenol resin	SP-1056 (Schenelectady Chem.)

^aML1+8 120°C, ^binclude 75 phr of oil,

^cASTM D1238 (230°C, 2.16kg), ^dviscosity gravity constant.

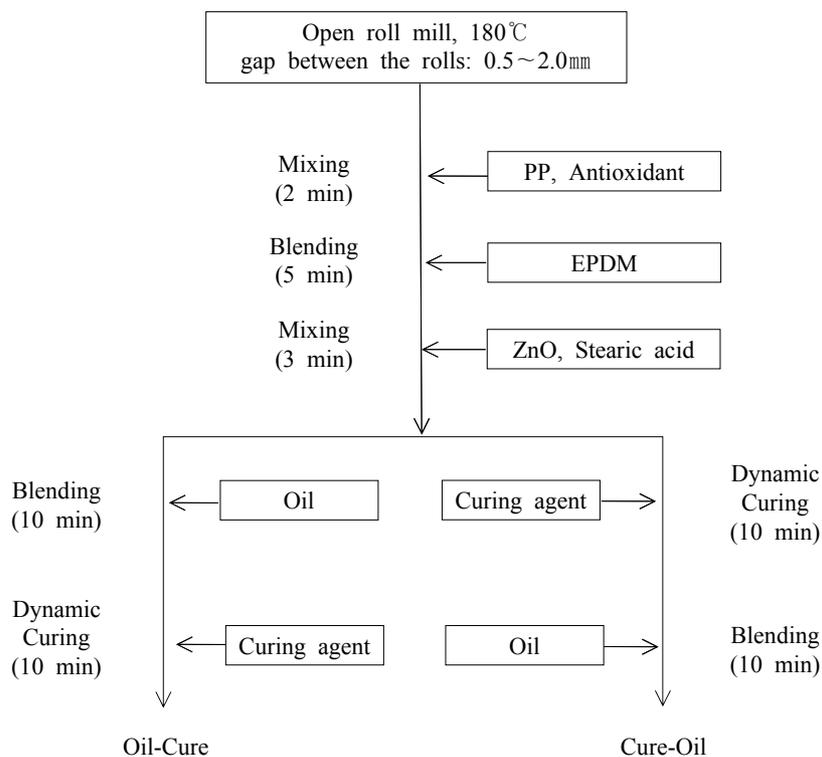


Figure 1. Schematic diagram of compounding procedure.

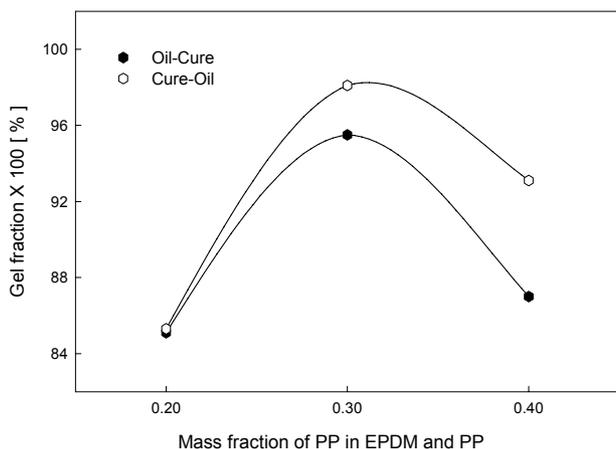


Figure 2. Gel fraction versus amount of PP in the EPDM/PP TPVs prepared using different blend modes for 50 phr of extender oil.

ization has been recognized as being important in determining properties of the resulting TPV.^{2,15} Figure 2 shows the gel fraction with the composition of EPDM and PP for the loading of 50 phr of extender oil. From this figure, it can be seen that the Oil-Cure materials have low gel fraction compared to the Cure-Oil ones. This indicates that a chemical cross-linking was hindered by the extender oil mixed before the addition of curing agent. The effects of the extender oil

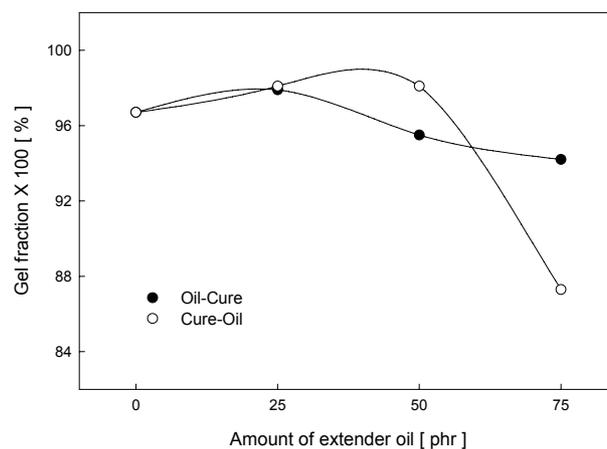


Figure 3. Gel fraction versus extender oil content for 70/30 EPDM/PP TPVs prepared using different blend modes.

contents on the gel fractions in 70/30 EPDM/PP TPVs prepared using the two modes are shown in Figure 3. The gel fraction of the EPDM increased to be a certain amount of oil due to the improved dispersion of curatives. However, the gel fraction decreased in the case of oil exceeded a critical amount, indicating that additional cross-linking in a partly cross-linked EPDM was reduced by significant amounts of extender oil.

2. Tensile property

Tensile strength and elongation at break of the TPVs with several compositions for the Oil-Cure mode are shown in Figure 4 and those for the Cure-Oil mode are shown in Figure 5. The values of tensile strength for the two modes decreased gradually with increasing amounts of extender oil. The 70/30 EPDM/PP TPVs for the composition ratio of EPDM/PP and the Cure-Oil samples for the blend mode of extender oil showed the higher tensile properties. These are due to the higher chemical cross-links in the corresponding samples and agree well with the gel fraction behaviors. In general, ultimate tensile properties are an inverse function of elastomer particle diameter and improve continuously as the chemical cross-link of the elastomer phase increases.^{6,16,17}

It is noted that, as shown in Figure 4, the vulcanizates provided ultimate elongation of 520% at 0 phr of extender oil, which decreased to 480% at 25 phr and then increased to 580% at 75 phr in the case of 70/30 EPDM/PP TPVs, representing a minima at intermediate oil contents in the Oil-Cure specimens. On the other hand, upon varying amounts of extender

oil in the Cure-Oil specimens, the ultimate elongations of 520, 690, 600, and 510% were obtained at 0, 25, 50 and 75 phr, respectively, showing convex upward elongation curves in Figure 5. These behaviors may be caused by a number of factors acting independently and simultaneously, including decreasing crystallinity of PP by blending with EPDM, mechanochemical degradation of PP, and chemical cross-linking of EPDM.¹² In addition to the above-mentioned factors, size and shape of dispersed phase, amount and location of extender oil, etc. may be included. In EPDM/PP/oil-based TPV,¹⁸⁻²⁰ the oil is generally believed to be predominantly absorbed by the EPDM phase. Some oil can reside in the amorphous region of PP phase. In this work, it would appear that in the Oil-Cure samples most oil was located in the EPDM phase because the dynamic curing was conducted after mixing the EPDM with the extender oil, whereas in the Cure-Oil samples some amounts of oil existed in an amorphous region of the PP phase and/or in a boundary between the EPDM phase and the PP phase because the extender oil was added to the partially cross-linked EPDM phase resulting from the dynamic curing. Even though this statement should need additional inves-

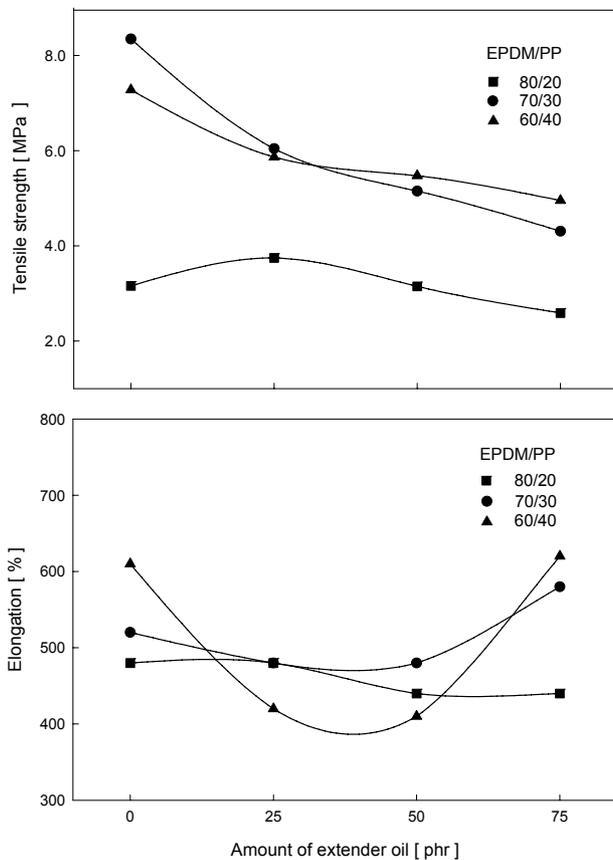


Figure 4. Effect of extender oil content on the tensile properties of EPDM/PP TPVs with various compositions for the Oil-Cure mode.

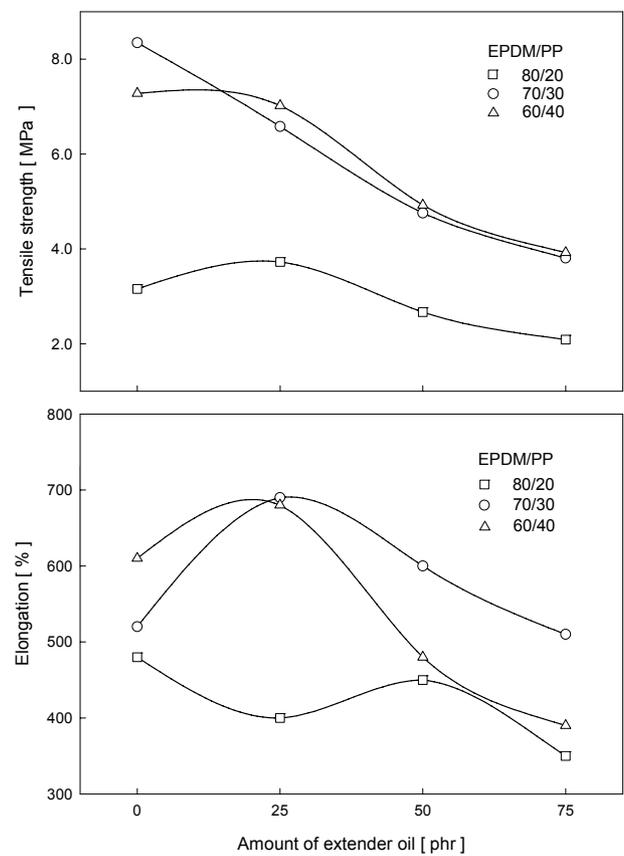


Figure 5. Effect of extender oil content on the tensile properties of EPDM/PP TPVs with various compositions for the Cure-Oil mode.

Table 2. Hardness Test Results

Blend Mode	EPDM/PP (wt./wt.)	Amount of extender oil (phr)			
		0	25	50	75
Oil-Cure	80/20	58	51	46	42
	70/30	75	68	63	57
	60/40	85	80	76	71
Cure-Oil	80/20	58	55	46	43
	70/30	75	69	64	60
	60/40	85	80	78	72

tigation, this distribution of oil over the EPDM and PP phases, together with other structural factors, would seem to lead to the variation of tensile property.

3. Hardness

The results of hardness testing are given in Table 2. As the amount of EPDM increased, the hardness of TPVs decreased. The decrease in hardness results from a rubbery nature of the EPDM. It is generally observed that as the ratio of EPDM to PP increases, the layer of PP between the EPDM phases becomes progressively thinner. Consequently, the TPV will become more rubber-like in properties, and less like a thermoplastic. Thus it will have a lower hardness and modulus, lower set, and a more linear tensile stress-strain curve.⁴ The hardness value also decreased straightforwardly with increasing amounts of extender oil. This is due to a plasticizing effect of extender oil.^{19,21,22} When the blend mode of extender oil was varied, however, the hardness was essentially unchanged. It is known that polypropylene/EPDM or ethylene-propylene rubber (EPR) combinations are especially useful as replacements for general-purpose vulcanized rubbers such as natural rubber, styrene-butadiene rubber, and EPDM.²³ To replace the thermoset rubbers, TPVs have to become a products having a lower hardness. It is considered that a composition ratio of EPDM/PP and amount of extender oil may be adopted to control the hardness of TPVs.

4. Thermal aging

Polymeric materials like rubbers usually suffer from oxidation degradation during processing, storage and end-use. Oxidation of rubber can result in loss of physical properties such as tensile strength, elongation, flexibility, and so on. In the case of a partly cross-linked PP/EPDM blends,²⁴ the samples showed a remarkable decrease in the tensile strength and elongation at break due to one year's exposure outdoors but the hardness and tensile modulus increased to some extent caused by desorption of oil during the exposure period. In

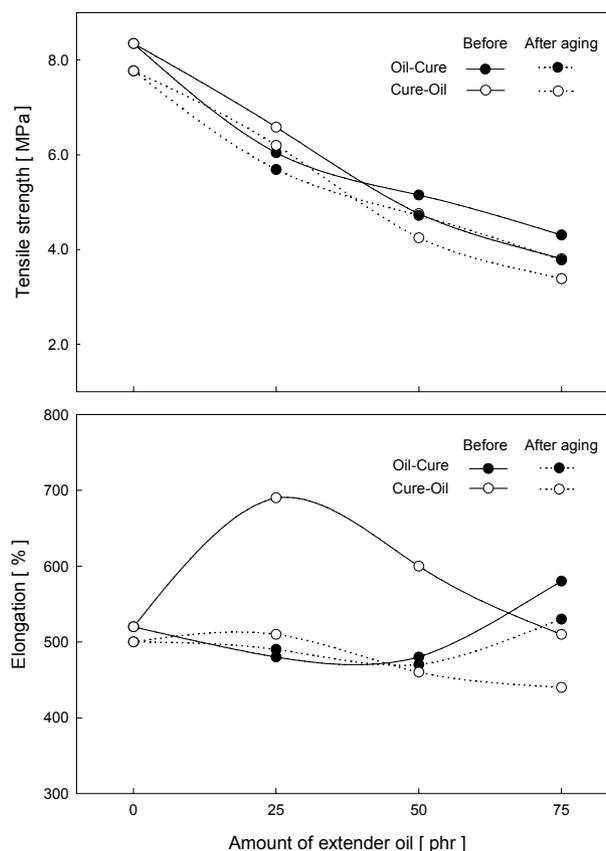


Figure 6. Variation of tensile properties as a function of extender oil content for 70/30 EPDM/PP TPVs before and after thermal aging.

this study, the samples prepared using the two modes were subjected to oxidation in an air-circulating oven at 135 °C for 168 h and mechanical properties were measured. The estimated tensile properties for the specimens before and after thermal aging are shown as a function of extender oil contents in Figure 6. Tensile strength of the original materials for 70/30 EPDM/PP TPVs varied from 8.35 to 3.81 MPa. After the exposure, the tensile strength values of all the specimens for the two modes decreased in similar amounts, about 0.35–0.53 MPa. The values of elongation at break in the Oil-Cure specimens decreased slightly as a result of the hot-air aging. However, the Cure-Oil specimens showed the marked decrease of 180, 140, and 70% for 25, 50, and 75 phr of extender oil, respectively. The reason may be that the oil located in an interface between the EPDM and the PP and/or in an amorphous region of PP migrated onto the surface of the TPVs during thermal aging and this should cause the decrease in the elongation values. Figure 7 is the hardness values both before and after aging for the Oil-Cure and Cure-Oil samples. After aging, there was no significant difference in the hardness for all the samples.

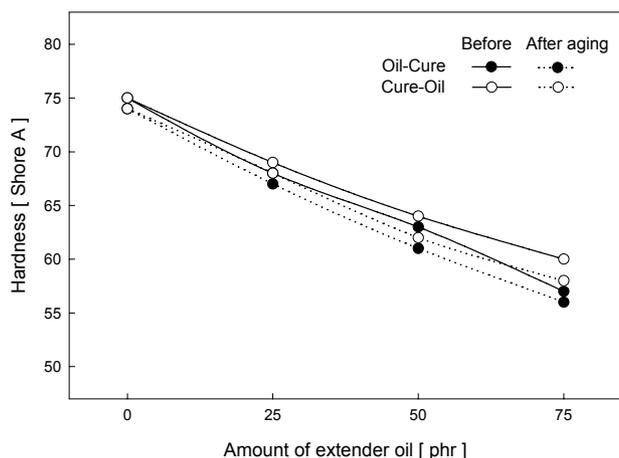


Figure 7. Variation of Shore A hardness as a function of extender oil content for 70/30 EPDM/PP TPVs before and after thermal aging.

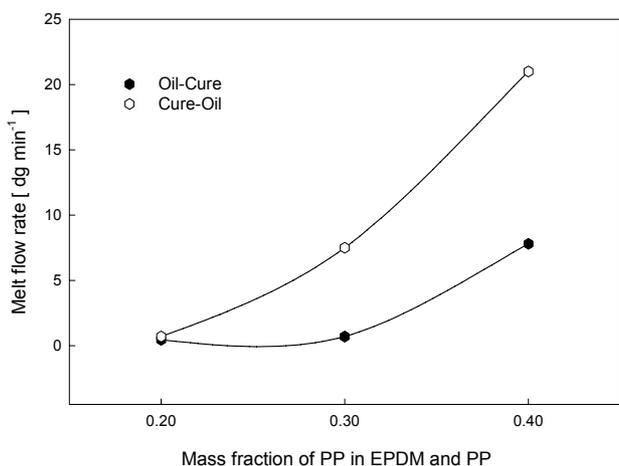


Figure 8. Melt flow rate versus amount of PP in the EPDM/PP TPVs prepared using different blend modes for 50 phr of extender oil.

5. Processability

Figure 8 shows the variation of melt flow rate with the composition ratio. The melt flow rate increased by increasing the amount of PP. This increase is attributed to the thermoplastic nature of PP. The effect of the amount of extender oil on the processing property of 70/30 EPDM/PP TPVs is shown in Figure 9. The melt flow rate of the Cure-Oil sample increased with increasing amounts of extender oil. The reason may be that some oil located in a region between the cross-linked polymer phases caused the increased processing property by a plasticizing effect. Whereas, the melt flow rate of the Oil-Cure sample was low and the amount of oil had little effect on the processing property. This may be that most oil

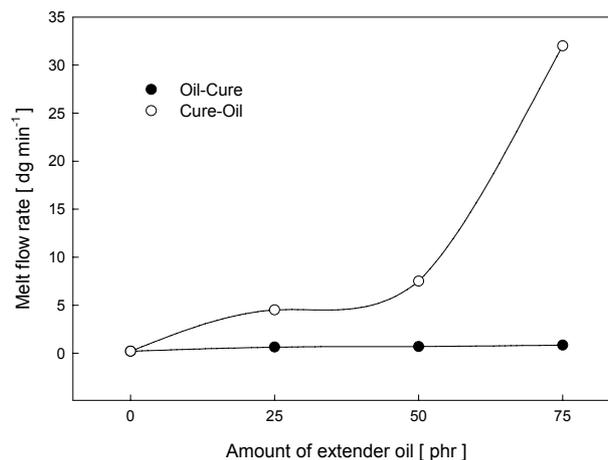


Figure 9. Melt flow rate versus extender oil content for 70/30 EPDM/PP TPVs prepared using different blend modes.

was located in the cross-linked rubber phase, hence the extender oil had no impact as a plasticizer between the cross-linked polymer phases. The processability data indicate that the sequence of extender oil addition has a significant effect upon the extent of melt flow index of the TPV.

A summary of the properties of 70/30 EPDM/PP TPV is given in Figure 10. Little influence of the blend mode of extender oil on the degree of cross-linking and mechanical behaviors is observed, as shown in Figure 10. It can be also seen, however, that the use of Cure-Oil mode in the preparation of EPDM/PP TPVs results in a marked increase in the level of processability as reflected by melt flow index, as compared to the use of Oil-Cure mode.

IV. Conclusions

The EPDM/PP TPVs were prepared using two different modes in blending sequence of paraffinic oil and phenolic curative, that is, the Oil-Cure mode (the oil was added prior to the adding of curing agent) and the Cure-Oil mode (the oil was added after blending curatives). The degree of cross-linking, and mechanical and processing properties of the TPVs prepared using the two modes were investigated and compared. The amount of extender oil had the strong influence on the mechanical properties, and the blending sequence of the extender oil and phenolic curative affected the processing properties of the TPVs greatly. In this work, TPVs with much improved processability without detracting in mechanical properties could be prepared using the Cure-Oil mode.

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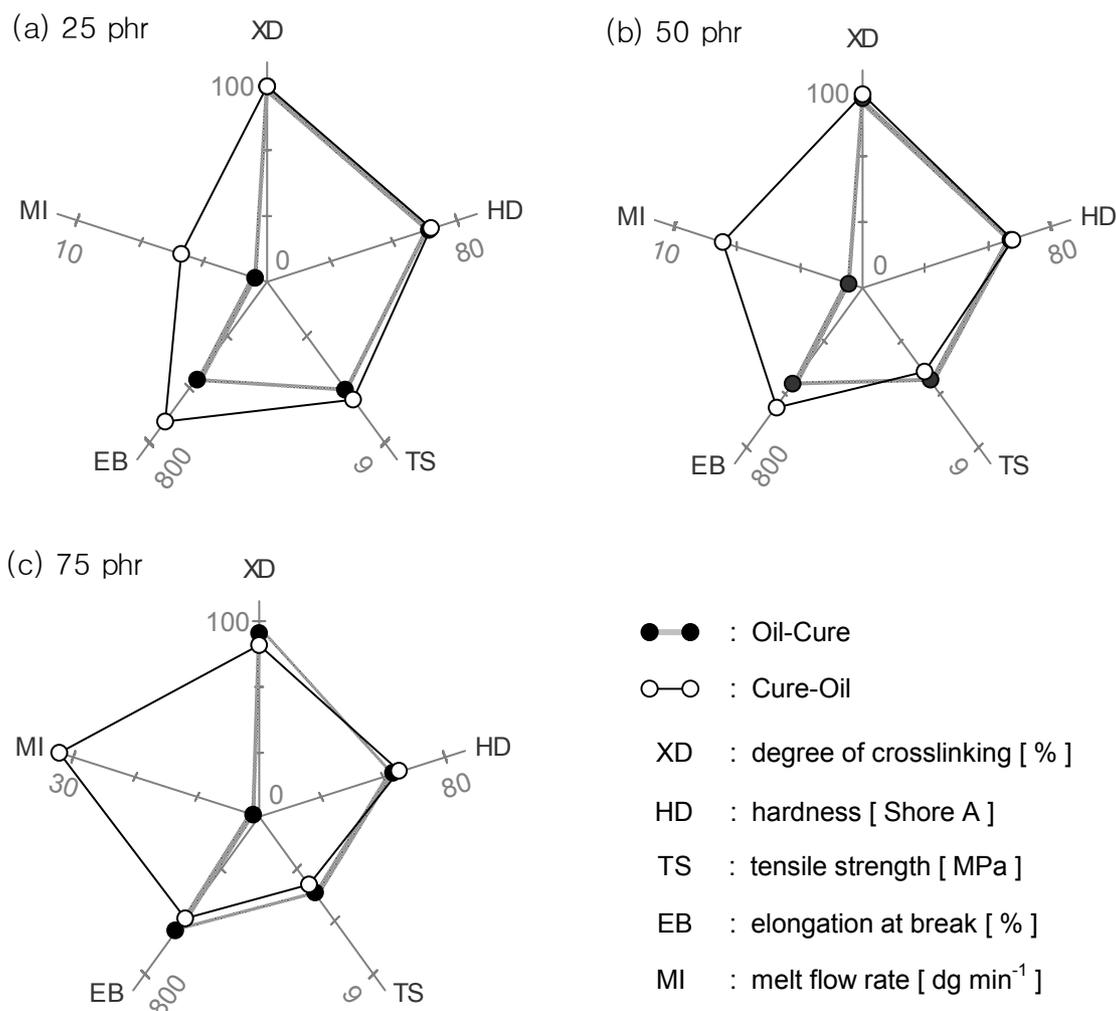


Figure 10. Changes in the properties of 70/30 EPDM/PP TPVs prepared using different blend modes for (a) 25, (b) 50, and (c) 75 phr of extender oil.

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