

Effect of Fillers on Thermal and Mechanical Properties of Polyurethane Elastomer

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ABSTRACT: The effects of five different types of fillers on the thermal and mechanical properties of hydroxyl-terminated polybutadiene-based polyurethane elastomers were explored to develop a filled polyurethane elastomeric liner for rocket motors with hydroxyl-terminated polybutadiene-based composite propellants. Two types of carbon black, silica, aluminum oxide, and zirconium(III) oxide were used as filler. Based on the improvement in the tensile properties and the erosion resistance achieved in the first part of the study, an ISAF-type carbon black was selected to be used as the main filler in combination with an additional filler. The second part involves the investigation of polyurethane elastomers containing a second filler in various amounts in addition to the ISAF-type carbon black used as the main filler. In addition to the thermal and mechanical properties, the processability of the uncured polyurethane mixtures were also explored by measuring the viscosity in this second part of the study. The studied fillers do not considerably change the thermal degradation temperatures and the thermal conductivity of the polyurethane elastomers with a filler content up to 16 wt %. The best improvement in the erosion resistance and tensile strength of the polyurethane elastomers with additional fillers is also achieved when filled with the ISAF-type carbon black, whereas the use of zirconium(III) oxide as additional filler provides almost no improvement in these properties. Viscosity of the uncured polyurethane mixtures increases with the increasing filler content and with the decreasing particle size of the filler. Aluminum oxide-filled elastomers seem to be the most suitable compositions having sufficiently high thermal and mechanical properties, together with the processability of uncured mixtures. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1057–1065, 1998

Key words: elastomers; polyurethane; HTPB; propellant; composite; thermal properties; mechanical properties; fillers

INTRODUCTION

Polyurethanes are probably the most versatile class of polymers due to the great variety of raw

materials that can be used in their formation.¹ The polyurethanes are usually used as adhesives, coatings, foams, and different kinds of plastics and elastomers, as well as rocket motor liners for securing the composite propellant grain within the rocket motor. Especially for hydroxyl-terminated polybutadiene (HTPB)-based composite solid propellants, polyurethane elastomers composed of the same HTPB prepolymer and diisocya-

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nate are widely used as rocket motor liners that can be prepared by casting or spraying.² Case bond liner systems for solid rocket motors have been formulated in a number of ways to maximize their design properties when interfaced with a propellant. Because a successful case bond liner system is one that fails cohesively in the propellant, any other mode of failure in the system is unacceptable. A recent article describes the improvement in the adhesive properties of polyurethane elastomers achieved by changing the NCO/OH and triol/diol ratios that primarily govern the crosslinking level.³ Considerable improvement in some of the thermal and mechanical properties of the polyurethane elastomers can also be achieved by using appropriate fillers of different type and amount.⁴ The effect of fillers on mechanical properties of other elastomers and the aspects of reinforcement have been studied in a general way.⁵⁻⁷ There have been some studies on the effect of fillers on tensile properties of polyurethane.^{8,9} The selection of fillers is also important to increase the erosion resistance of polyurethane elastomers.^{10,11} However, the effect of fillers on thermal degradation of polyurethane elastomers has not been studied extensively. In one of the existing studies on elastomers other than polyurethane, the fillers have been reported to cause only small changes in thermal stability of hydrocarbon elastomer.¹² Herein, we report the results of our extensive studies on the effects of five different type of fillers on the thermal and mechanical properties of HTPB-based polyurethane elastomers. The NCO/OH ratio was taken to be 1.1 as the optimum value determined in the previous study on the adhesive properties of polyurethane liner.³ Two types of carbon blacks, silica, aluminum oxide, and zirconium(III) oxide were used as filler in the HTPB polyurethane elastomers. Furthermore, the viscosity of uncured polyurethane mixtures was measured to investigate the effect of fillers on the processability of liner.

EXPERIMENTAL

Materials

HTPB (R-45M, number average molecular weight of 2700; ARCO Chemical Company, Philadelphia, PA), isophoron diisocyanate (Fluka AG, Buchs, Switzerland), triethanolamine (Merck, Darmstadt, Germany), carbon black (ISAF, Printex-U, 25 nm particle diameter, 98% carbon content,

0.7% sulfur content, 110 m² g⁻¹ surface area, pH 4, Degussa A. G., Frankfurt, Germany; MT, Thermax, 300 nm particle diameter, Cancarb Co., Medicine Hat, AB, Canada), methyl aziridiny phosphine oxide (MAPO; Arsynco, Carlstadt, NJ), silica (500 nm; Unimin Co., Elco, IL), aluminum oxide (5 μm particle diameter; Metco Co., Westbury, UK), zirconium(III) oxide (10 μm particle diameter, Metco Co.), and dioctyl adipate (Kimtaç, Istanbul, Turkey) were used.

Polyurethane Elastomer Preparation

The polyurethane-based elastomeric liners were prepared according to the route of a one-shot method described previously.¹³ All of the ingredients, except for the curing agent and the curing catalyst, are blended thoroughly in a horizontal mixer for a certain time period under vacuum at 65°C. After addition of curing agent to the slurry, the mixture is blended for another period under vacuum. Dry nitrogen gas blanket is maintained throughout the mixing. Freshly prepared polyurethane mixture is cast into Teflon molds and cured for 7 days at 65°C. The dog-bone-shaped elastomeric specimens are used in the tests.

Method of Testing

The thermal degradation temperatures of polyurethane samples were measured by using a Rheometric Scientific 1000M-type TGA instrument with a heating capability of up to 1000°C. The heating rate (10°C/min), the oven atmosphere (N₂ gas), and the sample weight (20 mg) were all kept constant for all of the samples. The erosion rate measurements were performed according to the ASTM Standard¹⁴ for oxyacetylene ablation testing of thermal insulation materials. In this test, the time needed for the penetration of the flame through the specimen is measured. The thickness of the specimen was measured and divided through the burn-through-time to obtain the erosion rate of the materials. The thermal conductivity of polyurethane specimens were measured by using a Kyoto Electronics Kemtherm QTM-D3-type instrument. The tensile properties of the polyurethane elastomers are determined in the form of dog-bone test specimens under predetermined conditions of pretreatment and temperature.¹⁵ The cured samples are tested for their mechanical properties (tensile strength, elongation at break) at room temperature and with a cross-head speed of 50 mm/min by using a conven-

Table I Compositions of Unfilled and Filled Polyurethane Elastomers

Composition	Filler Type	Filler Content (wt %)
UPR	—	—
CL-0	ISAF carbon black	10
SL-0	Silica	10
TL-0	MT carbon black	10

All elastomers have NCO/OH = 1.1, triol/diol = 0.1, and 6.12 wt % dioctyl adipate.

tional uniaxial testing system (Hewlett-Packard 1185-type Instron). The viscosity of the uncured polyurethane mixtures were measured with a rotational type of Brookfield Viscometer model DV-2 at a constant rotation speed of 10 rpm at ambient temperature.

RESULTS AND DISCUSSION

The filler content of elastomers is increased to improve their thermal, mechanical, and adhesive properties. However, this is restricted by maintaining the viscosity of the materials within workable limits, because reinforcement of the elastomer by increasing the filler content is accompanied by a concomitant increase in the viscosity. It has been shown that the use of combined mixtures of fillers enables higher loading to be conducted, while still maintaining the materials of workable viscosities.⁸ The challenge is to develop a polyurethane elastomeric liner prepared by using two different fillers to achieve high thermal stability, high tensile strength, and workable viscosity. Therefore, the investigation of the thermal and the mechanical properties of polyurethane elastomers was comprised of two parts. The first part involves the determination of the main filler that will be used together with a second additional filler. The compositions tested in this part contain 10% by weight one of three fillers as given in Table I. The second part involves the investigation of polyurethane elastomers containing a second filler in various amount in addition to the main filler determined in the first part. The polyurethane elastomer compositions with additional fillers are listed in Table II. For all of the compositions in both the first and the second parts, the NCO/OH and the triol/diol ratios were kept constant at 1.1 and 0.1, respectively, as determined in a previous

study on the adhesive properties of polyurethane elastomers.¹³

Determination of the Main Filler

This first part of the study includes the investigation on the effects of using two types of carbon blacks (ISAF or MT) or silica on thermal and mechanical properties of polyurethane elastomers for the purpose of selecting the main filler. The properties of the polyurethane elastomers containing the fillers were compared with those of the unfilled one. Thermal degradation temperatures, thermal conductivity, and erosion rates of unfilled and filled polyurethane elastomers are given in Table III. In thermal gravimetric analysis (TGA) experiments, the polyurethane elastomers show two main weight loss stages, implying the presence of two thermal degradation temperatures.¹⁶ Comparison of the thermal degradation temperatures given in Table III reveals that incorporation of the filler does not practically change the second-stage thermal degradation temperature. However, the use of ISAF-type carbon black as filler lowers the first-stage degradation temperature of

Table II Compositions of Elastomers with Additional Fillers

Composition	Extra Filler Type	Extra Filler Content (wt %)
CL-M	—	—
CL-1	ISAF carbon black	4
CL-2	ISAF carbon black	8
CL-3	ISAF carbon black	12
SL-1	Silica	4
SL-2	Silica	8
SL-3	Silica	12
SL-4	Silica	16
AL-1	Aluminum oxide	4
AL-2	Aluminum oxide	8
AL-3	Aluminum oxide	12
AL-4	Aluminum oxide	16
ZL-1	Zirconium oxide	4
ZL-2	Zirconium oxide	8
ZL-3	Zirconium oxide	12
ZL-4	Zirconium oxide	16
TL-1	MT carbon black	4
TL-2	MT carbon black	8
TL-3	MT carbon black	12
TL-4	MT carbon black	16

All elastomers have NCO/OH = 1.1, triol/diol = 0.1, 6.12 wt % dioctyl adipate, 2 wt % MAPO, and 10 wt % ISAF carbon black as main filler.

Table III Thermal Properties of Polyurethane Elastomers With and Without Base Fillers

Composition	First-Stage Degradation Temperature (°C)	Second-Stage Degradation Temperature (°C)	Thermal Conductivity (W m ⁻¹ K ⁻¹)	Erosion Rate (mm s ⁻¹)
UPR	379.5	498.9	0.1957	0.467
CL-0	374.4	498.6	0.2129	0.260
SL-0	379.5	498.3	0.2316	0.455
TL-0	381.1	499.2	0.2162	0.324

the elastomer by 5.1°C. This result is quite surprising, because ISAF-type carbon black would be expected to improve the thermal stability of elastomer due to the interaction of the functional groups of carbon black with the polymer matrix.¹⁷ The thermal conductivity of filled polyurethane elastomers is also not very different from that of the unfilled elastomer, despite the relatively high thermal conductivity of the filler materials, compared with the matrix. This behavior is most probably due to random dispersion of filler particles in the elastomeric matrix. The most significant change is observed in the erosion rate of the polyurethane elastomer upon adding filler. By using both types of carbon black as filler, considerable improvement is achieved in the erosion resistance of the elastomer, whereas the use of silica does not practically rectify this property. The improvement achieved in the erosion resistance of the carbon black filled elastomers can be attributed to the blockage of the flame by the carbon black particles and to the cooling effect of the evolving gases.

The tensile properties are the most important mechanical characteristics of elastomers serving as a structural parts or layers. Therefore, the effect of fillers on the tensile properties of polyurethane elastomers is also taken into consideration in selecting the main filler in the first part of the investigation. The tensile properties considered are the ultimate tensile strength, the elongation at break, and the elastic modulus (as given in Table IV). A brief inspection of the results immediately shows the conspicuous improvement in the tensile properties of polyurethane elastomer achieved by incorporating the ISAF-type carbon black. Taken together with the outcome of the thermal measurements, this result lets one select the ISAF-type carbon black as a main filler. The extent of the interaction of ISAF-type carbon black with the polyurethane matrix is obviously high enough to increase considerably the tensile strength and elongation of the elastomer. MT-

type carbon black and silica do not improve the tensile properties so much and may be due to the lack of interaction as strong as ISAF-type carbon black with the polyurethane matrix. The strong interaction of ISAF-type carbon black with polyurethane matrix stems from the small particle size (large surface area), proper wetting of carbon black with polyurethane matrix, and the presence of functional groups.¹⁸ The particle sizes of MT-type carbon black and silica are much higher than that of ISAF-type carbon black and, consequently, no significant reinforcement takes place.

Investigation of the Elastomers with Additional Fillers

After having selected the ISAF-type carbon black as the main filler, based on the results of erosion rates and tensile properties, the effect of additional fillers on the thermal, rheological, and tensile properties of polyurethane elastomers was studied in this second part of investigation by adding carbon black of two types, silica, aluminum oxide, or zirconium(III) oxide in various amounts into the polyurethane elastomers containing 10% (by weight) the ISAF carbon black as the main filler. In these polyurethane elastomers, the content of additional filler is increased by increments of 4% up to 16% by weight. Furthermore, these

Table IV Tensile Properties of Polyurethane Elastomers With and Without Main Fillers

Composition	Tensile Strength (MPa)	Elongation at Break (%)	Elastic Modulus (MPa)
UPR	0.567	153.5	0.361
CL-0	2.010	447.9	0.475
SL-0	0.901	198.4	0.629
TL-0	0.858	263.1	0.334

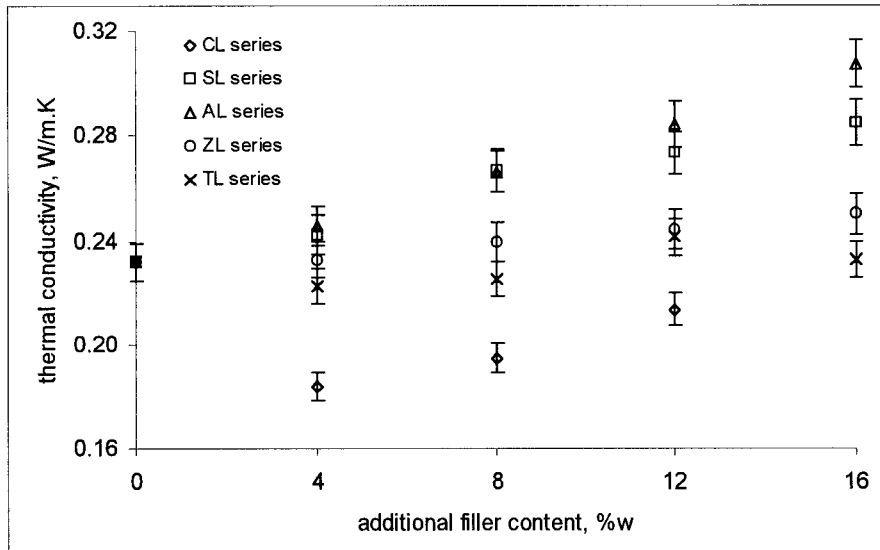


Figure 1 Effect of additional filler content on the thermal conductivity of elastomers.

elastomers contain MAPO used as bond promoter at a certain amount determined in a previous study on the adhesive properties of polyurethane elastomer.¹³ The results of TGA experiments show that the fillers do not considerably affect thermal degradation temperatures of elastomers as obtained in the first part of the study.

Figures 1 and 2 show the variations in thermal conductivity and erosion rate of the polyurethane elastomers, respectively, with the content and type of the additional filler. In general, the thermal conductivity of the elastomers increases slightly with the increasing amount of

filler. The highest thermal conductivities are observed for the AL series elastomers that contain aluminum oxide (Table II). This might be attributed to the higher thermal conductivity of aluminum oxide and to the ability of this material being finely dispersed in polyurethane matrix. CL and TL series elastomers (Table II) containing the ISAF- or MT-type carbon black as additional filler, respectively, show some deviations from the general trend. In particular, the contradictory decrease in the thermal conductivity of the CL series elastomers containing ISAF-type carbon black may result from the pos-

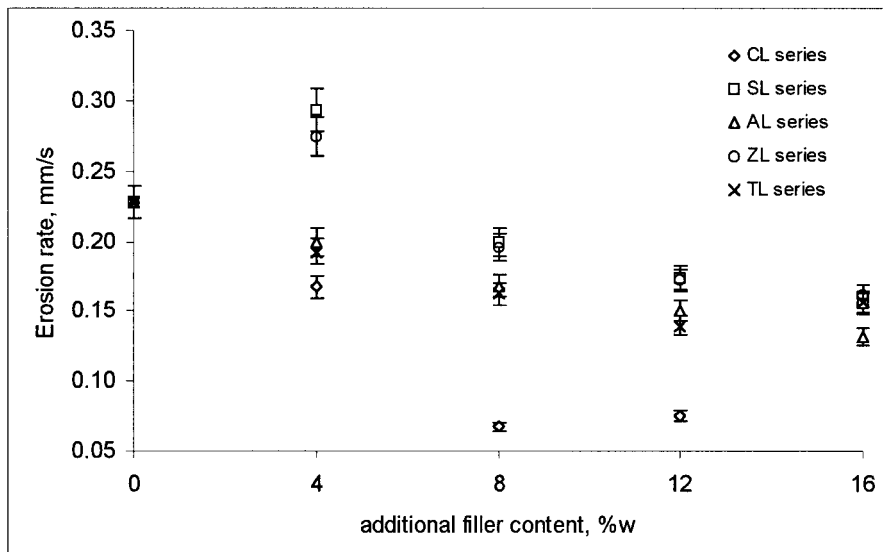


Figure 2 Effect of additional filler loading on the erosion rate of elastomers.

sible formation of air bubbles due to the high viscosity of uncured polyurethane mixture.

Although the additional fillers do not significantly affect the thermal degradation temperatures of polyurethane elastomers, noticeable improvements are achieved in the erosion resistance of the elastomers by increasing the filler content. The highest enhancement in erosion resistance is observed for the CL series elastomers containing the ISAF-type carbon black as additional filler up to 8 wt %. It is not possible to prepare the elastomer containing 16 wt % ISAF carbon black as additional filler due to the extravagant viscosity of the slurry. The negative effect of filler observed for the erosion resistance of the CL-3 elastomer containing 12 wt % the ISAF-type carbon black as additional filler may be attributed to the formation of air bubbles, even visually observed during and after curing, due to the high viscosity (improper mixing) of uncured polyurethane mixture. The least improvement in erosion resistance is observed in the ZL series elastomers (Table II) containing zirconium(III) oxide as additional filler, most probably due to weak interaction of the filler with the elastomer matrix. The erosion rate values of the other elastomers with the other three fillers are close to each others. The decrease observed for the SL-1 and ZL-1 elastomers (Table

II) containing 4 wt % silica or zirconium(III) oxide as additional filler is unexpected, because viscosity of the uncured mixture of these compositions is not so high as that of CL series elastomers. The last point that should be mentioned is the effect of particle size of the fillers on the erosion rates. That the CL series elastomers containing the ISAF-type carbon black as additional filler have lower erosion rates than the other compositions can be ascribed to the smaller particle size of the ISAF-type carbon black, compared with the other fillers and thus to the strong interaction with the polymer matrix. However, in the case of aluminum oxide and silica containing elastomers, a completely different effect is observed. The AL series elastomers containing aluminum oxide have lower erosion rates than the SL series containing silica, despite the fact that aluminum oxide has larger particle size than silica. This may be attributed to the better influence of aluminum oxide on the charring properties of elastomers than silica.

As in the erosion resistance, considerable improvements are achieved in the tensile properties of the polyurethane elastomers by incorporating the additional fillers (as shown in Table V). Figures 3 and 4 show the variation in the tensile strength and elastic modulus, respectively, with the increasing content of the additional fillers.

Table V Tensile Properties and Viscosity of Polyurethane Elastomers with Additional Fillers

Composition	Tensile Strength (MPa)	Elongation at Break (%)	Elastic Modulus (MPa)	Viscosity (Pa s)
CL-M	1.486	606.9	0.198	12.5
CL-1	2.055	486.0	0.378	49.6
CL-2	2.746	550.1	0.551	103.0
CL-3 ^a	1.870	447.3	0.715	—
SL-1	1.974	491.4	0.335	16.0
SL-2	2.311	556.3	0.366	20.8
SL-3	2.425	262.6	0.768	33.6
SL-4	2.658	471.7	0.480	36.8
AL-1	1.550	334.9	0.458	14.4
AL-2	2.006	428.9	0.446	21.6
AL-3	2.393	469.1	0.487	24.0
AL-4	2.075	413.2	0.429	32.0
ZL-1	1.620	509.5	0.297	16.0
ZL-2	1.674	443.8	0.338	20.0
ZL-3	2.139	437.2	0.524	24.0
ZL-4	1.983	362.8	0.554	32.0
TL-1	1.616	483.8	0.264	19.2
TL-2	2.424	420.6	0.631	49.0
TL-3	2.534	400.9	0.719	60.5
TL-4	2.451	423.4	0.537	82.0

^a Viscosity cannot be measured because of its excessive value.

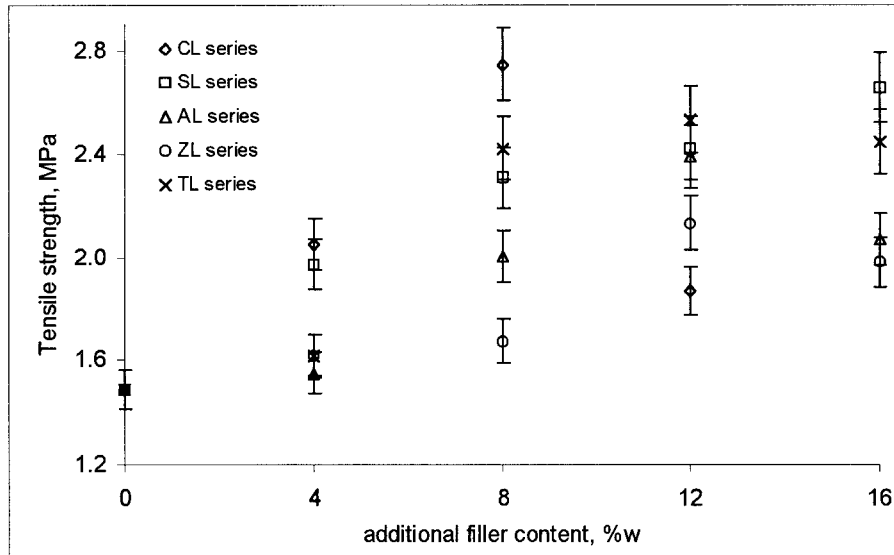


Figure 3 Effect of additional filler content on the tensile strength of elastomers.

Parallel to the results of erosion rate measurements, the highest tensile strength values are observed for the CL series elastomers containing the ISAF-type carbon black, and the lowest values are observed for the ZL series elastomers containing zirconium(III) oxide as additional fillers. In general, the tensile strength value of the elastomers increases with the increasing amount of additional filler up to a threshold limit, and then the tensile strength begins to decrease with the further addition of filler, except for the SL series elastomers containing silica as additional filler. The

values of elongation at break do not show a simple dependence on the additional filler content of the elastomers, only a decreasing trend is observed with increasing zirconium(III) oxide amount in the ZL series elastomers. The highest elongation at break is observed for the CL and SL series elastomers containing 8 wt % additional filler. The elastic modulus also shows variations with both the type and content of the additional filler. Only for the CL and ZL series elastomers containing the ISAF-type carbon black and zirconium(III) oxide, respectively, the elastic modulus

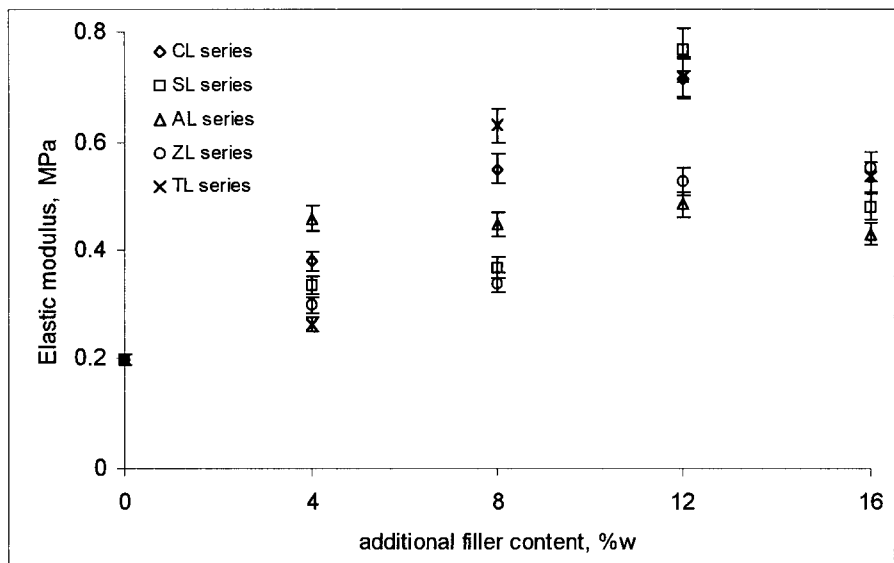


Figure 4 Effect of additional filler content on the elastic modulus of elastomers.

increases with the increasing amount of the additional filler. The particle size effect on tensile properties of elastomers is not so remarkable as in the case of erosion rates. The improvement in the tensile properties of the CL series elastomers is not as large as one would expect from the smaller particle size of the ISAF-type carbon black, compared with that of the other fillers. The achievement of a high value of the tensile strength by highly loaded CL series elastomer is actually not possible due to the excessive viscosity of ISAF-filled uncured polyurethane mixtures. Besides not achieving the desired levels of improvement in tensile properties, the processability of uncured polyurethane mixtures with ISAF carbon black is rather poor because of having very high viscosities. Related to the processability, the viscosity of uncured polyurethane elastomers with additional filler was measured to rank these compositions according to their fluidities. The results of the viscosity measurement are given in Table V. The CL series polyurethane mixtures containing the ISAF-type carbon black as additional filler have the highest viscosity values among the mixtures. The lowest viscosity values are observed for the AL and ZL series polyurethane mixtures containing aluminum oxide and zirconium(III) oxide as additional filler. From close inspection of these results, it can be realized that the viscosity of the polyurethane mixture increases with the decreasing particle size of the filler (or with the increasing surface area). However, there is no considerable difference between the viscosity values of AL and ZL series polyurethane mixtures, despite the fact that zirconium(III) oxide has two times larger particle size than aluminum oxide. For proper mixing and practical casting purposes, it is practically not possible to use polyurethane mixtures having viscosity values larger than 30 Pa s.

As a consequence of these investigations, the AL series elastomers containing aluminum oxide as additional filler seem to be suitable elastomer compositions having sufficiently high thermal and mechanical properties together with workable viscosities.

CONCLUSIONS

The investigation on the effects of the type and the amount of various fillers on the thermal and mechanical properties of the HTPB-based polyurethane was comprised of two parts. Results of

the first part allow the selection of the ISAF-type carbon black to be used as the main filler in the polyurethane elastomers. The second part involves the investigation of polyurethane elastomers containing a second filler in various amounts in addition to the ISAF-type carbon black used as the main filler. In addition to the thermal and mechanical properties, the processability of the uncured polyurethane mixtures was also explored in this second part of the study. The conclusions emerged from this study can be summarized as:

- Studied fillers do not considerably change the thermal degradation temperatures of the polyurethane elastomers with a filler content up to 16 wt %.
- Thermal conductivity of polyurethane elastomers is just slightly affected by addition of the fillers studied. For practical purposes, this effect is negligible.
- Improvement in tensile properties and erosion resistance achieved by using the ISAF-type carbon black enables one to use it as the main filler.
- The best improvement in the erosion resistance and tensile strength of the polyurethane elastomers with additional fillers is also achieved when filled with the ISAF-type carbon black. The use of zirconium(III) oxide as additional filler provides almost no improvement in these properties.
- Aluminum oxide-filled elastomers seem to be the suitable compositions having sufficiently high thermal and mechanical properties, together with the processability of uncured mixtures.

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