Effects of Cure Characteristics, Mechanical and Morphological Properties of Styrene Butadiene Rubber/Recycled Chloroprene Rubber (SBR/CRr) Blends

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The effects of tensile and morphological properties of styrene butadiene rubber/virgin chloroprene rubber blends (SBR/CRv) and styrene butadiene rubber/recycled chloroprene rubber blends (SBR/CRr) were investigated. The range size of CRr used in this study was 0.3 – 0.7 mm. Both SBR/CRv blends and SBR/CRr blends were prepared using two roll mill at room temperature with blend ratios 95/5, 85/15, 75/25, 65/35 and 50/50. It can be observed that, cure characteristics of SBR/CRr blends have lower cure time, t_{90} than SBR/CRv blends.SBR/CRr blends showed higher scorch time, t_2 and minimum torque (ML) compared to SBR/CRv blends at all blend ratios compared with the SBR/CRv blends. However, maximum torque (MH) of SBR/CRr blends exhibit the opposite trend compared with the SBR/CRv blends. It can be observed that, the tensile strength and elongation at break of SBR/CRr blends show higher value than SBR/CRv blends particularly up to 15 phr of CRr in the blends. However, SBR/CRr blends shows higher value of tensile modulus (M100) than SBR/CRv blends at all blend ratios. The scanning electron microscopy (SEM) of tensile fracture surface of SBR/CRr blends at 50 blend ratios illustrated a better adhesion and dispersion in comparison with SBR/CRv blends.

Keywords: chloroprene rubber, recycled chloroprene rubber, styrene butadiene rubber, tensile properties, SEM

Malaysia's glove makers produce about 65 percent of the world's capacity and Malaysia is the world's largest supplier of medical rubber gloves, catheters and latex thread and cord [1]. The medical devices industry in Malaysia is dominated by companies engaged in the production of medical gloves and other medical disposable products. Malaysia continued to maintain its position as the world's leading producer and exporter of medical gloves and catheters, supplying 80 per cent of the world market for catheters, and 60 per cent for rubber gloves [2].

In Japan, 'The Basic Law for Establishing the Recycling-based Society' was enacted in May 2000 with the aim of driving Japan toward a recycling-based society appropriate to the twenty-first century. The legislation sets out concrete proposals with the introduction of action plans for (1) reduction through restrictions in the generation of waste (2) reuse of materials (3) recycling and (4) appropriate disposal of waste [3-7].

Through the rubber recycling technology (the blending of polymer, especially elastomers together with recycled waste) can meet the performance and processing requirements to manufacture a wide range of rubber based products such as road and playground surfaces, recycled rubber flooring, adhesive glues, sporting mats, floats, marine and automotive parts [8-10]. The rubber waste is generated from objects that are not practical and discharged. The post industrial waste is generated during the processing and molding elastomers in the production line and in some situations the amount of waste can be equivalent with the production [11].

Currently, due to difficulty on reprocessing techniques, the vulcanized rubbers are a big problem in the recycle field. One of the main forms of discharge rubber is to use it as fuel to generate electricity and steam, this process is still in use but creates a new problem of air pollution and is also a low value to recovery process of the rubber waste [11]. Polymer blends are being used extensively in numerous applications. A blend can offer a set of properties that may give it the potential of entering application areas not possible with either of the polymers comprising the blend [12].

Among all types of rubber, the chloroprene (CR) is a prominent material. This rubber was the first market synthetic elastomer (1932) due to advantageous properties and has been investigated in the last years. CR are homopolymers of chloroprene. The polymer chains have an almost entirely *trans*-1-4-configuration. Because of this high degree of stereoregularity they are able to crystallize on stretching [12-13].

It is very versatile and can be cured with sulfur or organic peroxides and has the following characteristics: good elasticity, allows perspiration, resistance to oil, solvents, weather ageing, heat, oxygen, ozone and flame [14, 15]. In Malaysia, the output of CR catheters was found

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Table 1
CHARACTERISTICS OF THE MATERIALS

Materials	Description	Source
Styrene butadiene rubber (SBR)	1502	Bayer (M) Ltd
Virgin chloroprene rubber (CRv)		**Tosoh Asia Pte. Ltd.**
Recycled chloroprene rubber (CRr)	Size : 0.3 – 0.7mm	Teleflex Medical Sdn. Bhd.
Carbon black	N330	Malayan Carbon (M) Ltd
N-cyclohexyl-2-benzothiazyl sulfenamide (CBS), zinc oxide, stearic acid, sulphur and processing oil		Anchor Chemical Co (M) Ltd

Table 2
FORMULATION OF SBR/CRv AND SBR/CRr BLENDS

Ingredients(phr)	Blend				
	R05	R15	R25	R35	R50
SBR	95	85	75	65	50
CRv/CRr	5	15	25	35	50
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Sulfur	2	2	2	2	2
CBS	1	1	1	1	1
Processing oil	5	5	5	5	5
Carbon black (N330)	20	20	20	20	20

abundantly. Most of this material originates from medical, industrial as well as research activities. After a certain period of time these polymeric materials are not serviceable and mostly discarded. To solve this environmental issue, we have used recycled CR catheters (waste) obtained from industrial floor in an effort to create a value added instead of being scrapped [9, 11].

Styrene butadiene rubber (SBR), known as a non-polar rubber, has good mechanical properties and does not easily break down. Particularly, it has better ozone resistance, weatherability and abrasion resistance than natural rubber [10]. In this study, we selected commercial styrene-butadiene rubber (SBR), a typical unsaturated polyolefin, which has been widely used in the fabrication of automotive tire sidewalls, cover strips, wires, cables, footwear, roofing barriers and sporting goods [16, 17].

Butadiene and chloroprene (2-chloro-1,3 butadiene) are related monomers [18]. Blending of SBR with CR has been done to obtain better crystallisation resistance, better compression set resistance, lower brittleness temperature and enhanced resistance to sunlight deterioration as compared with CR alone. Other important properties, such as oil, heat, flame and ozone resistance, decrease as the amount of SBR increases [19]. It is possible to improve the phase morphology of SBR/CR blend by incorporating 5±10 phr of a modified copolymer that has segments chemically identical to SBR and CR phases. Addition of halocarbenes to polymers has been reported since a long time; however, available information on the commercial application on such modified polymers is limited [20].

To the best of our knowledge, no work has been done dealing with recycled CR waste yet. Many blends based on SBR and other polymers such as NBR [8-10], ENR [12], NR [21] and NR [23]. Blends of SBR and BR were found to be more compatible after vulcanisation [20, 22]. In this study,the comparison of the effects of tensile and morphological properties of SBR/CRv blends and SBR/CRr blends were reported.

Experimental part

Materials and methods

The materials and their characteristics used in this experiment are illustrated in table 1. The size of recycled chloroprene external catheters was 0.3 – 0.7 mm and was obtained by a mechanical grinding using Crusher model RT34 (Chyun Industrial Co. Ltd.) to achieve a polydispersed rubber powder.

Compounding, cure characteristics and vulcanizing

The formulation of both SBR/CRv and SBR/CRr blend ratios were 95/5, 85/15, 75/25, 65/35 and 50/50, as given in table 2. The rubber was pre-blended and the mixing procedure was carried out using a two-roll mill at room temperature. Cure characteristics were determined using a Monsanto Moving Die Rheometer (MDR 2000) at 160°C with about 4 g samples of the respective compound. Blends were compression molded in an electrically heated hydraulic press to 2 mm thickness at 160 °C according to respective cure time, t_{90} with force of 10 MPa.

Scanning electron microscopy

The blends were characterized using a JEOL (JSM-6490LV). The fracture surfaces of the tensile test pieces were mounted on aluminum stubs and the surface sputter coated with a thin layer of gold (2 nm thick), prior to scanning to avoid electrostatic charging and poor resolution during examination.

Results and discussions

Cure Characteristics

Table 3 shows the curing characteristics of CRv and CRr on the cure time, t_{90}, scorch time, t_2, minimum torque, and ML and maximum torque, MH of SBR/CRv and SBR/CRr blends respectively. It is clear that cure time, t_{90} and scorch time, t_2 decreased with increasing CRv and CRr content in both blends. This is due to the existence of precursors and unreacted curative in the recycled rubber which latter would accelerate the vulcanization process. However, at a similiar blends ratio, particularly up to 15 phr of CRr, SBR/CRr blends show longer t_{90} and t_2 compared to SBR/CRv blends. The longer t_{90} and t_2 of SBR/CRr blends compared to SBR/CRv blends were due to filler-related parameters, such as particle size, surface area, moisture content, surface reactivity, metal oxide content and other chemical composites in CRr which might interact with curatives and delay the total curing process.

Table 3
CURING CHARACTERISTICS OF SBR/CRv BLENDS VERSUS SBR/CRr BLENDS

Blends (phr/phr)	Cure time, t_{90}		Scorch time, t_2		Minimum torque, M_L		Maximum torque, M_H	
	SBR/CRv	SBR/CRr	SBR/CRv	SBR/CRr	SBR/CRv	SBR/CRr	SBR/CRv	SBR/CRr
R05	24.28	22.31	5.11	5.39	3.20	3.37	24.63	24.42
R15	23.93	19.89	5.20	5.75	3.26	3.77	24.93	21.69
R25	22.99	19.44	5.21	6.03	3.47	4.01	25.14	21.16
R35	22.68	17.35	5.25	6.46	3.74	4.46	25.28	18.80
R50	22.47	16.31	5.46	7.22	4.10	5.22	25.62	17.54

It is clear that the minimum torque, ML of SBR/CRv and SBR/CRr blends increased with increasing CRv and CRr contents. This exhibit that the processability of the blends becomes more dificult. Meanwhile, SBR/CRr blends show higher value than SBR/CRv blends. This is due to the presence of cross-linked CRr and other additives. The increasing in the ratio of SBR/CRr blends will reduce the flow of the blends, thus increasing the minimum torque. However in figure 4, the maximum torque, MH of SBR/CRr blends decreased with increasing CRr contents. The increasing of CRr in the SBR reduced the MH of SBR/CRr blends. It is already reported that the maximum torque is dependent on crosslink density and chain entanglement. As a result of the comparatively high molecular weight of SBR, the long chain tends to coil. The different portions of the chain entangle with chain of CR and its own chains. High extent of entanglement causes an increase in the maximum torque value [16].

Mechanical properties

The tensile strength of SBR/CRv and SBR/CRr blends is illustrated in figure 1. Result showed that the tensile strength of SBR/CRv and SBR/CRr decreased with increasing of CRv and CRr, respectively. The reduction of tensile strength was due to incompatibility in the SBR/CRv and SBR/CRr. This property gradually decreased when more CRv and CRr were added with SBR and reduced the compatibility between the blends. However strength of SBR/CRr blends were higher than SBR/CRv blends, particularly up to 15 phr of CRr, and then it decreased with further increasing CRr. It is believed that below 15 phr of SBR/CRr blends, smaller size and uniform dispersion of CRr contents in SBR/CRr blends are responsible for the better tensile strength of SBR/CRr blends over SBR/CRv blends, which were shown later in morphology studied.

Figure 2 shows that the Eb of SBR/CRv blends and SBR/CRr blends decreased with increasing CRv and CRr content. However Eb of SBR/CRr blends was higher than SBR/CRv blends, particularly up to 15 phr of CRr. This is due to smaller size and better dispersion of CRr in SBR/CRr blends, which consequently enhanced the interfacial adhesion between SBR and CRr. When more than 15 phr of CRr was added, poor interfacial adhesion between SBR and CRr occurred.

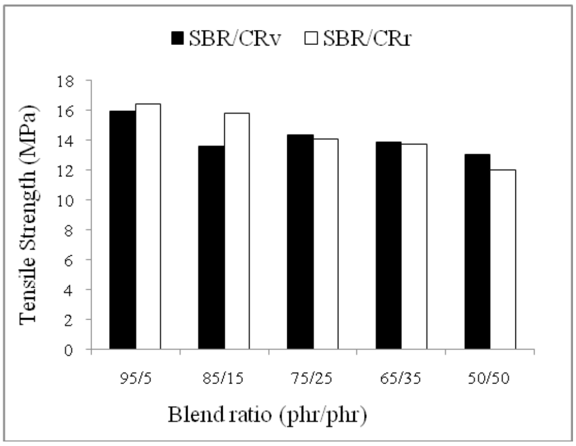

Fig. 1. Effects of CRv and CRr on tensile strength of SBR/CRv and SBR/CRr blends.

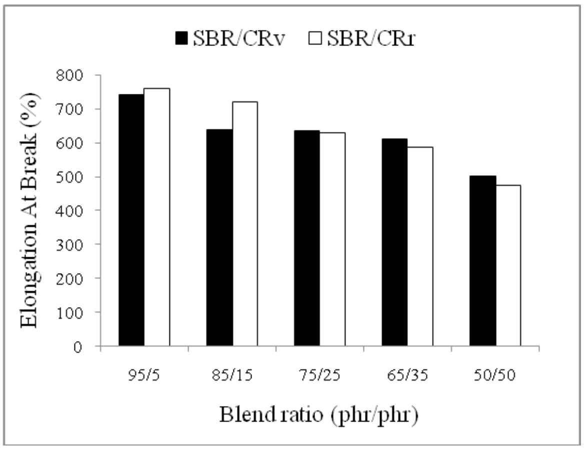

Fig. 2. Effects of CRv and CRr on elongation at break, E_b of SBR/CRv and SBR/CRr blends.

Figure 3 shows the effect CRv and CRr on M100 of BR/CRv and SBR/CRr blends respectively. It can be seen that for both SBR/CRv blends and SBR/CRr blends increased as CR content increased. The incorporation of CRr into the rubber matrix has increased the stiffness of the vulcanizates [25].

Morphology studies

Figure 5 shows the comparison of SEM tensile fracture surfaces of SBR/CRv and SBR/CRr blends at 85/15 and 50/50 blend ratios at 2000x magnification respectively. The micrograph of the failure surface of SBR/CRr blends in figure 5(a2 and b2) shows more rough surface with many tearing lines, which indicates more energy is needed to break the sample compared to SBR/CRv blends in figure 5(a1 and b1). The uniform dispersion of CRr in the SBR matrix altered the crack path, which leads to more resistance for crack propagation and, hence, higher tensile strength. The presence of more tear lines on the fracture surfaces of SBR/NBRr blends designates the effect of increased interaction between phases, thus improving the

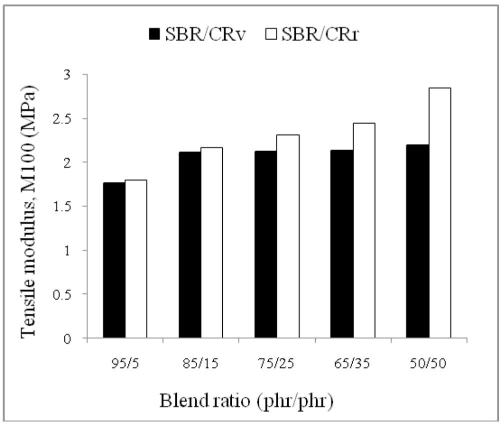

Fig. 3. Effects of CRv and CRr on M100 of SBR/CRv and SBR/CRr blends.

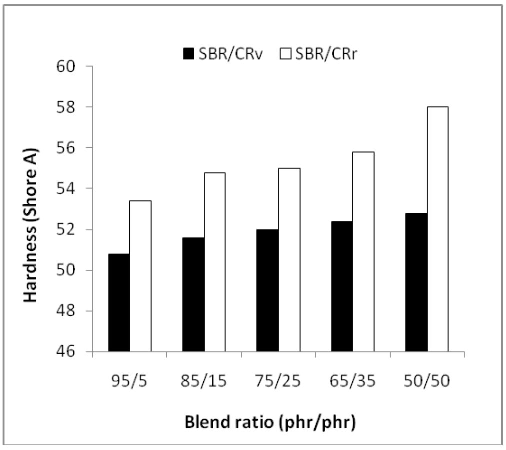

Fig. 4. Effects of CRv and CRr on hardness of SBR/CRv and SBR/CRr blends

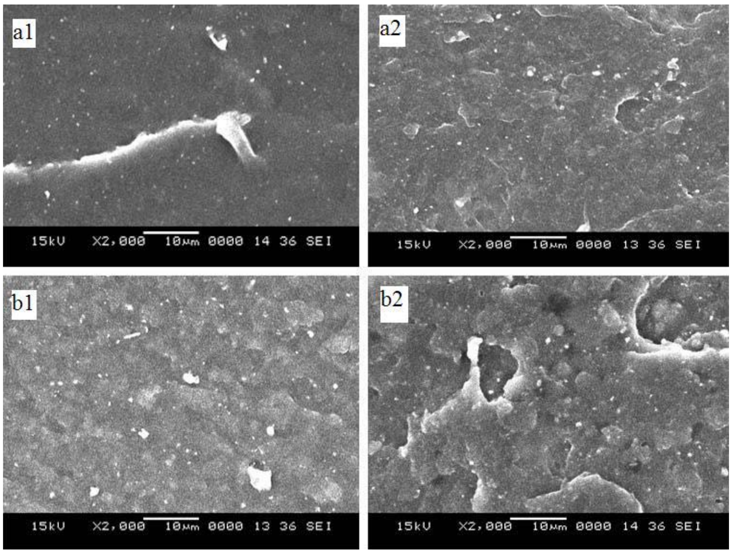

Fig. 5. Scanning electron micrograph of tensile fracture surface of SBR/CRv blends (a1) 85/15 and (b1) 50/50; and SBR/CRr blends, (a2) 85/15 and (b2) 50/50 at 2000x magnification

compatibility and enhancing the tensile strength. However as more CRr was added in SBR/CRr blends (fig. 5(a2 and b2)), the presence of many holes or loose CRr on the failure surface indicates a weak SBR-CRr interaction. At higher blend ratios, both blends (SBR/CRv and SBR/CRr) became stiffer (increaseing in tensile modulus) and a brittle failure occurred [18].

Conclusions

The scorch time, t_2, and cure time, t_{90}, were decreased with increasing CRv and CRr in SBR/CRv and SBR/CRr blends. However, at similar blend ratios, SBR/CRr blends show higher scorch time and cure time, particularly up to 15 phr of CRr.

TheML is increased with increasing CR contents in SBR/CRv and SBR/CRr blends. The SBR/CRr blends exhibited higher minimum torque at all blend ratios compared with the SBR/CRv blends. However, maximum torque in SBR/CRr blends showed the opposite trend compared with SBR/CRv blends. As more CRr was added with SBR, the maximum torque reduced.

The tensile strength and elongation at break of SBR/CRr blends show higher value than SBR/CRv blends particularly up to 15 phr of CRr in the blends. The stress at 100% elongation (M100) of SBR/CRr blends shows higher value than SBR/CRv blends at all blend ratios.The incorporation of CRr into the rubber matrix has increased the stiffness of the vulcanizates.

The tensile fracture surface of SBR/CRr blends at 15 and 50 blend ratios illustrated a better adhesion and dispersion in comparison with SBR/CRv blends.

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