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INVESTIGATION OF THE MECHANICAL PROPERTIES OF SILICONE RUBBER CONTAINING IMIDE-SILOXANE COPOLYMERS[1]

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Abstract

Prior to the present study, various imide-siloxane copolymers were prepared, the synthesis and characterization methods were described [1]. The experiments have been continued to provide a possibility by using these copolymers as additives in methylvinylsilicone rubber for high temperature vulcanizing (HTV) process. They are blended in varying proportions with methylvinylsilicone rubber. Investigation of the produced rubber demonstrates the effect of the imide content on the properties of silicone rubber.

Keywords: polydimethylsiloxane, siloxane, elastomers, copolymers.

1. Introduction

Silicones are unique among commercially important polymers both from the point of view of pure chemistry and their wide field of industrial applications [2]. There is a variety of interesting and useful properties exhibited by these materials which make them worthy of study and to develop new types of these compounds. Silicone polymers containing groups other than methyl were made in order to achieve improved properties [3-7]. In other cases, blending of silicone polymers with other organic polymers [8,9] gave elastomers with high thermal and chemical resistance and other interesting properties such as good mechanical properties. In these cases the polymer backbone contained both siloxy and other units such as sulfone, ethers, etc. Additives such as ferric oxide, ferrocene, etc. were used against thermooxidative degradation [10-12].

The aim of our further investigations was to clarify the effect of the imide-siloxane copolymers on the properties of siliconee rubber (mechanical, thermal properties and chemical resistance).

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2. Experimental

Process of vulcanization

The two types of siloxane-imide copolymer (from pyromellit-diimide referred to as (A) and benzophenontetracarboxylic-diimide referred to as (B)) were mixed with methylvinylsilicone rubber in different weight ratios (5-50 weight %). In all samples the same amounts of filler fumed silica (40%), anti crepe agent (20%), and 2,4-dichlorobenzoyl peroxide (1.5%) were used.

The finished batch was vulcanized in a closed system under pressure by using 2,4-dichlorobenzoyl peroxide as initiator, and we obtained sheets with 2 mm thickness. The time necessary for cross-linking was 10 min at 150 °C under 16.2 MPa (160 atm) pressure, and then the product was cured at a temperature of 200 °C in an air furnace for 4 hours to complete the vulcanizing process.

3. Characterization of Methylvinylsilicone Rubber Containing Imide-siloxane Copolymers

The most important properties of the produced rubber were investigated as follows.

3.1. Mechanical Properties

The mechanical properties as tensile strength, tear strength and elongation were determined by a ZMGi–250 type machine (with 250 mm/sec stretching speed). The mechanical properties of the prepared methylvinylsilicone-imide rubber mixtures are listed in *Tables 1* and *2*.

The data represent test-values of the pure methylvinylsilicone rubber as standard and those of the two different silicone-imide copolymer products. Tensile and tear strength determinations may have an error of 2% and that for elongation measurements is 3%.

Hardness (Shore A), tensile strength, elongation and tear strength values were compared with those of pure methylvinylsilicone rubber (*Tables 1* and *2*). It was found that with the exception of hardness, the mechanical properties were influenced even by small amounts of the imide additives.

The tensile strength shows a linear decrease with increasing imide content of the rubber. It is in good agreement with the fact that the tensile

Table 1
Mechanical properties of silicone rubber containing (A) copolymers

Copolymers wt%	Tensile strength Nmm^{-2}	Tear strength Nmm^{-1}	Elongation (%)	Hardness Shore A
5	8.4	19	420	67
10	8.0	22	440	67
15	7.6	25	445	67
25	6.8	32	480	67
30	6.5	37	490	66
40	5.2	28	430	66
50	4.5	18	350	66
0	8.8	17	400	67

Table 2
Mechanical properties of silicone rubber containing (B) copolymers

Copolymer wt%	Tensile strength Nmm^{-2}	Tear strength Nmm^{-1}	Elongation (%)	Hardness Shore A
5	8.3	21	430	67
10	7.7	26	455	67
15	7.3	30	480	67
25	6.4	39	535	66
30	5.8	35	510	66
35	5.2	29	485	66
40	4.5	24	450	66
50	3.4	17	380	66

strength of methylvinylsilicone rubber decreased with increased imidesiloxane oligomer content. Both the tear strength and elongation values attain a maximum for the 25 and 30 wt% imide-siloxane copolymer. Tensile strength, tear strength and elongation properties are shown in *Figs 1, 2* and *3*, respectively. The samples of methylvinylsilicone as standard, and methylvinylsilicone rubbers (containing 25 wt% of A and B imide) were aged at 200 °C for 24 48 and 72 hours, respectively. Their mechanical properties were compared with those of the unaged samples.

Earlier reports on polymethylvinylsiloxane rubber (with 0.5 mol% vinyl content) showed that the ageing of the samples at elevated temperature led to a deterioration of the mechanical properties. The mechanical properties after ageing are summarized in *Table 3*.

The results of thermooxidative ageing in *Table 3* as compared with data for pure methylvinylsilicone rubber show that even after a 72 hours

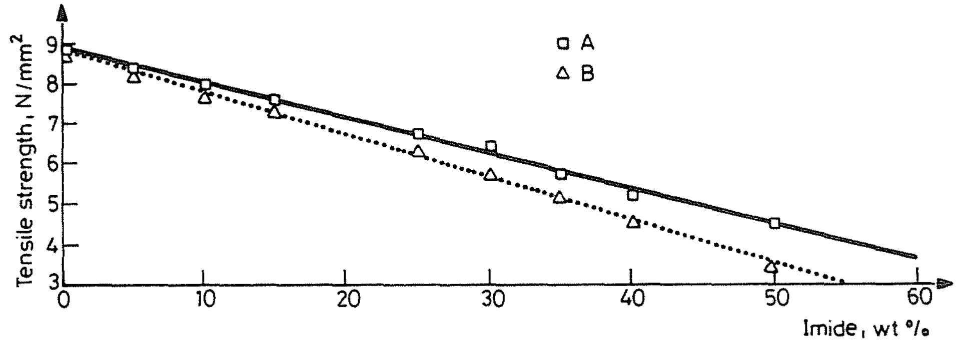


Fig. 1. Tensile strength - imide wt%

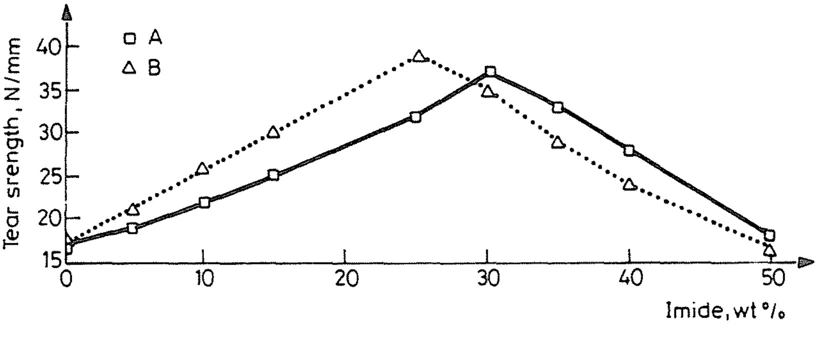


Fig. 2. Tear strength - imide wt%

treatment the mechanical properties of the rubbers containing imide-siloxane copolymer (B) are not changed. After longer treatments, it is supposed that the degradation process is accompanied by a cross-linking process. The resultant of the two processes explains the improvement of the mechanical properties.

3.2. Compression Set Measurements

The compression set is expressed as the per cent of retention of deformation for a test body after the sample has been heated for a specified time period and at given temperature under compression. The values of the compressibility are shown in *Table 4*.

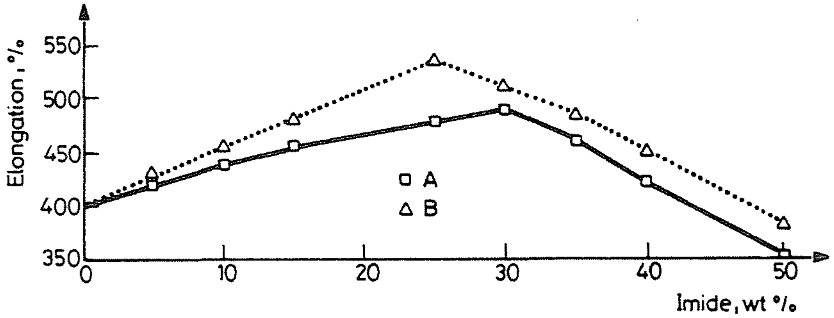


Fig. 3. Elongation - imide wt%

Table 3

Mechanical properties for samples of methylvinylsilicone rubber with 25 wt% imide A content and 25 wt% imide B content, respectively, before and after ageing at 200 °C

Ageing time at 200 °C (hours)	Mechanical properties	Methyl vinyl silicone rubber	25 wt% (A) imide	25 wt% (B) imide
	1. Tensile strength Nmm^{-2}	8.8	6.8	6.4
	2. Tear strength Nmm^{-1}	17	32	39
0	3. Elongation %	400	480	535
	4. Hardness (Shore A)	67	67	66
	1. Tensile strength Nmm^{-2}	8.8	7.0	7.0
	2. Tear strength Nmm^{-1}	16.8	32	39
24	3. Elongation %	400	425	525
	4. Hardness (Shore A)	68	66	66
	1. Tensile strength Nmm^{-2}	8.7	6.5	7.7
	2. Tear strength Nmm^{-1}	16.2	29	39
48	3. Elongation %	350	271	580
	4. Hardness (Shore A)	70	64	67
	1. Tensile strength Nmm^{-2}	7.5	5.4	8.1
	2. Tear strength Nmm^{-1}	14.9	29	38.4
72	3. Elongation %	250	271	500
	4. Hardness (Shore A)	72	64	67

The data in *Table 4* show that with increasing imide ratio in the methylvinylsilicone-imide rubber the compression set values decrease (indicating low compressibility). The imide (A) and (B) content in the per-

Table 4
Compression set % of the prepared imide-siloxane rubber (1)

Wt%	A	B	Me Vi
5	29.0	28.0	31.0
10	27.0	26.0	
15	26.0	24.0	
25	25.0	22.0	
30	24.0	21.0	
35	23.0	19.0	
40	20.0	17.0	
50	15.0	12.0	

(1) Each value is the average of five measurements, R.S.D. ±5%.

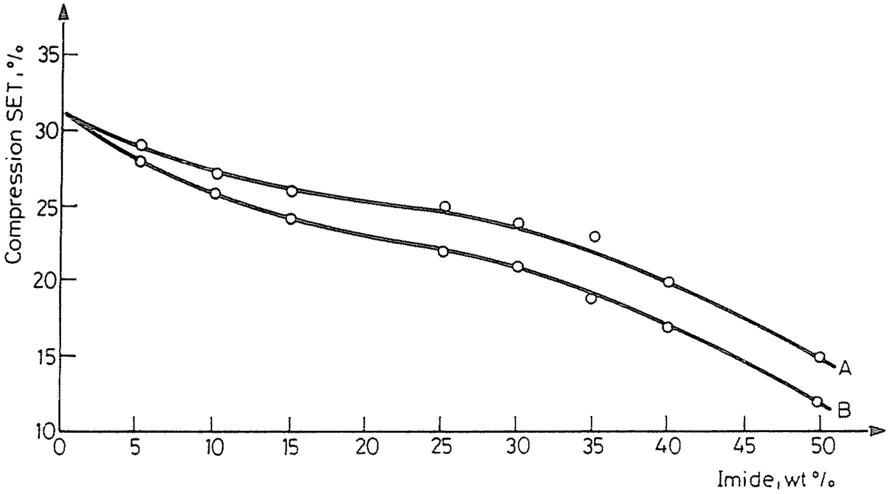


Fig. 4. Compression set - imide wt%

meation rubber is effective in improving the compression set. Compression set values versus imide content are shown in *Fig. 4*.

3.3. Water-vapour Permeation Measurements

To study the permeability of films to water vapour measurements were carried out by placing circular films over the mouth of a bottle, adhesive mixture was poured around the edge of the glass to seal off the edge of the films. Water was placed in the bottle, the circular area through which permeation took place was 4.0 cm^2. The thickness of the films was between 0.0035 and 0.0040 cm. The bottle was then placed into a desiccator. Phosphorus pentoxide was inserted in the bottom of the desiccator. Weighings were then performed after 24 hour periods. All measurements were made at 25.0±0.5 °C. The relative humidity in the bottle was 100%, however, inside the desiccator it was 0% at the external surface of the film. The surface of the liquid was in all cases 6.0 cm^2. Weighings were made by an analytical balance.

The rate of water-vapour permeation was given in g·cm (thickness)/cm^2·h. Hence, amounts of water-vapour passed through were plotted versus time; the relationship yielded a straight line, the slope of which gave the rate of water-vapour permeation through the rubber films. The rate of water-vapour permeation values for different types of rubber sheets are summarized in *Table 5*.

Table 5
Rate of water-vapour permeation g·cm/cm^2·h

	Imide weight per cent								
Imide % type	5	10	15	25	30	35	40	50	MeVi
A	7.457	7.558	7.745	7.937	8.151	8.272	8.502	8.75	7.358
B	7.549	7.737	7.921	8.154	8.355	8.69	8.87	9.268	

The data show that the rate of water-vapour permeation increases with increasing imide content in the sample. In the case of type (B) a large increase in the rate of water-vapour permeation was observed in comparison with type (A). These additives loosen the structure of the rubber (ruptures appear), and the long distances between chains ensure vapour transfer. The rate of water-vapour permeation versus the imide content is shown in *Fig. 5*.

3.4. Solvent Resistance of Silicone Rubbers

The solubility properties of siliconee rubber are best reflected in the swelling behaviour. Swelling measurements were made according to the following method.

Samples with approximately 1 cm^2 circular area were weighed before swelling, placed in the solvent for 7 days at room temperature (23±2 °C). After 24 hours of swelling the samples were removed and the excess solvent

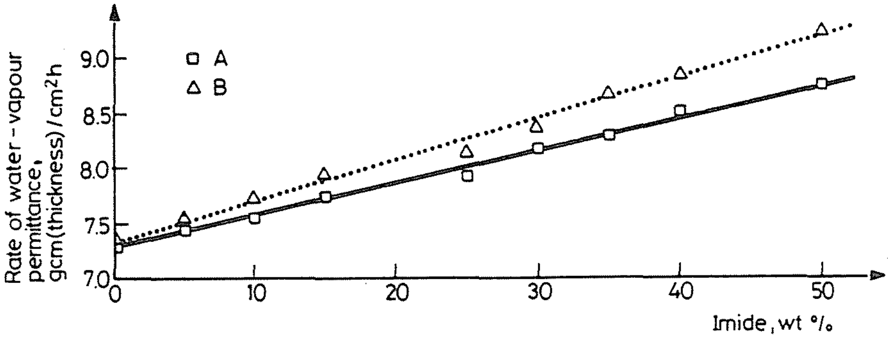
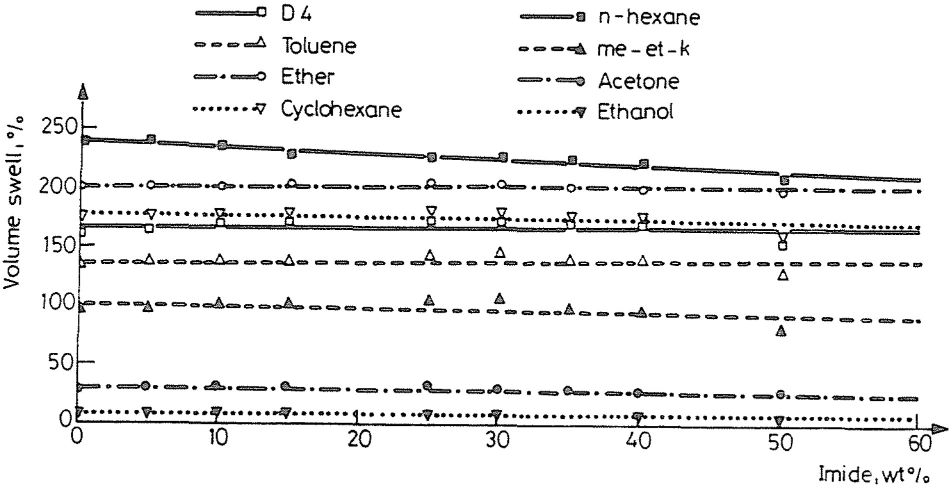


Fig. 5. Rate of water-vapour permeation - imide wt%

was quickly removed from their surface by blotting between sheets of filter paper. The swollen sample was weighed by an analytical balance. The samples were replaced in their respective solvents for another 24 hours and the procedure repeated, until the final swollen weight was obtained. The measurement of the degree of swelling used in the investigation was 'volume per cent swell'. The volume swell versus imide wt% (of A and B copolymers) shown in *Figs. 6* and *7*, respectively.



D4 : octamethyl-cyclo-tetrasiloxane
me-et-k: methyl-ethyl-ketone

Fig. 6. Volume swell - imide (A) wt%

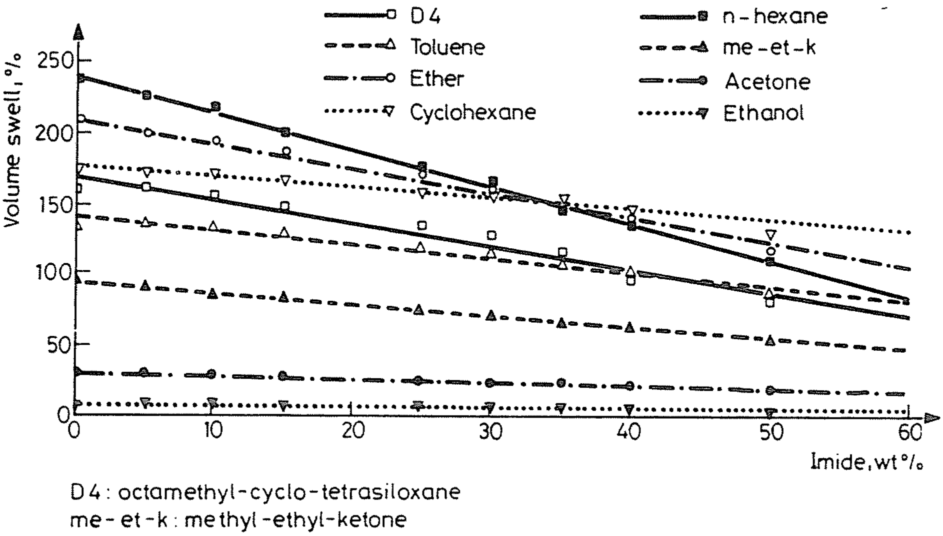


Fig. 7. Volume swell - imide (B) wt%

The incorporation of two different imide-siloxane copolymers into the methylvinylsilicone rubber affects the swelling resistance, and the swelling ratio decreases with increasing B-imide type content, but in the case of A-imide type, the swelling ratios increase with increasing imide content.

4. Conclusion

It can be stated that the imide-siloxane copolymer (A) influences the properties of methylvinylsilicone rubber only in small degree, but the copolymer (B) has a larger effect.

Acknowledgement

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