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THE USE OF THERMOGRAVIMETRY IN THE STUDY OF RUBBER DEVULCANIZATION

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Abstract

Thermogravimetry was employed to study the changes occurring in rubber vulcanizates during devulcanization carried out by microwave treatment, a new promising method of recycling rubber waste. The thermogravimetric parameters T_i, T_5 and T_p and the compositions of devulcanizates in comparison with vulcanizates were determined. The results obtained allowed estimation of the degree of destruction of the polymer chains in response to microwave treatment and permitted establishment of the most advantageous conditions of devulcanization in order to obtain the best properties of rubber devulcanizates for reuse in rubber processing.

The results demonstrated that thermogravimetry is a very useful method for investigation and control of the microwave devulcanization process.

Keywords: analysis of decomposition, microwave devulcanization, rubber recycling, rubber waste, thermal stability, thermogravimetry

Introduction

Devulcanization is one of the new methods of recycling waste rubber products. It can be carried out by different methods, e.g. chemical, ultrasound or microwave (MW) methods. The concept of 'devulcanization' means the cleavage of cross-linking sulphur bonds in rubber vulcanizates, without cleavage of the polymer chain bonds [1, 2]. Devulcanization is recognized as the best way of utilizing rubber waste because it assumes renewal of the original chemical formula of elastomers and provides a possibility of recovering elastomers from rubber vulcanizate waste. It allows cross-linking and the re-use of the recovered elastomers in rubber products.

Very important ecological aspects are also involved, particularly in the range of utilization of waste tyres.

In practice, however, a 'pure' devulcanization process is very difficult to achieve since many problems are caused by accompanying chemical transitions such as depolymerization, thermal destruction and oxidation, which worsen the properties of the recovered elastomers. In the technical literature, there is no information concerning the successful achievement of the devulcanization process on a large scale, but merely examples of laboratory trials [3, 4].

The main problem hampering the appropriate running of the devulcanization process is the very low thermal conductivity of rubber and in this connection the extremely

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difficult selective regulation of the quantity of energy carried to the cross-linking bonds. Theoretically, such energy should sufficient for the dissociation of cross-linking S–S bonds (271.7 kJ mol^{-1}) and C–S (301 kJ mol^{-1}), but at the same time too little for dissociation of the C–C bonds(347 kJ mol^{-1}) in the polymer chains. In practice, it is virtually impossible to achieve such levels of energy evenly distributed in all materials. It is necessary experimentally to find optimal devulcanization conditions, under which 'devulcanized' products with good properties can be obtained. In our Institute, experimental work has been performed with the application of MW energy for the devulcanization of rubber vulcanizates in order to obtain devulcanizates [5].

The purpose of this work is the application of thermogravimetry to study the changes occurring in cross-linked rubber vulcanizates under the influence of MW treatment with the aim of devulcanization. Thermoanalytical parameters such as thermal stability, the parameters of thermal destruction and the composition of vulcanizates before and after devulcanization were determined. The thermoanalytical data obtained allowed estimations of the degree of polymer destruction during MW devulcanization and permitted proposals concerning the optimal conditions of devulcanization.

Experimental

Materials

The subjects of investigation were granulated rubber vulcanizates cross-linked by sulphur systems and obtained from their devulcanizates.

The vulcanizates of the following elastomers were used natural rubber (NR), butadiene-styrene rubber (SBR) and ethylene-propylene-diene rubber (EPDM). The components of the vulcanizates in parts/100 parts of rubber are listed below:

1. NR (RSS) – 100, ZnO –5.0, stearine – 1.5, sulphur – 2.5, paraffin wax G –2.0, carbon black – 50, naphthaic plasticizer – 8.0, N-isopropyl-N'-phenyl-*p*-phenyldiamine (IPPD) – 1.5, N-cyclohexyl-2-benzothiazyl sulphenamide (CBS) – 0.6,
2. SBR (Ker 1500) – 100, ZnO – 5.0, stearine – 2.0, sulphur – 1.5, carbon black – 60, paraffin oil – 25, naphthaic plasticizer – 1.2, CBS – IPPD – 1.0, CBS – 1.4 paraffin wax G – 2.0,
3. EPDM (Keltan 512) – 100, ZnO – 5.0, stearine – 2.0, sulphur – 1.5, carbon black – 60, paraffin oil – 25, tetramethyl thiuram disulphide – 0.5, mercaptobenzothiazole – 1.0, zinc ethylphenyldithiocarbamate – 1.5.

The devulcanizates were obtained from the above vulcanizates by treatment with different quantities of MW energy during devulcanization.

Methods

Thermogravimetric investigations were performed with a Perkin Elmer Thermobalance TGS under the following conditions:

Samples of about 10 mg were heated at a heating rate (β) of 10°C min^{-1}, first in nitrogen atmosphere from ambient temperature (25) to 600°C, to achieve constant mass, and the residues were next cooled to 300 and again heated in air to 800°C, to total destruction.

The TG and DTG curves were recorded. The following thermoanalytical data were determined:

T_i – initial temperature of decomposition,
T_5 – thermal stability index at the temperature of 5% mass loss,
T_p– temperature of decomposition peak.

The contents of organic ingredients, polymers, organic non-polymeric substances, carbon black (soot) and ash in the vulcanizates were determined on the basis of the $-\Delta m_x/m_s$ values, according to the method described in ISO/DIS 9224-1 [6] and used in our previous work [7].

Results and discussion

Thermogravimetric investigations of rubber vulcanizates subjected to previous MW treatment revealed distinct changes in comparison with untreated samples, the changes depending on the MW energy used in the devulcanization process.

Examples of TG and DTG curves obtained during the heating of vulcanizates of NR and its ‘devulcanizates’ are presented in Fig. 1. The TG data clearly indicate the changes in the shape of the thermal curves of the vulcanizates and devulcanizates and in their characteristic decomposition temperatures.

The regions of decomposition of non-polymeric substances and polymers for devulcanizates were not separated as in the curves of the vulcanizates, but overlapped. This may suggest that intermediates with lower molecular masses than those of the initial elastomers occur in the rubber devulcanizates as a results of degradation of the polymer chains under the influence of MW action.

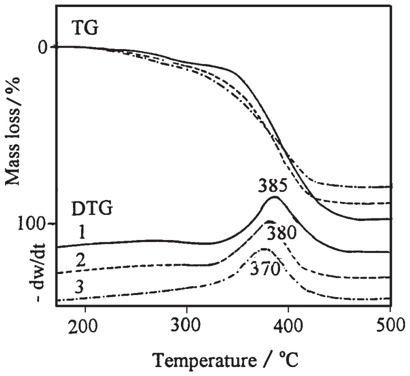

Fig. 1 TG and DTG curves of NR vulcanizate (1) and its ‘devulcanizates’ (2, 3), recorded in N_2 atmosphere, β=10°C min^{-1}

Table 1 Comparison of thermogravimetric data for vulcanizates before and after microwave (MW) treatment (in MW devulcanization process)

Vulcanizates		MW energy/ kJ kg^{-1} of sample	Thermal stability indices in nitrogen/°C			Temp. of destruction of carbon black (soot) and carbon residue in air/°C
			T_o	T_5	$T_{DTG\ max}$	
NR after MW*		0	180	290	385	510–615
	1	540	160	265	380	450–625
	2	612	140	260	370	440–635
SBR after MW*		0	200	290	465	500–610
	1	360	190	285	465	490–620
	2	435	180	280	460	460–630
	3	540	170	275	450	440–655
	4	612	140	270	450	420–650
EPDM after MW*		0	200	280	480	500–600
	1	650	185	275	470	490–615
	2	935	180	265	470	480–625

*Samples 1–4 vulcanizates treated with increasing amounts of MW energy

Significant decreases in the initial temperature of mass loss T_i and the thermal stability index T_5 of the vulcanizates before and after MW treatment were observed (Table 1). Examples of the determination of the compositions of devulcanizates in comparison with the data obtained for the raw vulcanizates are presented in Table 2. The following changes in composition of the devulcanizates were found as a result of MW action.

1. decrease in the total content of organic component,
2. decrease in the amount of polymer,
3. increase in the amount of organic non-polymeric substances,
4. increase in the total amount of carbon black (soot) and carbon residue,
5. decrease in the ash content.

The above phenomena were more marked when the vulcanizate samples were treated with higher MW energies. The data presented in Table 2 testify that extensive destruction of the polymers took place. The ‘devulcanizates’ obtained under these conditions of MW devulcanization can be expected not to have properties appropriate for their re-use in rubber technology. To obtain devulcanizates containing less destroyed polymers, the MW energy used in the devulcanization process or the time of expositure of the vulcanizate samples should be decreased.

Results on the devulcanizate compositions obtained under adjusted optimal parameters of the devulcanization process are illustrated by the data in Table 3. It follows from the data that the changes in the thermal stability indices and in the compositions of the devulcanizates in comparison with the vulcanizates in this case are rela-

Table 2 Compositions of vulcanizates, before and after microwave (MW) treatment, determined by TG

Sample	*	MW energy/ kJ kg^{-1}	Contents of ingredients/%									
			$\sum$ Organic ingredients		Rubber		Organic non-polymeric ingredients		Carbon black+ carbon residue		Ash	
			theor.	exper.	theor.	exper.	theor.	exper.	theor.	exper.	theor.	exper.
SBR			68.6	68.5	56.9	56.5	11.7	12.0	28.5	29.0	2.9	2.5
	1	380		65.6		52.1		13.5		32.0		2.4
	2	435		55.8		39.8		16.0		42.8		2.4
	3	540		51.6		35.3		16.3		46.0		2.4
	4	612		50.5		33.0		17.0		47.0		2.4
NR			68.9	68.5	58.8	60.4	10.1	8.1	28.2	29.4	2.9	2.5
		540		61.1		47.6		13.5		36.5		2.4

*Samples 1–4=SBR vulcanizates treated with increasing amounts of MW energy

Table 3 Thermogravimetric data and compositions of vulcanizates (V) and devulcanizates (DV) obtained under optimal conditions of microwave (MW) devulcanization process

Sample	MW energy/ kJ kg^{-1} of sample	Temp./°C		Contents of ingredients/%									
				$\sum$ Organic ingredients		Rubber		Organic non-polymeric ingredients		Carbon black + carbon residue		Ash	
		T_o	T_5	theor.	exper.	theor.	exper.	theor.	exper.	theor.	exper.	theor.	exper.
V-NR		180	290	68.9	68.5	58.8	60.4	10.1	8.1	28.2	29.4	2.9	2.1
DV-NR	320	160	285		67.5		58.0		9.5		30.0		2.5
V-SBR		200	290	68.6	68.3	56.9	56.5	11.7	12.0	28.5	29.0	2.9	2.5
DW-SBR	350	190	285		65.5		52.5		13.0		32.3		2.1
V-EPDM		200	280	66.7	68.5	51.1	52.4	15.6	16.5	30.7	29.4	2.6	2.1
DV-EPDM	600	190	275		61.8		46.4		15.4		35.8		2.4

tively small, which shows that destruction of the polymer chains occurred to a very slight degree.

Conclusions

Thermogravimetry has been successfully employed to analyse rubber devulcanizates obtained during microwave devulcanization, applied for the recycling of rubber waste. The thermogravimetric data permit an evaluation of the degree of thermal destruction of the polymers in devulcanizates by comparison of the thermal parameters and compositions of vulcanizates before and after treatment with microwaves. TG data are very useful to establish the optimal parameters of the devulcanization process in order to protect against the accompanying disadvantageous reactions such as depolymerization or thermal destruction of the polymer chains during the devulcanization process.

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