THERMAL STABILITIES OF VARIOUS RUBBER VULCANIZATES CURED BY SULFUR, PEROXIDE AND GAMMA-RADIATION

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ABSTRACT

Sulfur and peroxide-cured rubber vulcanizates of NR and EPDM were obtained by blending the elastomers with fillers, antioxidants and appropriate accelerators, followed by vulcanization at 150 – 160 °C. Blends of the same elastomers with appropriate co-agents and additives were also cured by gamma radiation at 150 and 200 kGy. A comparison of the thermal stabilities of these vulcanizates prepared by different curing techniques has been made by thermogravimetric analysis (TGA), assessed on the basis of comparison of DTG peak maxima, temperature for loss of 50% mass and actual thermal curves. The comparison reveals that the sulfur-cured vulcanizates are less thermally stable than their peroxide-cured counterparts. This may be attributed to the presence of a stronger C-C bond in case of peroxide-cured vulcanizates compared to weaker C-S_x-C bond in case of sulfur-cured vulcanizates. However, compared to peroxide-cured vulcanizates, radiation-cured formulations demonstrated much improved thermal stability. This may originate from the existence of more uniformly distributed crosslinks and the enhanced rate of crosslink formation in the radiation process as compared to peroxide curing. In all the formulations whether sulfur, peroxide or radiation-cured, the natural rubber vulcanizates were found to be thermally much inferior to the synthetic contender, EPDM. Influence of variation of the amount of coagent and other additives on the thermal stabilities of formulations of radiation cured NR and EPDM vulcanizates was also investigated.

1. INTRODUCTION

One important application of the TG-DTG technique is the determination of the thermal stability of polymers. Thermal stability of polymers including PE, SBR and PVC was assessed by Smith (1) using TG-DTG technique based on temperature of original weight loss. A detailed review of TG technique by Troops (2) shows how to apply TG to predict the service life of wire enamel. A comparison of thermal stability of sulfur-cured formulations with their peroxide counterparts was reported earlier by the authors of this paper (3). Here we report the comparison of thermal stability of radiation-cured formulations with their peroxide and sulfur-cured counterparts for which the best thermally stable formulations from each group were selected. It was envisaged that such comparison would help us to assess the relative merits of radiation curing over conventional sulfur and peroxide curing. A distinct feature of the approach adopted for assessing comparative thermal stabilities involves the use of temperature for loss of 50% mass of the sample, in addition to record of DTG peak maxima. This is especially advantageous for selecting the best among formulations demonstrating close thermal stability due to overlap of DTG peaks. In addition, this observation is objective and does not suffer from the subjective errors likely to occur while recording DTG peak maxima.

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2. EXPERIMENTAL

Materials

The elastomers used in this study were commercial grade, natural rubber (NR type SMR-20) and ethylene-propylene diene monomer rubber (EPDM type Kelton 720) with ethylene/propylene ratio: 72/28. All the materials including elastomers, fillers, antioxidants accelerators, etc. were supplied by Amiantit Rubber Co., Saudi Arabia.

Compounding and Vulcanization

The various formulations utilized in this study are proprietary and a general list of constituents are presented in Table I. A Brabender Plasticorder Model PL-2000 and an internal mixer Model 350 S were used. The compounding was carried out in accordance with ASTM D-3182. A hydraulic hot press by PHI Co. Model G236 H was used to press and vulcanize rubber sheets with an average thickness of about 2 mm in accordance with ASTM D-3191. The formulations containing sulfur were vulcanized at 150 °C for 30 minutes and the ones containing peroxide were vulcanized at 160 °C for 60 minutes.

Table I. Formulations of Different Rubber Vulcanizates.

Notation	Ingredients (phr)							
	Elastomer	Carbon black/silica	Oil	ZnO	Stearic acid	Anti-oxidants	Anti-Ozonant	Curing agent and coagent
S-Cured EPDM	100	130	110	5	0.5	4	0	Sulfur
S-Cured NR	100	46	10	5	2	5	1	Sulfur
Peroxide-Cured EPDM	100	130	110	5	1	4	0	Peroxide
Peroxide-Cured NR	100	46	10	5	2	5	1	Peroxide
Radiation-Cured EPDM	100	45	0	0	0	2	1	Radiation / SR-517[a]
Radiation-Cured NR	100	45	0	0	0	0	0	Radiation / SR-633[b]

a= SR-517 (trimethacrylic ester), b = SR-633 (zinc diacrylate).

Irradiation

The compressed sheets were irradiated in nitrogen atmosphere at a dose rate of 13 kGy / h to an absorbed dose of 150 kGy, and 200 kGy.

Thermogravimetric and Derivative Thermogravimetric Analysis:

A Perkin Elmer TGA-7 was used. Sample weight was generally from 8-13 mg. A standard heating rate of 5 °C /min. was used. The general procedure was to program-heat from ambient to 800 °C under a nitrogen atmosphere. Carrier gas flow was constantly monitored with flow meter and maintained at 40 cm^3/min. throughout the run.

3. RESULTS AND DISCUSSION

Thermal Stability Study of Radiation-Cured NR, EPDM Formulations

Thermal stabilities were assessed on the basis of comparison of DTG peak maxima, temperature for loss of 50% mass and temperature for onset of degradation.

Thermal Stabilities of Radiation-Cured EPDM Formulations Containing Different Concentrations of Coagent Type SR-633 and Fillers.

It is common practice in industry to add to the polymer, polyfuctional monomers containing two or more ethylenic bonds to enhance radiation crosslinking (4,5,6). Use of crosslinking

agent can help reduce the dose required for corsslinking (7,8) and the detrimental influences associated with high dose irradiation can be avoided. For this study, influence of addition of varying amounts of coagent SR-633 containing two double bonds was investigated by comparing DTG peak maxima. On the basis of DTG peak maxima and the temperature of onset of degradation, the EPDM formulations (loaded with carbon black) having 2 and 4 phr of the coagent appear to possess the best thermal stability (see Fig.1). Their DTG maxima are 533 °C and 535 °C respectively. On the basis of temperature for loss of 50% weight, the formulation containing 4 phr of the coagent can be considered as the best thermally stable in the group. No correlation between the amount of coagent and the thermal stability was found.

Fillers or reinforcement aids such as carbon black, clays and silica are added to rubber formulations to meet material property targets such as tensile strength and abrasion resistance etc., Addition of silica to a rubber compound offers a number of advantages such as improvement in tear strength, reduction in heat build up and increase in the compound adhesion in multicomponent products such as tires (9). It was considered important to explore the influence of silica loading on the thermal stability of EPDM rubber.

When silica was used as filler instead of carbon black, formulations possessing compatible thermal stability (see Fig.2) appear to have been attained. Again, there is no correlation between the amount of coagent and the thermal stability, though in general, formulations containing 3, 4 phr are better than the rest. On the bais of combined evidence, the formulation containing 4 phr of coagent SR-633, is the best thermally stable formulation.

An intercomparison of the various above mentioned temperatures selected as the creiteria for comparing thermal stablilties shows that in the series of EPDM formulations, the formulation containing 4 phr of coagent type SR-633 (containing 45 phr of silica) is the most thermally stable.

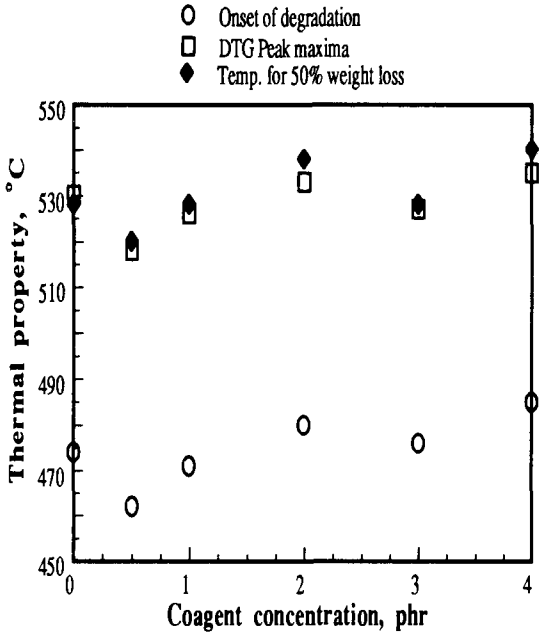

Fig.1: Thermal stabilities of EPDM formulations containing 45 phr of HAF-carbon black, different concentrations of coagent type SR-633,1 phr of antioxidant and irradiated to 150 kGy.

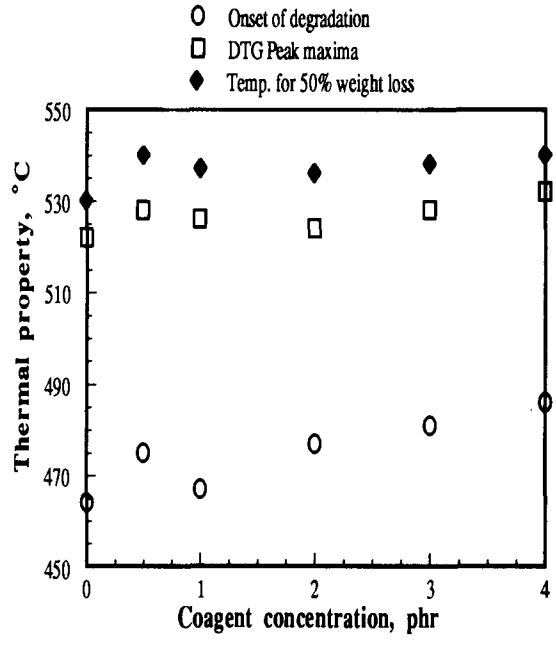

Fig.2: Thermal stabilities of EPDM formulations containing 45 phr of silica, variable concentrations of coagent type SR-633 and irradiated to 150 kGy.

Thermal Stabilities of NR Formulations Containing Different Concentrations of Coagent Type SR-517 and Carbon Black or Silica as Fillers

On the basis of the comparison of the onset of degradation, temperature for the loss of 50% mass and DTG peak maxima, it can be inferred that the NR formulation containing 3 phr of the coagent SR-517 (loaded with carbon black) is the most thermally stable in the group (see Table II). The presence of the coagent at levels higher than 3 phr appears to exert a significant detrimental influence on thermal stability. This is expected as the excessive amounts of unreacted coagent are likely to generate free radicals on radiolysis. The interaction of these radicals with the elastomer presumably, results in retardation of degree of curing. Formulations possessing much lower thermal stability were obtained by replacing carbon black with silica (see Table III). Formulation containing 3 phr of the coagent SR-517 along with IPPD, TMQ (antioxidant and antiozonant) appears to be the most thermally stable in the group. Here again a pronounced detrimental influence on the thermal stabilities was observed when amounts of the coagent used were in excess of 3 phr.

Table II. Thermal Stabilities of NR Formulations Irradiated to 200 kGy Containing Various Concentrations of Coagent Type SR-517 and 45 phr Carbon Black and other Additives (Antiozonants and Antioxidants).

Concentration of Coagent (phr)	Onset of Degradation (°C)	DTG Peak Maxima (°C)	Temperature for Loss of 50% mass (°C)
3	356	417	412
4	349	411	407
5	349	412	408
6	354	414	410
5a	348	412	407
5b	346	413	407

a: Formulation contains 1phr IPPD, 1 phr TMQ and 0.5 phr paraffin wax
b: Formulation contains 1phr IPPD, 1 phr TMQ and 1phr paraffin wax

Table III. Thermal Stabilities of NR Formulations Irradiated to 200 kGy Containing Various Concentrations of Coagent Type SR-517 and 45 phr Silica and Other Additives (Antiozonants and Antioxidants)

Concentration of Coagent (phr)	Onset of Degradation (°C)	DTG Peak Maxima (°C)	Temperature for Loss of 50% mass (°C)
3	337	404	400
4	314	374	375
5	314	378	370
6	305	368	362
3a	354	410	404
3b	347	393	386

a: Formulation contains 1phr IPPD, 1 phr TMQ and 0.5 phr paraffin wax
b: Formulation contains 1phr IPPD, 1 phr TMQ and 1.0 phr paraffin wax

Intercomparison of Thermal Stabilities of Radiation-Cured EPDM and NR Formulations

In general, all the NR formulations exhibit much lower thermal stabilites than the EPDM counterparts. This originates from the intrinsic thermal stabilities of the two types of rubbers (see Table IV).

Comparison of Sulfur-Cured Vulcanizates with Peroxide-Cured Counterparts

When compared, sulfur-cured EPDM and NR vulcanizates individually with their counterparts in peroxide-cured systems, peroxide-cured rubbers exhibit marginally higher thermal stabilities (see Table IV) with the exception of temperature for onset of degradation for EPDM rubber. This is expected due to the higher bond strength of C-C bonds in peroxide-cured system compared to C-S_x-C bond strength which is of lower order.

Table IV. Comparison of Thermal Stabilities of Radiation-Cured EPDM and NR Vulcanizates with Sulfur and Peroxide-Cured Counterparts.

Sulfur-Cured Vulcanizates			
Rubber Type	DTG Curve due to Elastomer ,T_{max} (°C)	Temperature for 50% Weight Loss (°C)	Temperature for Onset of Degradation (°C)
EPDM	483	487	374
NR	395	410	352

Peroxide-Cured Vulcanizates			
Rubber Type	DTG Curve due to Elastomer ,T_{max} (°C)	Temperature for 50% Weight Loss ((°C)	Temperature for Onset of Degradation (°C)
EPDM	496	497	341
NR	400	410	354

Radiation-Cured Vulcanizates			
Rubber Type	DTG Curve due to Elastomer ,T_{max} (°C)	Temperature for 50% Weight Loss (°C)	Temperature for Onset of Degradation (°C)
EPDM	535	540	486
NR	410	405	355

Intercomparison of Thermal Stabilities of Sulfur, Peroxide and Radiation-Cured Vulcanizates

A combined picture based on comparison of DTG curve maxima, temperature for loss of 50% mass and temperature of onset of degradation shows that in case of EPDM the thermal stabilities of radiation-cured formulations are quite superior when compared to the sulfur and peroxide-cured counterparts (see Table IV). This is reflected by much higher temperatures observed individually in case of DTG maxima, temperature of loss of 50% mass and temperature for onset of degradation for the radiation-cured vulcanizates when compared to the same temperatures observed in case of sulfur and peroxide-cured vulcanizates. Radiation-cured NR formulations did not demonstrate any significant gain in thermal stability when compared to sulfur or peroxide-cured counterparts. This may be related to the loss and isomerization of double bond due to radiation and also the formation of a less relaxed network in the irradiated crystallizable NR, which may influence its thermal stability (10).

4. CONCLUSIONS

The following conclusions can be deduced:

1. Acombined comparison based on DTG peak maxima,temperature of onset of degradation and temperature for 50% weight loss gives good indication of thermal stability of rubber compounds.

2. EPDM formulations filled with 45 phr of either carbon black or silica in the presence of 4 phr of XL-coagent and irradiated to 150 kGy possess the best thermal stability among the investigated formulations.

3. Silica filled EPDM rubber is more thermally stable than carbon black filled counterpart.

4. NR formulations filled with 45 phr of either carbon black or silica in the presence of 3 phr of XL-coagent and irradiated to 200 kGy possess the best thermal stability among the investigated formulations.

5. Carbon black filled NR rubber is more thermally stable than silica filled counterpart.

6. Radiation-cured EPDM formulations are more thermally stable than sulfur or peroxide-cured counterparts, whereas no significant improvement was realized in radiation-cured NR formulations.

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