Effect of Plasticizer and Curing System on Freezing Resistance of Rubbers

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ABSTRACT: At glass transition temperature, T_g the rubber compound becomes stiff and brittle and it loses all its rubbery characteristics. This article deals with the changes in T_g of rubber blends based on natural rubber and polybutadiene rubber of varying vinyl content having different types and content of plasticizers, different curing systems and its effect on physico-mechanical properties to improve its freezing resistance. The plasticizers used were dioctylphthalate (DOP), tricrecylphosphate (TCP), dioctyladipate (DOA), and oil type plasticizers like parafinic oil (P#2) and aromatic oil (A#2). Among the plasticizers, when DOP and DOA content was high, an appreciable decrease of T_g was found compared to TCP. Moreover, there was a remarkable decrease of T_g using DOA plasticizer, which shows more effective on freezing resistance. However, there was not much change in T_g with oil-type plasticizers with high oil content compared to TCP plasticizer. The effect of cross-linking systems such as conventional sulfur vulcanization (CV), efficient sulfur vulcanization (EV), and dicumyl peroxide (DCP) and rubber blends with varying vinyl content in polybutadiene rubber were also carried out. It was found that T_g in different cross-linking system decreased in this order: $CV < EV < DCP$. It reveals that DCP cross-linking system affect more for improving freezing resistance. Physico-mechanical properties such as tensile strength, tear strength, hardness were also measured. The ratio of initial slope (M_0) to steady-state slope (M_1), M_0/M_1 in tensile curves of different blends were verified, which in turn related to the physico-mechanical properties and freezing resistance of rubber compounds. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39795.

INTRODUCTION

Most of the polymers that has high molecular weight is used for wide temperature range.[1,2] Reducing the temperature of the environment surrounding the rubber article will have a negative impact on the rubber properties. With decreasing temperatures, the movements of the molecular chains are reduced. At a certain temperature the molecular chains will no longer be able to move and the rubber losses all its rubbery characteristics. The rubber will be embrittled and become plastic like, reducing or eliminating the ability of the material to act as a seal or cause fracture by external forces like deflection or shock.

Some elastomers posses inherently good low temperature properties, whereas others do not. Silicones and fluorosilicones generally have very good low temperature characteristics, with low range operating temperatures being as low as $-72°C$ and below.[3,4] EDPM materials are also pretty good with lower temperatures being in the -60 to $-45°C$ range. On the other hand, most fluoroelastomers and perfluoroelastomers become stiff at temperatures above $-18°C$ with some even above $0°C$. Most of the other elastomers are ranged somewhere between these two extremes. A couple of them including neoprenes, require extended time to become completely stiff at lower temperatures.[5] Viscoelastic properties of an elastomer depend on type of rubber, the content of plasticizer, and also type of filler.[6] As T_g decreases, there is an improvement in freezing resistance. The rubber become harder at low temperature and also on crystallization as it is related with the microbrownian motion of polymer chain molecules. Considering the relationship between molecular structure of rubber and freezing resistance, nonpolar rubbers like NR, BR, SBR, EPDM has low molecular cohesive energy and superior freezing resistance. On the other hand, polar rubbers like CR, NBR, and Acryl rubber have inferior freezing resistance.

Choice of rubber and compounding additives are a prime factor to have a good freezing resistance. Among the additives, plasticizers, and softeners have a leading role.[7–13] They should have low volatility, superior and compatible with the rubber(s). In addition, it is also important to choose type of vulcanizing system and rubber–rubber blend system. For example, if the degree of cross-linking increases, the glass transition temperature of NR also increases and the tendency of crystallization became less.[14,15] To design a rubber compound for freezing resistance purpose one should have rubber of low T_g, noncrystallizable and should be compatible with other rubber in the blend system. Care should be taken also for choosing type and amount of reinforcing additive in the compounding recipe as T_g increases with the addition of reinforcing filler. The role of plasticizers in freezing resistance is that it enters between the polymer molecules and reduces interaction among the molecules which in turn decrease the cohesive energy.

The rubber materials with improved freezing resistance can be used for aero tires, air spring of express trains in railways, track mat of railway, automobiles, etc. A rubber without freezing resistance can affect not only uncomfortableness but also safety. So, the role of freezing resistance of rubber materials is of great importance.

It has been suggested that the cold resistance is quite sensitive to the physical networks including weal intermolecular bonds, faint links of rubbers with carbon black particles, and physical networks among carbon black particles.[16] The initial tensile modulus (M_0) of a tensile curve (Figure 1) incorporates the physical and chemical networks in the rubber compounds. The steady-state modulus (M_1) at certain deformations elongations is dominated from more chemical networks than physical networks. The ratio of M_0 to M_1 (M_0/M_1) represents a relation between nonequilibrium and equilibrium modulus components. Thus, the higher the ratio, the greater the role of the physical network, indicating poorer cold resistance. Thus it is expected that any compositional and structural parameters affecting the physical and chemical networks of the rubber vulcanizates might play a role in cold resistance.
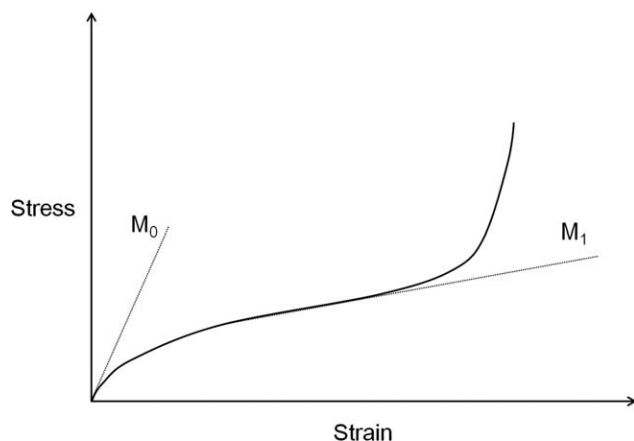
The aim of present study is to investigate the effects of plasticizers (chemical structure and loading), cross-link system (sulfur and peroxide), and rubber blend system (NR and BR in this study). The cure characteristics, glass transition temperature (T_g), tensile, and tear properties were investigated as a function of compositional parameters mentioned above. The cold resistance based on the glass transition temperature, T_g was attempted to correlate with the relative contribution between physical and chemical networks, defined as M_0/M_1.

EXPERIMENTAL

Materials
Natural rubber (NR, STR-20, ML_{1+4}, $100°C = 60$) and polybutadiene rubber (BR) composed of two different vinyl contents of 0 (CBR, KBR-01, ML_{1+4}, $100°C = 45$, Kumho Petrochemical, Korea) and 14.5% (VBR, KBR-710S, ML_{1+4}, $100°C = 50$, Kumho Petrochemical, Korea) were selected as rubber materials. Accelerator activators like zinc oxide and stearic acid were obtained from Hanil, Korea, and Pyungwha, Korea, respectively. An accelerator N-t-butyl-2-benzothiazole sulfenamide and a vulcanizing agent of sulfur were procured from Flexsys, USA, and Seikwang, Korea, respectively. A dicumyl peroxide (DCP, purity >98%, Sigma Aldrich) was also used for curing the rubbers to form C–C cross-link network. Polymerized 2, 2, 4-trimethyl-1,2-dihydroqinoline was used as antioxidant and was obtained from Kumho-Monsanto, Korea. Plasticizers used for this work were di-2-ethyl hexyl phthalate (DOP), di-2-ethyl hexyl adipate (DOA), and tricrecyl phosphate (TCP) and procured all from Aldrich Chem. USA. Also, oil type plasticizers like paraffin oil, P#2 and aromatic oil A#2 were obtained from Kumho Petrochemical, Korea.

Mixing Procedure
An internal mixer (Haake Rheocord 9000, Germany) and a two-roll mixing mill (8422 Farrel, USA) were used for mixing. Two different vinyl content polybutadiene rubbers, viz., 0% and 14.5% vinyl content, were blended with natural rubber followed by addition of ZnO and stearic acid. Next plasticizer/oil was incorporated to the mixer followed by addition of antioxidants to prepare master batch. Finally different cross-linking systems like conventional, efficient, and DCP were incorporated into the master batch for final mixing as given in Table I. Rheometer (ODR, Alpha Technologies, USA) was used to find the optimum cure time of the compounds and finally curing of the compound were carried out in a molding press (Carver, WMV50H, USA).

Glass Transition Temperature
Differential scanning calorimeter, DSC (TA Instruments, USA) was carried out with 7 mg ($\pm$ 0.3 mg) noncross-linking rubber compounds at a heating rate of $20°C/min$ in the temperature range from -150 to $250°C$ under N_2 gas purging. The experiment was repeated twice, and final glass transiston temperarure was recorded for each rubber compound.

Physico-Mechanical Properties
The basic physical properties like tensile strength, tear strength, hardness, and stiffness were carried out for the vulcanized rubber samples. Tensile tests were carried out according to ASTM

Figure 1. Sketch of initial slope (M_0) and steady-state slope (M_1).

Table I. Composition of Mixes

Ingredients	Loading (phr)	Type of Cure System		
		CV	EV	DCP
NR	100	X[a]	X	X
BR		100-X	100-X	100-X
ZnO	10	5	5	
Stearic acid	2	3	3	
Plasticizer[b]	0 to 60			
RD	1	2	2	
NS[c]	0.7	1	2.6	
S	2.25	2	1	
DCP				1

[a] X:100, 70, 50, 30, 0.
[b] Plasticizer:Dioctyl phthalate(DOP), Dioctyl adipate(DOA), Tricrecyl phosphate (TCP), Paraffin oil (P#2), Aromatic oil (A#2).
[c] NS:N-t-butyl-2-benzothiazole sulfonamide.

D 412 on dumbbell-shaped specimens (punched out from the molded sheet using ASTM Die-C) using stretcher (STM-10, USA) and an uniaxial tension mode at a constant crosshead speed of 500 mm/min. The tests were performed at 25°C. For each samples, the averages of four tests were reported.[17–19] The hardness of the samples was measured using Shore A-type hardness scale (Model Kobunshi Keiki, Japan) according to ASTM 2240 at ambient temperature. The average value was determined by measuring hardness in five spots of same specimen. Young's modulus was measured by monitoring the elongated length (strain) of a rectangular strip (50 × 5 × 1 mm) with changing the stress.

Tear strength was performed in the same stretcher (STM-10, USA) like tensile test using Trouser test of specimen size of 100 × 25 × 1 mm according to ASTM D 624 at ambient temperature at a cross-head speed of 50mm/min. To avoid the extension of legs during tear experiments, a narrow backing cloth (weak textile) was employed in the legs parallel to the tearing direction, and the tear specimens were compression-molded for vulcanization. In this case, we can simply calculate the tearing energy by $2F/t$, where F is averaged tearing force and t is thickness.[20,25]

To determine the relative information of physical to chemical network (M_0/M_1), a rectangular strip (100 × 10 × 1 mm) was extended up to 100% with a speed of 10 mm/min without prestretching to avoid Mullin's effect. Then the initial and steady-state slopes were determined from the curves.

RESULTS AND DISCUSSION

Cross-Linking Properties

Some useful physically-meaningful parameters can be extracted from the rheometer curves, which are necessary to describe the microstructural characteristics of cured rubber compounds. One of the methods to access the cross-link density is to find out differences between the maximum value of torque, M_H and the

minimum value, M_L. Therefore, $M_H - M_L$ is a qualitative assessment of the crosslink density of a rubber vulcanizate. So, it is an efficient means of measuring the effects of additives on the cure efficiency. Actually the M_L exhibits the torque of the compounds in the cure curves where no vulcanization reaction has started. Therefore it can be a measure of viscosity of unvulcanized compounds. Accordingly, it is clearly evidenced that the incorporation of the reinforcements increases always the viscosity of the rubber. This behavior has already been observed frequently by others in many rubber-filler systems,[21,22] which is often attributed to the strong interaction at the rubber–particle interfaces.[23,24] Crosslink density values from Flory-Rehner model corresponds with the variation of torque difference. Figure 2 shows the effect of various plasticizer content on the differences between the maximum value of torque, M_H and the minimum value, M_L i.e., $M_H - M_L$ of NR/BR blend vulcanizates. The percentages of $M_H - M_L$ values (apparent crosslink density) decreases with the plasticizer content regardless the type of plasticizer whether it is phosphate or adipate or oil type. This means that more and more slippage between the polymer chains occurs with the reduction of crosslink density. It can be visualized that the cross-linking time becomes longer with the higher content of the plasticizer.

The effect of variation of polybutadiene rubber of two different vinyl contents, viz., 0 and 14.5% in the NR/BR blends with the variation of $M_H - M_L$ percentages have also been presented in Figure 3. Among the three different types of curing systems in the rubber vulcanizates the degree of cross-linking became higher with increasing amount of BR content in the NR/BR blends regardless of types of curing system and BR types. Moreover, cross-linking density of DCP-cured blend compound shows remarkable increase with the increase of BR content in the blend.

Glass Transition Temperature

Glass transition temperature, T_g of a polymer generally decreases with the addition of a plasticizer as it increases the flexibility of a polymer and which can retain its rubbery behavior even at low
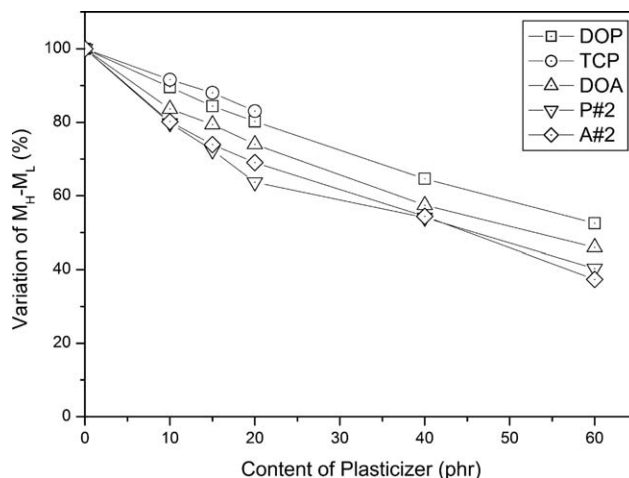
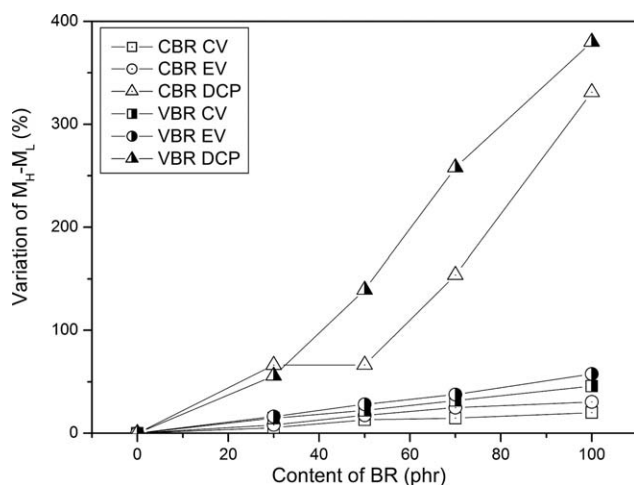**Figure 2.** Variation of $M_H - M_L$ with plasticizer types and content.

Figure 3. Variation of $M_H - M_L$ with BR types and content.

Table II. Change of T_g with Plasticizer Types and Content

Content of Plasticizer (phr)	Glass Transition T_g (°C)				
	DOP	TCP	DOA	P#2	A#2
0	–	–	−54.4	–	–
10	−55.9	−54.8	−56.7	−55.6	−53.7
20	−58.5	−54.4	−60.8	−55.2	−53.1
60	−63.3	–	−73.6	−56.8	−52.4

temperature. If the polymeric materials are heated, the stiffness will be disappeared at a certain temperature. Generally, T_g of polymer is defined as the temperature at which segmental motion ceases. The segmental length varies from about 10 to 50. T_g of polymer is affected by chemical structure, and it changes remarkably according to the size of substituent and geometrical coordination. In the relationship between glass transition temperature and freezing resistance, if the glass transition temperature goes down, the resistance property in a low temperature will be improved, and accordingly the freezing resistance will be enhanced.

In the present study, development of NR/BR blends of low T_g is the prime goal for freezing resistance materials. Differential scanning calorimeter (DSC) was used to measure low T_g of the compounds. For each specimen DSC run was performed twice. Figure 4 shows the DSC thermograms of NR/BR compounds having different phr of TCP type plasticizer. It was visualized from the first scan of both the samples that there were reaction peak of moisture as well as additives at a certain temperature
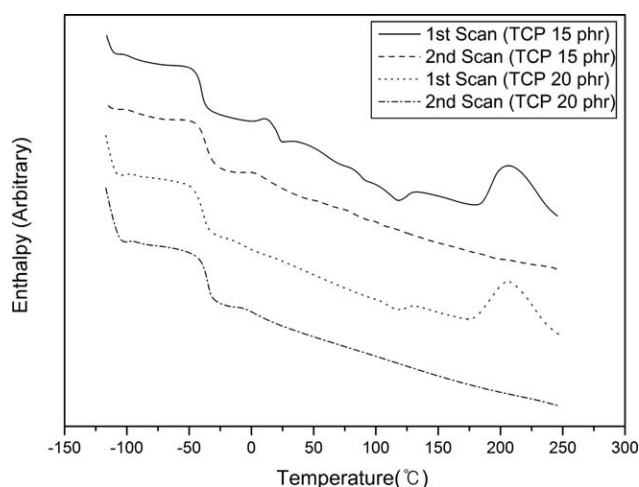
and a cross-linking peak at around 200°C. However, all these peaks vanishes in the second scan of DSC run and only a prominent peak of glass transition temperature appears. Table II shows the changes of measured glass transition temperature of the compounds with different plasticizers and Table III shows the changes of glass transition temperature in NR/CBR and NR/VBR blends with different cure systems. First of all, in Table II when the content of DOA and DOP was high, the glass transition temperature of compound was decreased and in particular, there was an appreciable reduction of glass transition temperature using DOA plasticizer in the compound. Considering the molecular structure of TCP, it contains bulky group, which cannot be compatible with natural rubber, and it does not affect the main rubber chain. Also, oil-type plasticizers like paraffinic oil, P#2 and aromatic oil, A#2 have compatibility with rubber. However, it did not affect much of the main chain of rubber matrix chemically. So, it is well understood that DOA was the most proper plasticizer for improvement of freezing resistance of rubbers.

The changes in glass transition temperature, T_g because of different cross-linking systems was reported in Table III. The order of cross-linking system that affects the decrease of glass transition temperature was conventional sulfur vulcanization (CV) < efficient sulfur vulcanization (EV) < DCP. The glass transition temperature of compounds containing BR with higher vinyl content was decreased remarkably. Because the degree of cross-linking in cross-linked compound was increased because of the vinyl content in BR. Compounds that contained BR with less vinyl content shows high cross-linking density compared to previous cross-linking property. Generally, it is known that if the degree of cross-linking is more, the flexibility of the molecule reduces in compounds and at the same time the glass transition temperature was increased. Although the cross-linking density was increased, compounds of DCP cross-linked system had the lowest glass transition temperature. So it can be concluded that not only the degree of cross-linking but also other factors plays a great role in reducing glass transition temperature of a rubber compound. From these reasons, we plan to look into the changes of the glass transition temperature according to size of molecule by GPC (Gel permeation chromatography) to verify molecular weight of each compound in the future work.

Mechanical Properties

Figure 5 shows the stress–strain curves of NR compounds with different types and content of plasticizers namely DOA and P#2

Figure 4. Typical DSC thermograms of 1st and 2nd scans of TCP-contained rubber compounds.

Table III. Change in T_g of NR/CBR and NR/VBR Blends with Different Cure Systems of Conventional Sulfur Vulcanization (CV), Efficient Sulfur Vulcanization (EV), and Dicumyl Peroxide (DCP) Cure

Blend Ratio		Glass Transition T_g (°C)		
		CV	EV	DCP
NR/CBR	100/0	−51.0	−54.7	−55.9
	50/50	−51.5 (−91.8)	−55.4 (−95.2)	−57.7 (−98.5)
	0/100	(−91.5)	(−95.3)	(−97.5)
NR/VBR	100/0	−54.5	−55.8	−57.8
	50/50	−55.5 (−78.2)	−56.9 (−79.8)	−58.6 (−79.9)
	0/100	(−78.7)	(−79.9)	(−78.4)

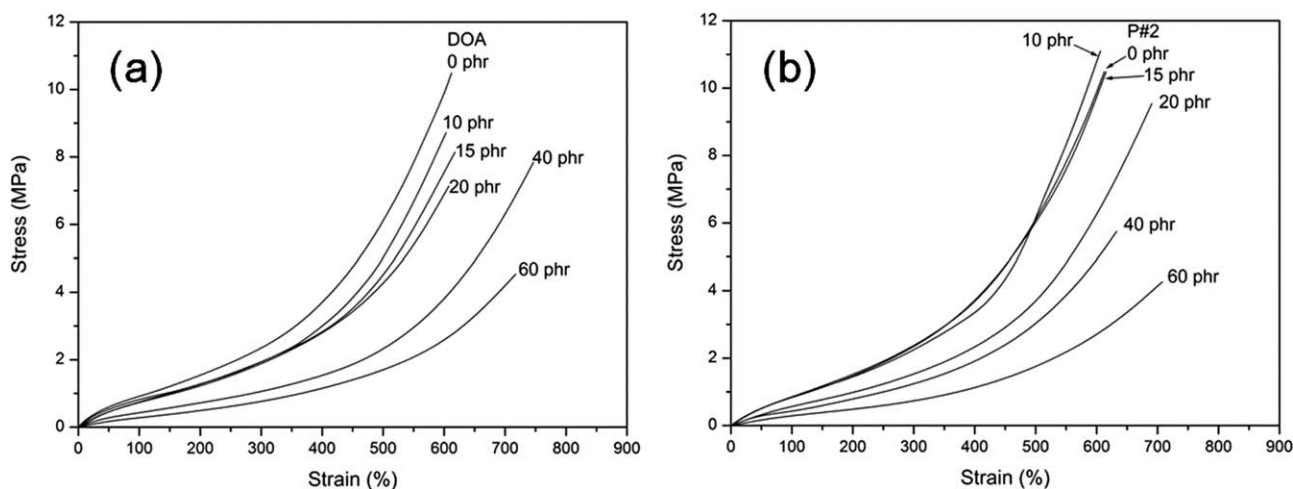No plasticizer was used in this experiment. Parentheses Indicate T_g of BR.

to verify their effect on tensile properties of the compounds. In both the plasticizers used for this experiment, it was found that there were decreasing trend of tensile strength and increasing trend of elongation when the amount of plasticizers were gradually increased. This is because of the fact that hardness gradually decreases with the addition of more and more plasticizer loading. As more and more plasticizers were added, the compound became softer, so the degree of hardness was decreased too and as a result tensile strength decreased. Similar trends were also observed with the remaining three plasticizers that with the increasing amount of plasticizers, the tensile strength was gradually decreased, whereas the elongation was gradually increased.

In NR/CBR blend system, as visualized in Figure 6, the stress–strain curves were obtained for different curing systems like, CV, EV, and DCP. As the amount of CBR was increased, both the tensile strength and elongation were found to decrease in all the cross-linking system. The compound that was cross-linked by DCP showed this phenomenon more clearly. These results clearly manifest that load carrying capacity of NR rich blends were more in all the cross-linking system. Similar results were
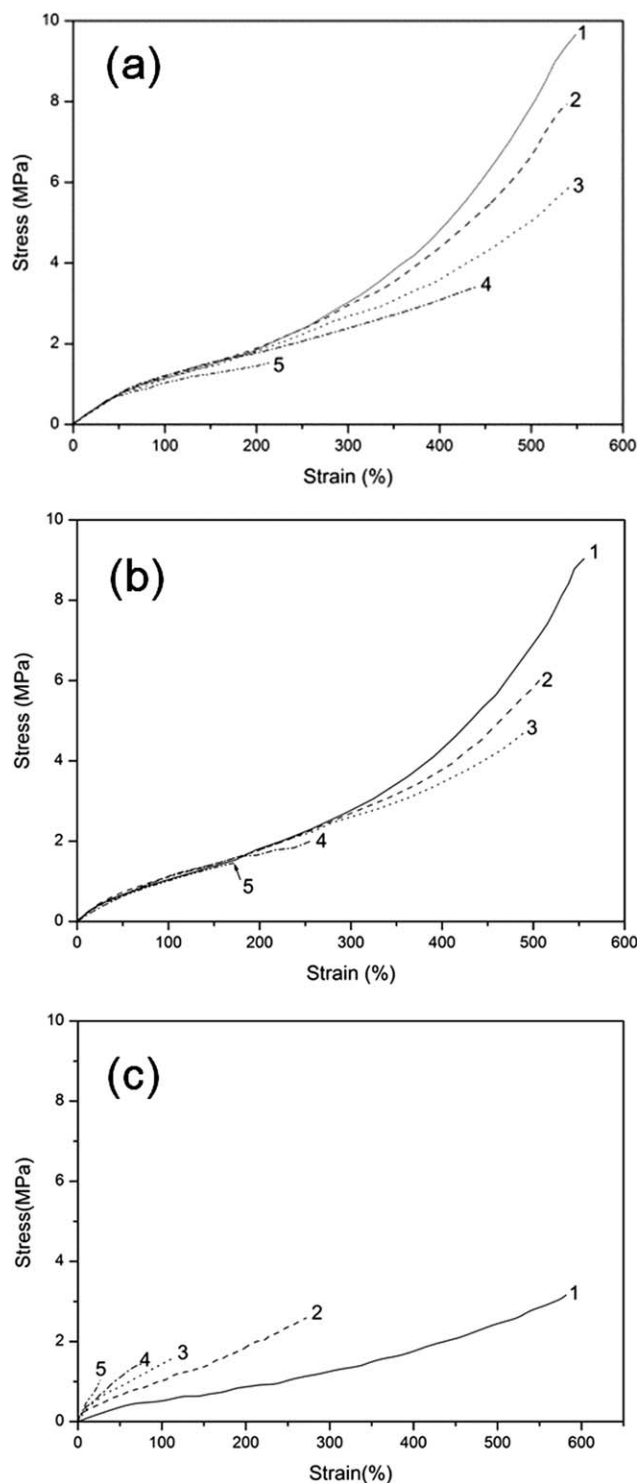
obtained in the NR/VBR compounds with VBR (14.5% vinyl content).

Figure 7 shows the effect of different types and content of plasticizers on tear strength of NR/CBR blend compounds. It was found that the compounds having low level of plasticizers had similar tearing strength until the amount of plasticizers reached to 20 phr. The tear strength was decreased beyond 20 phr plasticizer loading. In general, when the amount of plasticizers was increased, tear strength was decreased. In addition, Figure 7 also reveals that the values of tear strengths were similar among the different plasticizers. However, in compounds containing oil-type plasticizers the amount of decrease in tear strength was less compared to nonoil type plasticizers with increasing amount of plasticizer loading.

Figure 8 shows the changes of tear strength values of the NR/CBR and NR/VBR blend compounds with composition in different cure systems. It was clearly visualized that as the amount of CBR and VBR was increased tear strength was decreased in both conventional and EV cross-linking system. However, in DCP cross-linking system, the decrease was more. When the
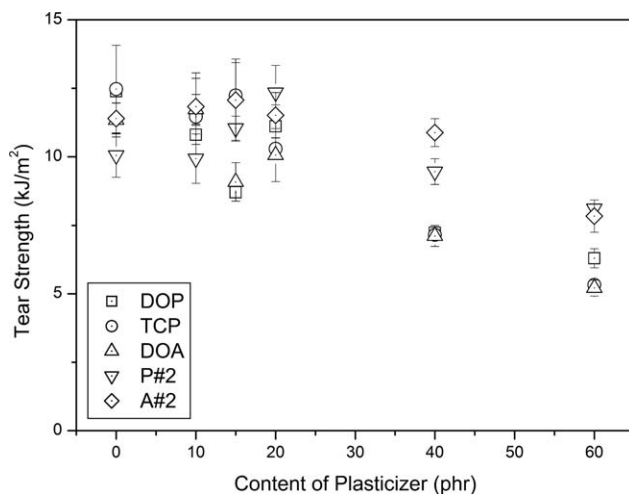

Figure 5. Stress–strain curves of NR compounds with (a) DOA and (b) P#2.
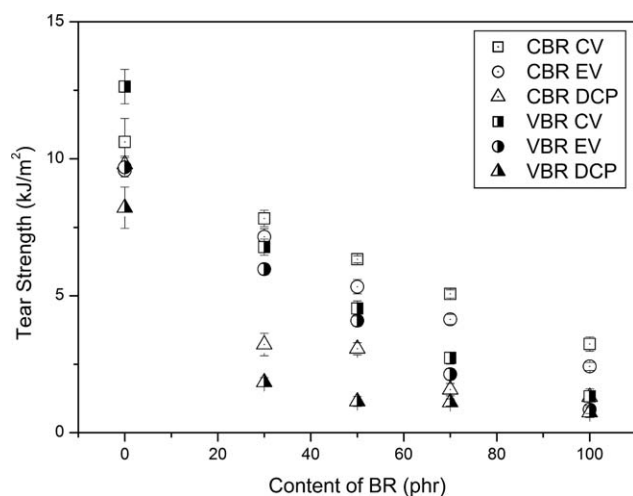
Figure 7. Tear strength of NR/CBR compounds with plasticizer types and content.

shows less tear strength than sulfur cross-linking system might be because of the crosslink nature of two cure systems. The major component of polysulfide bonds in the CV can be rearranged to mono- and/or di-sulfide bonds, even after breaking initial polysulfide bonds, leading to a higher resistance to tearing.[25] This effect is less for the EV composed of mainly mono- and di-sulfide cross-links. There is no such effect for DCP cure having no sulfide links. A similar behavior was also observed for NR/VBR blend.
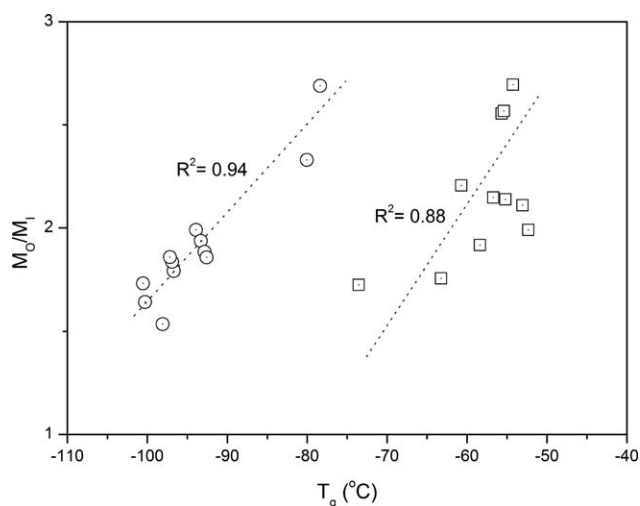
Figure 9 depicts the changes of Shore A hardness and Young's modulus values with VBR content in NR/VBR blend compounds for different cure systems. As the amount of VBR was increased, the degree of stiffness (hardness and Young's modulus) was enhanced. Moreover, the enhancement was more pronounced in DCP cured system than sulfur cure systems (CV and EV). This can be explained by the results from cure-rheometer results ($M_H - M_L$) representing the degree of cross-link (Figure 3). The crosslink density increased with increased CBR and VBR content and this effect was more and more with the DCP cured system. It is well known that degree of hardness and modulus depends on number of cross-links present in the vulcanized state.

Relationship Between M_0/M_1 and T_g

The ratio of initial to steady-state moduli (M_0/M_1) from the tensile curves was measured for NR/BR blend compounds with different plasticizers. Figure 10 exhibits the relationship between M_0/M_1 and glass transition temperatures. The initial modulus (M_0) includes both the chemical and physical networks. The equilibrium modulus (M_1) represents the chemical network dominantly because the physical networks including Mullin's effect break at higher elongations. Thus it is speculated that the higher values of M_0/M_1 represent greater role of physical networks to confine the molecular segmental motions at T_g. Figure 10 shows the relationship between M_0/M_1 and T_g. Two linear relationships were found between them at the temperature ranges close to T_g's of CBR (-95°C) and VBR (-79°C) and

Figure 6. Stress–strain curves of NR/CBR blends with different cure systems: (a) CV, (b) EV, and (c) DCP. The blend ratio of NR/CBR was indicated by curve 1 for 100/0, 2 for 70/30, 3 for 50/50, 4 for 30/70, and 5 for 0/100.

minimum amount of CBR and VBR rubber of 30 phr was added, the tear strength was remarkably decreased. Moreover, tear strength has been appeared same up to CBR and VBR rich compounds. The main reason that DCP cross-linking system

Figure 8. Tear strength of NR/CBR and NR/VBR blends with different cure systems.

Figure 10. Correlation between T_g and M_0/M_1.
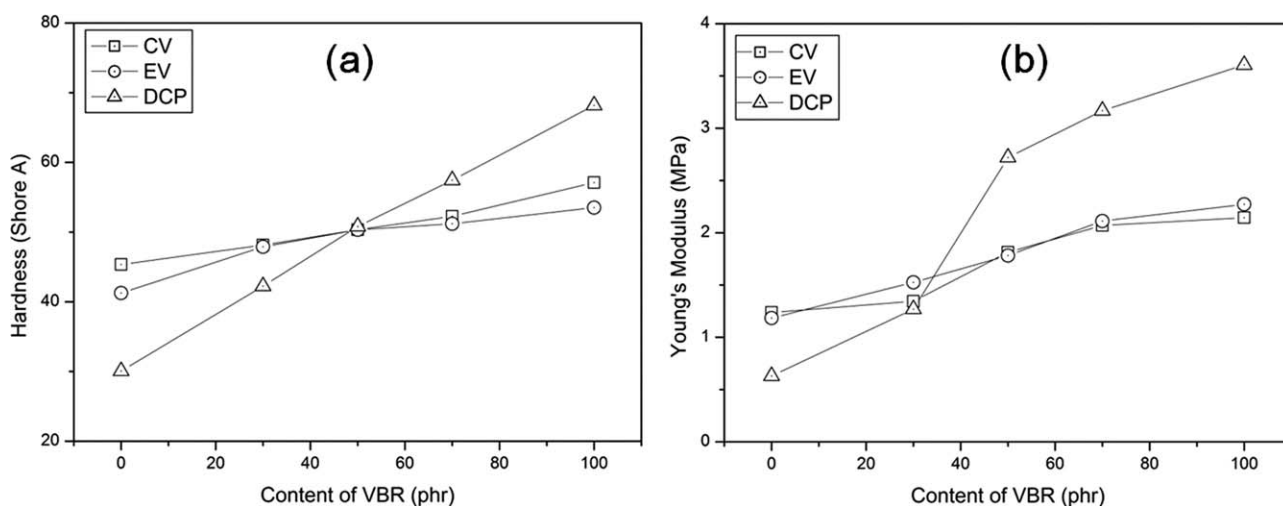
Figure 9. Hardness and Young's modulus of NR/VBR blends.

NR (-55°C). The lower temperature relation showed much higher correlation ($R^2 = 0.94$) than that of higher temperature relation ($R^2 = 0.88$). The lower T_g is corresponding to the lower M_0/M_1 values, as the physical entanglements are decreased because of increased role of plasticizers.

CONCLUSIONS

The glass transition temperature of rubber compound was decreased as the amount of DOP and DOA was increased. However, in case of plasticizers like TCP, P#2, and A#2, there was not much effect on glass transition temperature. Tensile properties, tear strength, hardness, and Young's modulus were decreased when the amount of plasticizers was increased.

In NR/CBR and NR/VBR blends, the glass transition temperature was decreased in this order: CV < EV < DCP. When the amount of CBR and VBR was increased, tensile properties, hardness, and Young's modulus were enhanced, whereas tear strength was reduced.

The modulus ratio M_0/M_1 was related with the glass transition temperature. As the value of M_0/M_1 was smaller (majority of chemical network), the freezing resistance was improved.

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