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Abstract

Elastomeric materials have viscoelastic properties and can be designed for numerous applications, tires production, vibration isolation and damping. These properties can be tailored for a wide temperature range and in ozone-rich atmospheres. Processing capacity of a rubber compound can be predicted by their vulcanization properties. In goals of raising environmental demands rubber manufacturers are now focusing on the uses of recycled product. Re-use, recycle, pyrolysis and recovery are the common methods in sustainable management of waste elastomeric products. Waste rubber can be used in civil engineering, for composite material preparation, as energy source, for sport devices, tires fabrication. The goal of this applicative work was to estimate vulcanization behavior of rubber compounds based on recycled rubber powder and triple rubber matrix NR/BR/SBR which is used for tire tread manufacturing. It was estimated that the values of optimum vulcanization time decrease with the increase of recycled rubber powder amount.

Key words: rubber blend, elastomers, waste rubber, recycling, composites,

INTRODUCTION

Crosslinking of rubbers as network precursors causes substantial changes at the rubber macromolecules. The long rubber macromolecules (molecular weight usually between 100,000 and 500,000 daltons) become linked together with junctures (crosslinks) spaced along the chains with the average distance between junctures corresponding to a molecular weight between crosslink points of about 4000 and 10,000 daltons. Because of network formation, the material becomes essentially insoluble, and cannot be processed by methods that requires it to flow (processing in a mixer or extruder; on a mill or calendar; or during forming, or molding. It is substantial that crosslinking occur only after the rubber product is in its final geometric shape. Effects of vulcanization on elastomeric material final properties are given in the Figure 1. The static modulus increases with crosslinking to a greater level than does the dynamic modulus. The dynamic modulus is a composite of viscous and elastic behavior, whereas static modulus is largely a measure of only the elastic component of rheological behavior. Dynamic modulus is determined by the imposition of a sinusoidal small strain in the frequency range from 1 to 100 Hz. Crosslink point formation reduces hysteresis. Hysteresis is the ratio of the rate dependent or viscous component to the elastic component of deformation resistance. It is also a measure of not stored deformation energy, but is converted to heat. Vulcanization then causes a trade-off of elasticity for viscous or plastic behavior. Toughness and tear strength are related to the breaking energy. Values for these properties enlarge with small amounts of crosslink points but they are diminished by further crosslink point formation [1].

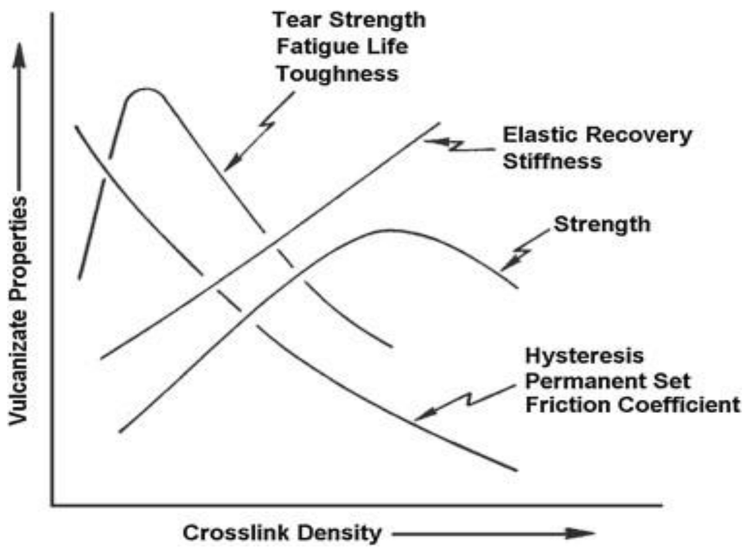

Figure 1 *Typical changes of elastomeric material properties as a function of the obtained crosslinking density (vulcanization level).*

The majority of rubber blend have been found to be multiphase either completely immiscible or multiphase with limitations. This is due to the small mixing combinatorial entropy of the dissimilar macromolecules. The remaining portions are single phase, melt-miscible mixtures. Compatibility is a concept depending on the scale of a particular experimental method. Thus, a rubber blend can be compatible when tested for mechanical properties or incompatible as revealed by structural assessments (glass transition determination, SEM. For industrial purposes blends as compatible when they show a synergistic behaviour in some valuable properties, incompatible when they show a minimum in some property-composition curves, and semi-compatible when the properties are intermediate for used rubbers [2]. Incompatible blends are heterogeneous, but only the compatible blends on a molecular scale are homogeneous. Different rubbers have specific unsaturation and may require the special crosslinking agents which may have different solubility in continuous or discontinuous domains. The structure of *cis*-1,4-polybutadiene is very similar to that of the natural rubber macromolecule (NR). Both network precursors are non-saturated hydrocarbons but for the natural rubber the double bond is activated by the existence of a methyl group. The polybutadiene macromolecule is without this group, and thus less reactive. The methyl side groups stiff the polymer chains and thus the polybutadiene glass transition temperature (T_g) is consequently smaller than NR glass transition. This lower T_g has a number of limitations to the polybutadiene rubber properties. At room temperature polybutadiene rubber compounds have a higher resilience than natural rubber compounds. , On the other hand elastomers based on this network precursor, have poor tensile strength and tear resistance. For example, they are blended with NR in the fabrication of truck tyres and with SBR for passenger car tyres. Rubber compounds based on general purpose network precursors (NR, SBR, BR) or its blends use curing packages based on sulfenamide accelerators. The selection of the crosslinking package is based on processing safety, curing rate index and ultimate modulus buildup per accelerator loading (activity). It is applied to the loss of network structures by thermal nonoxidative ageing. It is associated with isoprene rubber used as network precursor crosslinked by sulfur package. It can be the result of the over-curing or of thick section hot ageing [3]. Sometimes the term reversion is concerned to other types of non-oxidative deterioration (mainly for network precursor not based on isoprene. For example, thermal aging of SBR which can cause increased crosslink point density and hardening is called reversion, since it can be the result of over-curing and can also degrade a elastomeric product. In focus of raising environmental demands manufacturers are now forced to use recycled product. Re-use, recycle, recovery and pyrolysis are the common methods in sustainable management of waste elastomeric products. De-vulcanization is a fabrication process in which crumb rubber is subjected to thermal treatment, pressure or the addition of softening agents to regenerate the rubber compound to its original plastic state. Fabrication of rubber powder from waste tyres is a three-stage procedure primarily shredding, after that granulation and lastly fine grinding. The process of cryogenically freezing scrap rubber and crushing the rubber to the particle size desired. Dry method is procedure that mixes crumb rubber modifier with rubber aggregate before the mixture is combined with asphalt binder. This process applies only to hot-mix asphalt production. Tyre in general consists of pollutants and heavy metals thus there is a potential risk for the introduction of toxins into the soil and ground water. The solubility of these materials varies with the pH of soil and characteristics of local water. Research has estimated that insignificant leaching occurs when shredded tires are used as land fill materials. Sometimes eco-toxicity may be a serious problem. Studies have been assessed that ingredients such as zinc, heavy metals leach into water. Shredded tire particles leach more, forming a bigger concern via the increased surface area on the pieces. Ecology is now the crucial part of the elastomeric materials design. The automobile tire technology is obliged to reduce the fuel consummation via the fabrication of tires with less rolling resistances [4]. The viscoelastic behavior of elastomeric materials results in an energy loss during a cycle of extension-contraction (called hysteretic loss). This property is related to the rolling resistance of tire (the fuel consumption). In the Table 1. are listed the typical rubbers for passenger and truck tire parts manufacturing. The progress in waste rubber recycling is focusing to the incorporation of recycled rubber powder (RRP) or partially de-vulcanized elastomer (PDE) into polymer or rubber matrix and a new sustainable material creation for technological purposes. PDE and RRP are frequently blended with other network precursors such as natural rubber, styrene butadiene rubber, polybutadiene rubber and acrylonitrile butadiene rubber (NBR).

Table1 *Typical rubbers for tire part fabrication*

	Tread	Belt	Carcass	Sidewall
Passenger tire	SBR-BR	NR	NR-SBR-BR	NR-BR or NR-SBR
Truck tires	NR-SBR or BR-BR	NR	NR-BR	NR-BR

The compatibility of these rubbers with these recycled materials should be satisfied as they are among the major rubber components used in tire recipes. The goal of this work was to determine crosslinking behavior of compounds based on recycled rubber powder and triple rubber matrix NR/BR/SBR. It was estimated that the values of optimum vulcanization time (t90) decrease with the increase of recycled rubber powder amount.

EXPERIMENTAL

Network precursors were: (a) Malaysian natural rubber (NR SMR-20) (b) polybutadiene rubber (BR SKD-Nd, producer Nizhnekamsk) (c) Styrene-butadiene rubber (SBR Intol1783). Carbon black was used as active filler. The content of recycled rubber powder was varied. The sulfur vulcanization package was used. Naphthenic oil was used as plastificator (10 phr), The network precursor ratio in triple rubber matrix NR/BR/SBR was 10/10/80 (w/w/w). Rubber compounds were homogenized using laboratory roll mill in the temperature region 60-70°C. The sheeted rubber compounds were conditioned at 23 ± 2° C prior to crosslinking behavior assessment at 160 °C using oscillating disk rheometer (Figure 2).

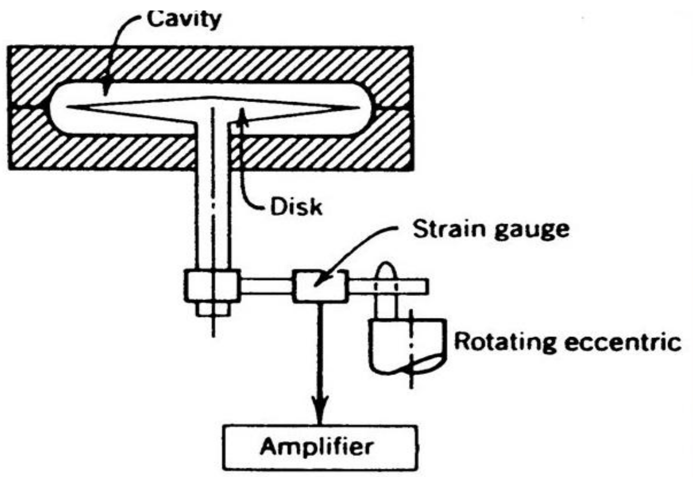

Figure 2 *The scheme of oscillating disk rheometer*

RESULTS AND DISCUSSION

Elastomeric materials based on triple rubber matrix of SBR and highly unsaturated NR and BR are common materials for tire manufacturing (applicative temperature from -40°C to 70°C). In the Figure 3. are given the preliminary structures of hybrid materials based either, partially de-vulcanized elastomer (PDE) or on recycled rubber powder (RRP) like in our experimental study.

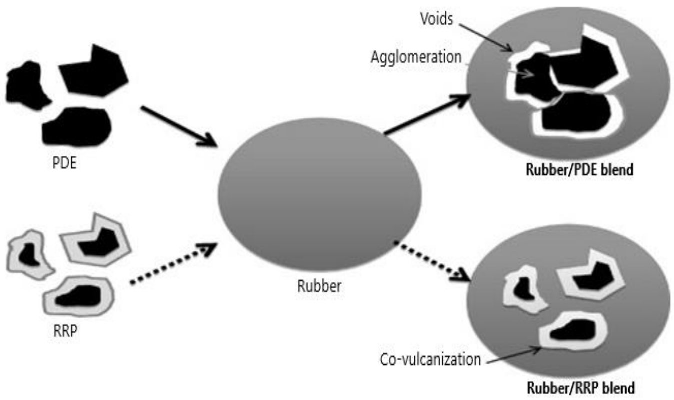

Figure 3 *The typical structure of hybrid elastomeric materials based either on recycled rubber powder (RRP) or partially de-vulcanized elastomer (PDE).*

For saving energy it is important to assess the optimum vulcanization time. With crosslinking time reduction at the same time there is a diminishment of heat losses to the surroundings, which enables the energy consumption to be reduced significantly. In curing behavior assessment the minimum torque is a measure of stock viscosity.

$M_{t90} = (M_h - M_l) \times 0{,}9 + M_l$ (1)

where M_h is the maximum torque, and M_{t90} a new torque reading corresponding to 90% cure in the rubber were determined from the cure traces generated at 160. The curing rate index (CRI) is the measure of rate of vulcanization based on the difference between optimum cure time of vulcanization t_{c90} and the scorch time t_{s2}. It can be calculated from the relation:

$CRI = 1/t_{c90} - t_{s2} \times 100$ (2)

The data for evaluated optimum crosslinking duration and index CRI are summarized in the Table 2. Scorch safety during vulcanization can be controlled by the selection of the primary accelerator used in the cure system. Sulfenamide accelerators are the most commonly selected primary accelerator for general purpose rubber compounds because, as a class, they give the best processing. It is known that the increase of the minimum torque for RRP/rubber blend compounds is significantly higher compared to PDE/rubber blend compounds. This is related to the substantial structure where RRP is vulcanized material and PDE is partially de-vulcanized network. Due to such structure RRP acts like soft fillers which agglomerates in the rubber matrix and does not flow. The increase in viscosity translates to increase in the minimum torque. The data for evaluated optimum crosslinking duration and index CRI are summarized in the Table 2. Scorch safety during vulcanization can be controlled by the selection of the primary accelerator used in the cure system. Sulfenamide accelerators are the most commonly selected primary accelerator for general purpose rubber compounds because, as a class, they give the best processing. In curing behavior assessment by oscillating disk rheometer the minimum torque is a measure of stock viscosity. The increase of the minimum torque for RRP/rubber blend compounds is significantly higher compared to PDE/rubber blend compounds. This is related to the substantial structure where RRP is vulcanized material and PDE is partially de-vulcanized network. Due to such structure RRP acts like soft fillers which agglomerates in the rubber matrix and does not flow. The increase in viscosity translates to increase in the minimum torque.

***Table 2**. Crosslinking characteristics for elastomeric composites based on triple rubber matrix NR/BR/SBR, carbon black particles and recycled rubber powder (RRP).*

Sample	Carbon black (phr)	RRP (phr)	M_L (dNm)	M_H (dNm)	t_{C90} (min)	CRI (min^{-1})
NR/BR/SBR	60	0	1.94	15.83	0.66	303.03
NR/BR/SBR /RRP5	55	5	2.21	15,00	0.70	294.12
NR/BR/SBR/RRP10	50	10	2.05	13.87	0.67	312.50
NR/BR/SBR/RRP20	40	20	1.84	11.29	0.56	434.78

With reduction in the crosslinking time there is a reduction in heat losses to the surroundings. It should be mentioned that used RTR particles contains and some amounts of processing oil which could facilitate the reduction of the minimum torque. Presence of filler such as carbon black in recycled rubber particles also contributes to the increase in the minimum torque. Lower minimum torque of RTR shows, it has better processability compared to GTR. It was assessed that the values of optimum crosslinking time (t90) decrease with the increase of recycled rubber powder content. For saving energy it is obligative to assess the optimum vulcanization time for each rubber compound recipes.

CONCLUSION

The goal of this work was to estimate the influence of recycled rubber powder on the crosslinking characteristics, such as maximum torque (M_h), minimum torque (M_l), torque reading corresponding to 90% cure in the rubber (M_{t90}), curing rate index (CRI) and optimum crosslinking time (t90) on triple rubber matrix NR/BR/SBR to assess the best recipes for rubber compound preparations. Materials based on triple rubber matrix are used for tire tread fabrication. It was estimated that the optimum crosslinking time (t90) decrease with the increase of recycled rubber powder content. For saving energy it is important to assess the optimum vulcanization time. With crosslinking time reduction at the same time there is a diminish of heat losses to the surroundings, which enables the energy consumption to be reduced significantly.

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