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Optimisation of accelerators and vulcanising systems on thermal stability of natural rubber/recycled ethylene–propylene–diene-monomer blends

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ABSTRACT

The present paper concerns the thermal stability of natural rubber/recycled ethylene–propylene–diene-monomer (NR/R-EPDM) blends. The blends were prepared using various accelerators and vulcanising systems. Four types of accelerators were selected, i.e., N-tert-butyl-2-benzothiazyl-sulphonamide (TBBS), N-cyclohexyl-benzothiazyl-sulphenamide (CBS), tetramethylthiuram disulphide (TMTD) and 2-mercaptobenzothiazol (MBT). Subsequently, semi-efficient vulcanisation (semi-EV), efficient vulcanisation (EV), peroxide and mixed sulphur/peroxide vulcanising systems (semi-EV/Peroxide and EV/Peroxide) were observed in the latter study. Two methods of thermal analysis namely, thermo-oxidative ageing and thermogravimetric analysis were conducted. The results indicated that TMTD and MBT-vulcanised blends showed slightly higher thermal stability than that of CBS and TBBS vulcanised blends however, CBS-vulcanised blends exhibited satisfactory overall mechanical and thermal stability in comparison to the other accelerators used. In the case of optimisation of vulcanising systems, semi-EV showed the highest un-aged tensile strength when compared against semi-EV/Peroxide, EV, EV/Peroxide and peroxide vulcanising systems, respectively. However, EV, EV/Peroxide and peroxide vulcanising systems provided slightly higher thermal stability, due to the blends consisted of more stable monosulphidic and carbon–carbon linkages in the vulcanised network. The activation energies of degradation of the blends were determined by applying the Coats–Redfern's method. It can be verified that the activation energies observed in the blends were in good agreement with the thermogram results.

1. Introduction

Mostly, polymeric materials are subjected to oxidation. The rate of oxidation depends on the polymer type, processing method and end-use conditions. Oxidation of rubber can result in the loss of physical properties such as tensile strength, elongation and flexibility. Hence, the service life is determined by the oxidation stability [1–4]. Thermal properties are relevant to the potential use of polymeric materials in many consumer oriented applications. Thermogravimetric analysis (TGA) and thermal ageing have proven to be successful techniques in determining the thermal stability of polymers and polymer blends [5]. The assessment of thermal stability is one of the most important applications of TGA in the study of polymers. Thermogravimetric curves provide information about the decomposition mechanisms for various materials [6]. Both thermogravimetry (TG) and derivative thermogravimetry (DTG) will provide information about the nature and extent of degradation of the material.

Development of an effective recycling technology continues to be an interesting motive because earlier efforts to recycle rubber wastes, such as incineration, pyrolysis and landfills, end up with ecological and environmental quality problems [7,8]. There have been great deals of interest in the polymer industry on the development of cost effective techniques to convert waste and used rubber into a processable form [9–11]. Blending is an easy and cost effective way to produce new combination properties of recycled rubber waste. The purpose of blending the rubber is to improve the physical and mechanical properties as well as modify the processing characteristics and reduce the cost of the final product [12]. The utilisation of waste rubbers (whether powdered rubber or reclaimed rubber) in virgin polymer materials has been given much attention because it is the most effective way to reduce disposal problems and environmental pollution.

Reuse of EPDM rubber is an interesting topic with regards to the continuous market growth of EPDM. To solve this environmental issue, we have utilised waste EPDM in an effort to create value added rubber materials based on the blended waste of EPDM and NR, with the aim to combine the excellent physical properties of NR as well as the ozone resistance of waste EPDM. The blending

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of natural rubber/recycled ethylene–propylene–diene monomer (NR/R-EPDM) was studied previously [13,14]. However, it was focused only on the mechanical and thermal properties in various blend ratios. To extend our work, the optimisation of accelerators and vulcanising systems, on the thermal stability of the blends, was carried out. Two methods of thermal analysis namely thermo-oxidative ageing and thermogravimetric analysis were employed to study the knowledge of how polymers break down when heat is applied to materials during production or use.

2. Materials and methods

2.1. Materials

The Rubber Research Institute of Malaysia (RRIM) supplied natural rubber of SMR 5L grade. The recycled ethylene propylene diene monomer (R-EPDM) that was obtained from the gaskets and O-ring products was supplied by Zarm Scientific (M) Sdn. Bhd. R-EPDM was ground into powder form using a Table Type Pulverizing Machine from Rong Tsong Precision Technology Co. Ltd., Taiwan to acquire particles approximately 10–200 μm in size prior to blending. R-EPDM was in an irregular, rough shape and a typical particle in an aggregate that was broken by a mechanical crusher. The specific gravity of the powdered recycled EPDM was found to be 1.06 g/cm^3. The carbon black content in R-EPDM was obtained around 29.33% from the TGA results. The physical characteristics of R-EPDM have been reported in our previous study [13]. Cabot Corporation supplied the N330 grade carbon black. The trimethylolpropane triacrylate (TMPTA) was purchased from UCB Asia Pacific Ltd., Malaysia. Other compounding ingredients such as zinc oxide, stearic acid, N-tert-butyl-2-benzothiazyl sulphenamide (TBBS), N-cyclohexyl-benzothiazyl-sulphenamide (CBS), tetramethylthiuram disulphide TMTD), 2-mercaptobenzothiazol (MBT), dicumyl peroxide (DCP) and sulphur were purchased from Bayer (M) Ltd.

2.2. Compounding, curing characteristics and vulcanisation

All materials were used as supplied. The compositions were prepared according to the formulations presented in Tables 1 and 2. A semi-efficient sulphur vulcanisation system (semi-EV) was employed for the study on the accelerator types (the chemical structures of respective accelerators used in this study are shown in Fig. 1). Then, the CBS-vulcanised blend was again selected to study various vulcanising systems on the thermal stability of the blends. A fixed blend ratio of 70/30 (phr/phr) was produced using a laboratory-sized two-roll mixing mill (Model XK-160). N330 grade carbon black was also incorporated into the blends. The blended compounds were then compression moulded at 150 °C with a force of 10 MPa using a hot press according to the respective curing times (tc_{90}), determined by the MDR 2000. In addition to this study, conventional vulcanisation (CV) was not selected because the purpose of blending of natural rubber and recycled ethylene–propylene–diene-monomer is mainly to reduce compounding cost as well as eliminate the waste rubber. The minor objective is to improve the thermal properties towards natural rubber by using recycled EPDM in the second phase. In natural rubber, semi-efficient vulcanisation (semi-EV) and efficient vulcanisation (EV) can provide remarkable resistance to reversion and

Table 1
Formulations of the blends vulcanised using various accelerators.

Materials (phr)	Sample codes			
	TBBS	CBS	TMTD	MBT
SMR L	70.0	70.0	70.0	70.0
R-EPDM	30.0	30.0	30.0	30.0
N330	30.0	30.0	30.0	30.0
ZnO	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
TBBS	1.2	–	–	–
CBS	–	1.2	–	–
TMTD	–	–	1.2	–
MBT	–	–	–	1.2
Sulphur	1.8	1.8	1.8	1.8

SMR L = Standard malaysian rubber L.
R-EPDM = Recycled ethylene-propylene-dienen rubber.
ZnO = Zinc oxide.
TBBS = N-tert-butyl-2-benzothiazyl sulphenamide.
CBS = N-cyclohexyl-benzothiazyl-sulphenamide.
TMTD = Tetramethylthiuram disulphide.
MBT = 2-mercaptobenzothiazol.

Table 2
Formulations of the blends vulcanised using various vulcanising systems.

Ingredients (phr)	Sample code				
	Semi-EV	Semi-EV/ Peroxide	EV	EV/Peroxide	Peroxide
Sulphur/ peroxide ratio	3:0	1.5:1.5	3:0	1.5:1.5	0:3
SMR L	70.0	70.0	70.0	70.0	70.0
R-EPDM	30.0	30.0	30.0	30.0	30.0
N330	30.0	30.0	30.0	30.0	30.0
ZnO	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
CBS	1.2	0.6	2.5	0.25	–
Sulphur	1.8	0.9	0.5	1.25	–
DCP	–	0.6	–	0.25	1.2
TMPTA	–	0.9	–	1.25	1.8

DCP = Dicumyl peroxide.
TMPTA = Trimethylolpropane-triacrylate.

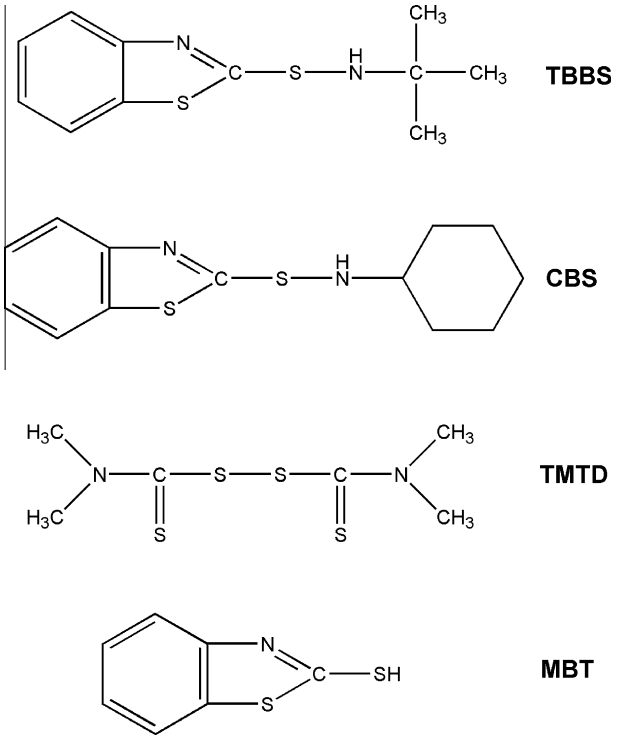

Fig. 1. Chemical structures of N-tert-butyl-2-benzothiazyl-sulphonamide (TBBS), N-cyclohexyl-benzothiazyl-sulphenamide (CBS), Tetramethylthiuram disulphide (TMTD), and 2-mercaptobenzothiazol (MBT).