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Evaluation of Surface-Active Agents by Mechanical Properties of Highly filled Composites

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Synopsis

Mechanical spectroscopy is used to study the behavior under accelerated aging of surface-active additives in highly filled composites using a binder based on an hydroxyl-terminated polybutadiene. First, the mechanical properties of composites containing an amine polyester or an aziridine polyester are compared to those of a composite without any surface-active agents. It is thus confirmed that the aziridine polyester is a better surface-active agent than the amine polyester. The improvement in properties from the aziridine polyester is not affected by accelerated aging at 333°K. It was also established that composites with a mixture of both polyesters showed adequate initial mechanical properties and maintained those properties upon accelerated aging. Various hypotheses are proposed to explain the behavior of surface-active agents.

INTRODUCTION

In a previous article,[1] mechanical spectroscopy was used to evaluate the efficiency of various surface-active additives at the binder–filler interface of highly filled composites. Empirically, the surface agent efficiency was found to be inversely proportional to the height of the mechanical absorption peak at a temperature slightly higher than the glass transition temperature (T_g). This meant that the heights of tan δ and loss modulus (E'') peaks were inversely related to the quality of the solid–binder interface, a good interface being one where it is difficult to create voids.

It was thus suggested to relate the peak heights of tan δ and E'' to differences in void concentrations, ΔC, between composites 1 and 2 by the following equations:

$$\ln \frac{(\tan \delta_1)}{(\tan \delta_2)} = -k\Delta C \qquad (1)$$

in which k is a constant.

Murayama and Lawton[2] have suggested an equation which predicts a lower tan δ for a composite with perfect adhesion than for an experimental composite composed of tire cord and rubber.

This efficiency criterium is used in this paper to study the behavior of surface-active additives in solid composite propellants. The effects of various experimental parameters on tan δ and E'' were briefly studied as the opportunity

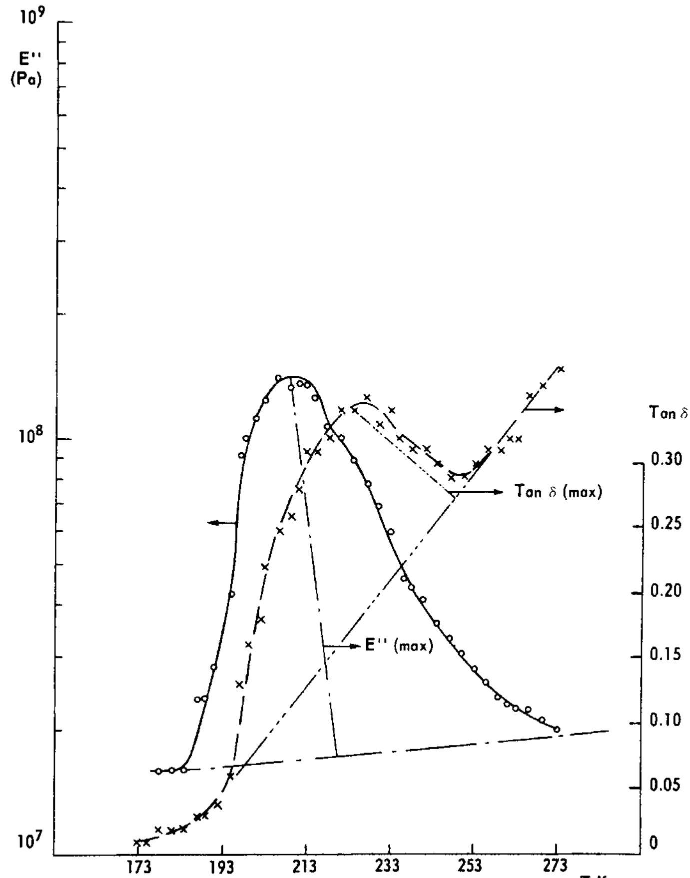

Fig. 1. Mechanical spectrum of sample 1.2 PAZ/0.2 PAM at 110 Hz.

arose from technological requirements, but the emphasis is put on the aging characteristics of composites as shown by the mechanical spectra. In each case, tensile mechanical properties measured on the Instron are discussed in relation to dynamic mechanical properties measured on the Rheovibron instrument.

EXPERIMENTAL

Preparations of composite propellants, measurements of dynamic mechanical properties with the Rheovibron instrument, and determinations of tensile mechanical properties on the Instron have been described.[1] However, in this work, the heights of the mechanical absorption maximum, given in various tables as tan δ(max) and E''(max) for the loss angle (δ) and the loss modulus (E''), respectively, were measured at the maximum perpendicularly to the baseline as shown on Figure 1. The temperature (T) is taken directly at the maximum of the peak.

Aging

For the aging tests on the Instron tensile machine, slabs of propellant in a polyethylene bag are kept in an oven at 60°C without any other control on the environment. After the desired period of time, "dumbbell" samples are punched and lamellae are machined for the Rheovibron trials.

Products

The prepolymer used to obtain the binder of the composites is the α,ω-hydroxypolybutadiene R-45M (HTPB) from Arco Chemical. The curing agent is the dimeric diisocyanate DDI 1410 from General Mills, Inc., and the plasticizer,

TABLE I
Binder Formulations

Sample	HTPB %	HTPB Batch	DDI, %	IDP, %	R
1.2 PAZ/0.2 PAM	63.9	006121	12.1	22.6	0.90
1.2 PAZ/0.2 PAM(–Fe_2O_3)	63.9	006121	12.1	22.6	0.90
0.9 PAZ/0.3 PAM(–Fe_2O_3)	64.0	006121	12.1	22.6	0.90
0.9 PAZ/0.2 PAM	62.9	212285	12.1	23.9	0.85
0.9 PAZ/0.2 PAM(344° K)	62.9	212285	12.1	23.9	0.85
0.9 PAZ/0.2 PAM(Prep)	63.6	006121	11.4	23.9	0.85
0.6 PAZ/0.4 PAM(–Fe_2O_3)	64.2	006121	12.2	22.6	0.90
0.6 PAZ/0.2 PAM(R = 0.8)	63.5	212285	11.5	24.2	0.80
0.6 PAZ/0.2 PAM(R = 0.85)	62.9	212285	12.1	24.2	0.85
0.6 PAZ/0.2 PAM(R = 0.9)	62.3	212285	12.7	24.2	0.90
0.1 PAZ/0.2 PAM	62.3	212285	12.7	24.7	0.90
2.4 PAZ	63.6	006121	11.4	22.6	0.85
2.4 PAZ (–Fe_2O_3)	63.0	006121	12.0	22.6	0.90
0.4 PAM	64.7	006121	12.3	22.6	0.90
0 PAZ/0 PAM	65.0	006121	12.4	22.6	0.90

TABLE II
Influence of PAM or PAZ on Dynamic Mechanical Properties at 110 Hz

Sample	Aging, days	tan δ(max) T, °K	tan δ(max) —	E''(max) T, °K	E''(max) Pa × 10^{-8}
0 PAZ/0 PAM	0	230 ± 3	0.12 ± 0.01	220 ± 3	0.8 ± 0.11
	14	230	0.15	217	0.9
	28	236	0.12	216	0.8
	56	233	0.16	221	0.9
0.4 PAM	0	227 ± 1	0.17 ± 0.01	217 ± 1	1.0 ± 0.03
	14	229	0.17	218	1.0
	28	236	0.11	218	0.9
	56	228	0.14	218	0.75
2.4 PAZ(–Fe_2O_3)	0	233	0.09 ± 0.01	220 ± 1	0.8 ± 0.08
	14	232	0.09	216	0.8
	28	240	0.09	217	0.7
	56	229	0.07	220	0.7

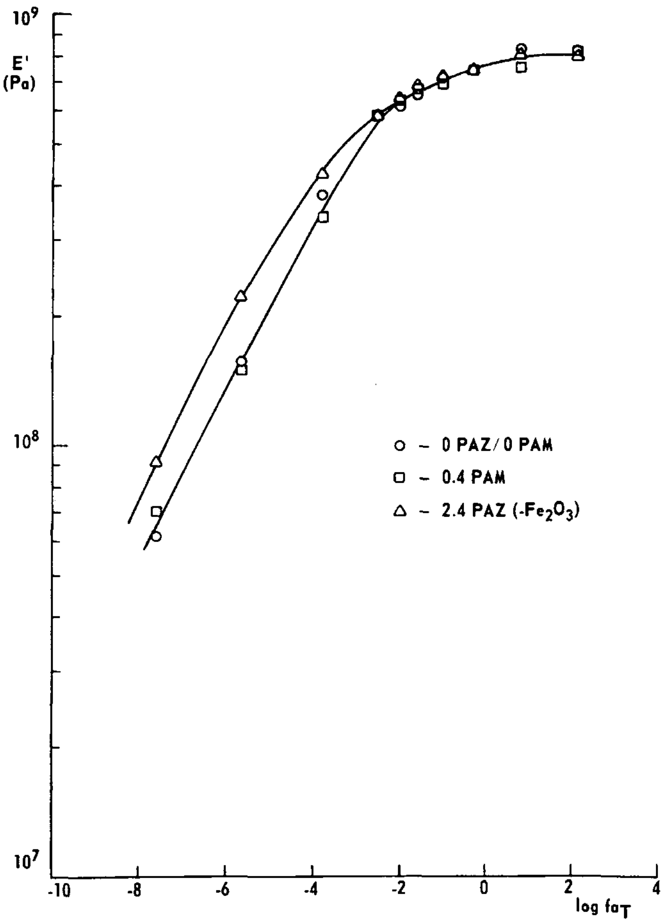

Fig. 2. Effect of surface agents on reduced storage moduli.

isodecyl pelargonate (IDA). Two surface-active agents were studied: one is an aziridine polyester (PAZ) which has been described in a U.S. patent,[3] the other is an amine polyester (PAM) which has been used in previous work.[4]

TABLE III
Influence of PAM or PAZ on Tensile Mechanical Properties at 22.8° C

Sample	Aging, days	σ_m, MPa	ϵ_m, %	E, MPa	ϵ_m/ϵ_r at 227.8° K
0 PAZ/0 PAM	0	0.37	16.5	4.59	7.0/7.5
	14	0.42	16.3	5.66	—
	28	0.40	15.3	5.44	8.5/9.0
	56	0.45	15.0	6.47	7.4/7.4
0.4 PAM	0	0.30	21.4	3.27	33.9/37.3
	14	0.36	22.0	4.56	—
	28	0.33	18.6	4.46	15.8/28.0
	56	0.36	19.5	5.17	9.9/28.3
2.4 PAZ(–Fe_2O_3)	0	0.79	22.8	8.22	36.2/37.0
	14	0.95	21.0	11.37	—
	28	0.86	17.8	10.42	30.4/31.2
	56	0.95	28.0	11.19	39.6/40.5

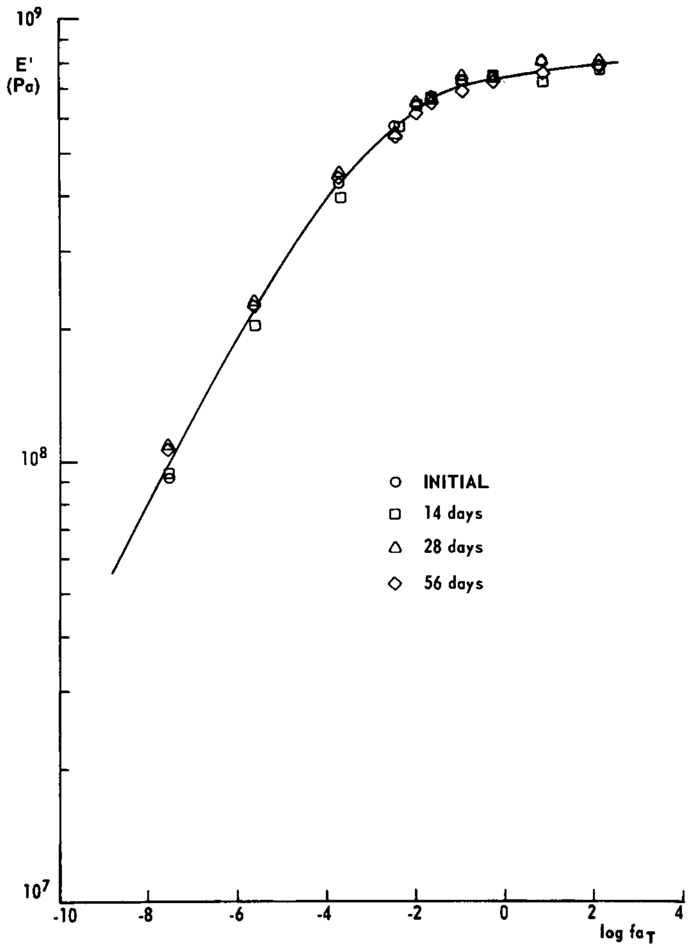

Fig. 3. Aging behavior of sample 2.4 PAZ($-Fe_2O_3$).

Formulations

Since the aim of the work was to study surface agents, all the various composites which were prepared are differentiated by the percentages and nature of surface agents. Thus, composite 1.2 PAZ/0.2 PAM contains 1.2% PAZ and 0.2% PAM in the binder. However, if many composites having the same amount of surface agents have been prepared to study the effect of experiment parameters, the main parameter under study is put inside brackets at the end of the appellation.

All propellants have a solid content of 88%, composed of 69.4% NH_4ClO_4, 18% Al, and 0.6% Fe_2O_3, except composites 1.2 PAZ/0.2 PAM ($-Fe_2O_3$), 0.9 PAZ/0.3 PAM ($-Fe_2O_3$), 0.6 PAZ/0.4 PAM ($-Fe_2O_3$), 2.4% PAZ ($-Fe_2O_3$), 0.4 PAM and the sample without any surface agent (0 PAZ/0 PAM) which are made of 70% NH_4ClO_4 and 18% Al, the absence of Fe_2O_3 being indicated by ($-Fe_2O_3$).

The formulations of the binders are given in Table I. In this table, the amount of surface agent is given only by the sample appelation. All the samples were cured at 60°C to constant hardness, except sample 0.9 PAZ/0.2 PAM which obviously was cured at 71°C. The NCO/OH ratios for each sample are given as R in the last column.

RESULTS AND DISCUSSION

Influence of Surface Agents PAM or PAZ on the Initial Properties of Propellants

Two propellants, 2.4 PAZ(−Fe_2O_3) and 0.4 PAM, were prepared and compared to a propellant without any surface agent, 0 PAZ/0 PAM.

Mechanical properties measurements on initial samples before aging were done with two different batches of propellants of the same formulation giving a reproducibility of about ±10% on both tan δ(max) and E''(max) (Table II) which is the same as reported previously.[1]

The results of dynamic mechanical properties in Table II confirm that PAZ is a better surface agent than PAM. Indeed, the tan δ(max) and E''(max) values

TABLE IV
Effect of Fe_2O_3 on Dynamic Mechanical Properties

Sample	Aging, days	tan δ(max) T, °K	tan δ(max) —	E''(max) T, °K	E''(max) Pa × 10^{-8}
1.2 PAZ/0.2 PAM(−Fe_2O_3)	0	237	0.10	226	0.7
	28	240	0.09	218	0.8
	56	240	0.14	220	0.7
1.2 PAZ/0.2 PAM	0	227	0.14	206	1.2
	28	227	0.20	209	1.5
	56	227	0.18	213	1.5
2.4 PAZ(−Fe_2O_3)	0	233	0.09	219	0.8
	14	232	0.09	216	0.8
	28	240	0.09	217	0.7
	56	229	0.07	220	0.7
2.4 PAZ	0	230	0.13	209	1.7
	14	227	0.15	209	1.6
	28	227	0.15	211	1.6
	56	233	0.19	209	1.7

TABLE V
Tensile Mechanical Properties of Sample 0.6 PAZ/0.2 PAM at Different R

R	Aging, days	σ_m, MPa	ϵ_m, %	ϵ_m/ϵ_r at 228°K	E, MPa
0.8	0	.32	59	44/92	1.25
	28	.33	58	—	1.11
	56	.34	48	41/82	1.24
0.85	0	.48	55	72/82	2.12
	28	.52	52	—	2.21
	56	.44	30	12/53	2.25
0.9	0	.64	45	53/64	2.93
	28	.68	43	—	2.90
	56	.54	29	19/32	2.59

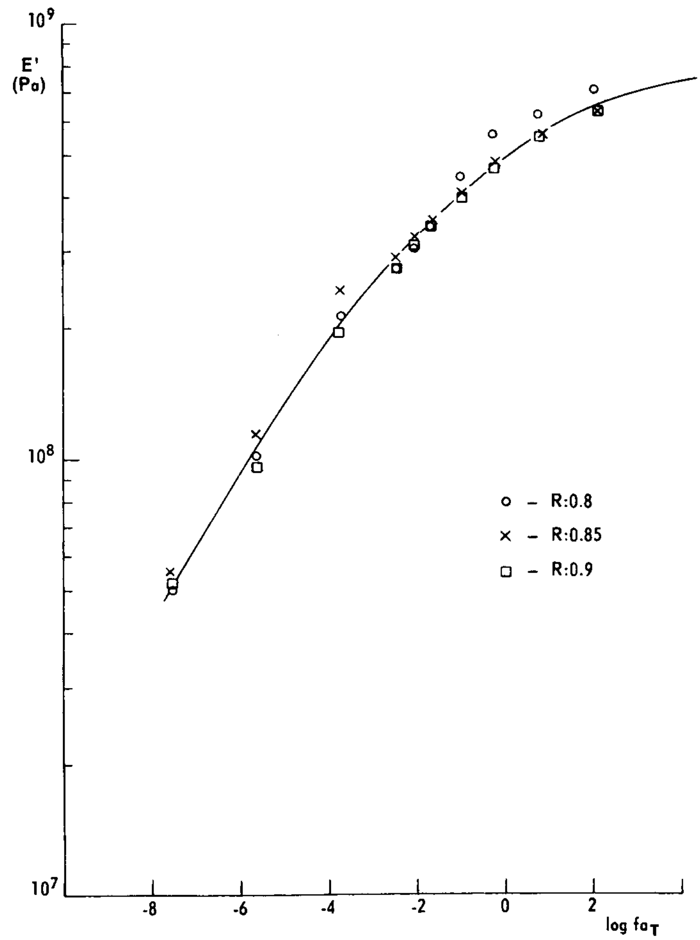

Fig. 4. Reduced storage moduli of sample 0.6 PAZ/0.2 PAM at different R values.

for sample 2.4 PAZ($-F_2O_3$) are lower than the corresponding ones for both samples 0.4 PAM and 0 PAZ/0 PAM. This conclusion is amply verified by the tensile mechanical properties of Table III for these products. At 22.8°C, for the same strain at maximum stress (ϵ_m), sample 2.4 PAZ($-Fe_2O_3$) has a maximum stress (σ_m) more than twice as high as samples 0.4 PAM and 0 PAZ/0 PAM.

TABLE VI
Dynamic Mechanical Properties of Samples 0.6 PAZ/0.2 PAM at Different R

R	Aging, days	tan δ(max)		E''(max)	
		T, °K	—	T, °K	Pa × 10^{-8}
0.8	0	233	0.22	206	1.2
	28	228	0.27	210	1.1
	56	229	0.24	206	1.0
0.85	0	215	0.21	203	1.2
	28	231	0.18	204	1.0
	56	—	0.14	210	1.0
0.9	0	233	0.28	211	0.9
	28	214	0.23	205	1.2
	56	233	0.28	209	1.0

However, the values of tan δ(max) and E''(max) for unaged sample 0 PAZ/0 PAM (Table II) which does not contain any surface agent are lower than those of sample 0.4 PAM, indicating that with freshly prepared composites based on the R-45M/DDI binder, PAM is detrimental to the quality of the solid–binder interface. Again, the tensile mechanical properties (Table III) emphasize the fact that, regarding properties at room temperature, there is nothing to gain by the incorporation of PAM in samples. However, at a temperature of 227.8°K which is just slightly higher than the T_g as measured by dynamic mechanical properties (Table II: ≃218°K), the composite containing PAM retains its strain while the sample without surface agent shows a dramatic loss of strain capability. These results are an example of the complementary nature of the dynamic and tensile mechanical properties measured on the Rheovibron and the Instron. The Rheovibron works at small elongation (0.3%), whereas the ϵ_m and the strain at rupture (ϵ_r) are obtained at much higher elongation.

Additional information on these surface-active agents can be obtained from the reduced curve of the storage modulus (E') for the same three composites using the WLF shift parameter (Fig. 2). Both reduced curves for samples 0 PAZ/0 PAM and 0.4 PAM are superposable, while the 2.4 PAZ($-Fe_2O_3$) reduced curve is definitely higher. The same trend can be observed from the Young modulus (E) (Table III). This is strong evidence that surface agent PAZ does increase the amount of crosslinking in the matrix or the reinforcement of the matrix by the solid, while PAM does not have any of these effects.

TABLE VII
Effects of Curing temperature on Dynamic Mechanical Properties

Sample	Aging, days	tan δ(max)		E''(max)	
		T, °K	—	T, °K	Pa × 10^{-8}
0.9 PAZ/0.2 PAM	0	216	0.20	207	1.7
	14	211	0.21	—	1.9
	28	218	0.23	209	1.6
	56	215	0.23	207	1.6
0.9 PAZ/0.2 PAM (344°K)	0	215	0.23	208	1.9
	14	218	0.22	207	1.9
	28	219	0.20	209	1.8
	56	215	0.18	209	1.1

TABLE VIII
Effect of Curing Temperature on Tensile Mechanical Properties

Sample	Aging, days	σ_m, MPa	ϵ_m, %	ϵ_m/ϵ_r at 228°K
0.9 PAZ/0.2 PAM	0	0.79	37	59/60
	14	0.82	36	—
	28	0.79	36	53/54
	56	0.79	36	49/50
0.9 PAZ/0.2 PAM(344°K)	0	0.75	38	60/62
	14	0.79	37	56/57
	28	0.76	37	51/53
	56	0.76	36	48/49

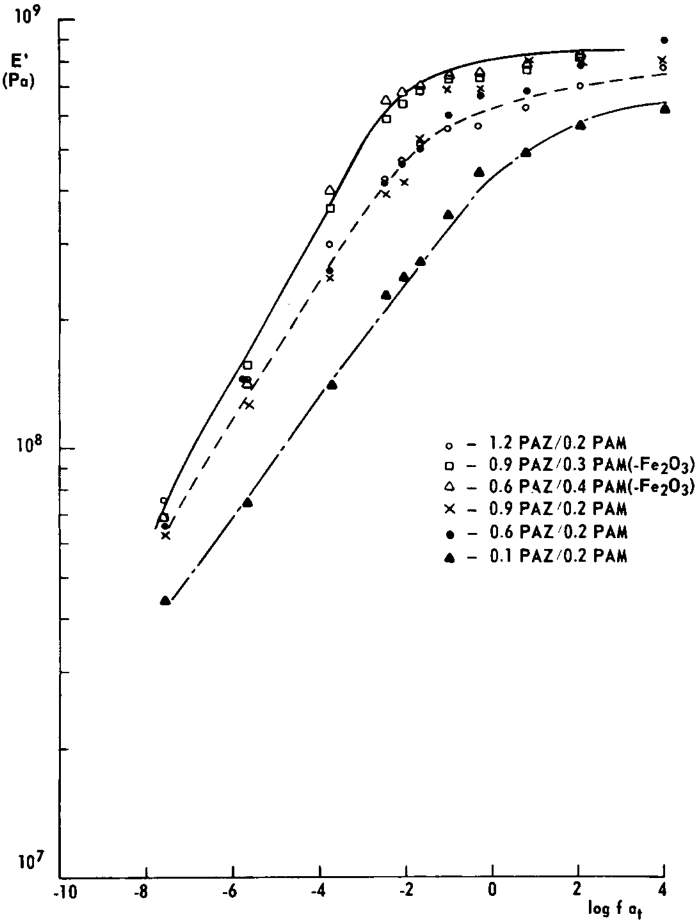

Fig. 5. Reduced storage moduli of sample with various ratios of surface-active agents.

So, in this R-45M HTPB binder, PAZ improves mechanical properties over the whole range of temperature and strains studied. The beneficial effect of PAM is only apparent at low temperature and under strains close to rupture.

TABLE IX
Effect of Prepolymer Batch on Dynamic Mechanical Properties

Sample	Aging, days	tan δ(max)		E''(max)	
		T, °K	—	T, °K	Pa × 10^{-8}
0.9 PAZ/0.2 PAM	0	220	0.23	209	1.9
	14	220	0.22	208	1.9
	28	221	0.20	209	1.8
	56	227	0.18	209	1.1
0.9 PAZ/0.2 PAM(Prep)	0	—	—	—	—
	14	218	0.22	203	1.7
	28	220	0.23	205	1.7
	56	218	0.21	206	1.4

Influence of PAM or PAZ on the Properties of Aged Propellants

For samples 0 PAZ/0 PAM, 0.4 PAM, and 2.4 PAZ($-Fe_2O_3$) aged at 60°C in an oven for 14, 28, and 56 days, the results of both the dynamic and the tensile mechanical properties do not follow any consistent trend (Tables II and III), except for the ϵ_m at 227.8°K of sample 0.4 PAM, which shows a considerable decrease. Accelerated aging does not seem to affect significantly the mechanical properties of those composites. The reduced curves lead to the same conclusion indicating no apparent aging effect. Figure 3 gives the typical reduced curve of sample 2.4 PAZ($-Fe_2O_3$).

Incorporation of Fe_2O_3

For ballistic purposes, it was necessary in the course of this study to incorporate small amounts of Fe_2O_3 in the propellant. This gave us the opportunity to note an effect of Fe_2O_3 on the dynamic mechanical properties which was impossible to foresee even though Fe_2O_3 had previously been demonstrated to intervene on the curing reaction.[5]

Two composites were formulated especially to determine the effect of Fe_2O_3. Table IV summarizes dynamic mechanical properties for samples 1.2 PAZ/0.2 PAM and 2.4 PAZ with and without Fe_2O_3. It is obvious that the incorporation of Fe_2O_3 causes a marked increase of both tan δ(max) and E''(max). If the ratios of the mechanical absorption maxima of samples with Fe_2O_3 over samples without Fe_2O_3 is averaged for composites aged during the same period, the following results are obtained:

$$\tan \delta(\max)/\tan \delta(\max)(-Fe_2O_3) = 1.8 \pm 0.4$$

and $E''(\max)/E''(\max)(-Fe_2O_3) = 2.0 \pm 0.2$. This shows that the incorporation of 0.6% Fe_2O_3 doubles the tan δ and E'' peak heights.

Also, the incorporation of Fe_2O_3 shifts the mechanical absorption peak to higher temperatures by about 10°, an effect which is not noticeable on the T_g as measured by a differential scanning calorimeter. The reduced curves for E' are slightly lower for samples without Fe_2O_3 in the vicinity of the mechanical absorption as expected from the increase of the loss modulus.

However, as can be seen from Table I, it should be noted that samples 1.2 PEZ/0.2 PAM($-Fe_2O_3$) and 1.2 PAZ/0.2 PAM were formulated at the same NCO/OH ratio (R = 0.9), while samples 2.4 PAZ and 2.4 PAZ($-Fe_2O_3$) were

TABLE X
Effect of Prepolymer Batch on Tensile Mechanical Properties

Sample	Aging, days	σ_m, MPa	ϵ_m, %	E, MPa	ϵ_m/ϵ_r at 228°K
0.9 PAZ/0.2 PAM	0	0.75	38	3.68	60/62
	14	0.79	37	3.87	57/58
	28	0.76	37	3.75	51/53
	56	0.76	36	4.14	48/49
0.9 PAZ/0.2 PAM(Prep)	0	0.67	39	3.24	61/63
	14	0.70	37	3.59	—
	28	0.72	39	3.47	61/61
	56	0.75	38	3.58	53/55

prepared at NCO/OH ratio of, respectively, 0.85 and 0.9. The problem is to decide whether it is preferable to compare samples with exactly identical formulation or samples which have been empirically optimized around preferred mechanical properties at room temperature of σ_m = 0.6–0.9 MPa and ϵ_m = 40%. As in previous works,[1] it was decided to compare samples with "optimized" formulation which are, in fact typical of products in use. But, as will be described in the following section, samples were formulated at different R values to collect information on the effect of the NCO/OH ratio on the dynamic mechanical properties.

Effect of the NCO/OH Ratio (*R*)

A variation of R from 0.80 to 0.85 and 0.90 gives large differences in the tensile mechanical properties of three 0.6 PAZ/0.2 PAM samples (Table V). As usual, when R is increased, both E and σ_m increase while ϵ_m decreases. The aging behavior of composites having R = 0.8 and 0.9 was poor after 56 days, as shown by every parameter.

The tan δ(max), E''(max), and T are about equal for all three compounds (Table VI), and it is impossible to establish any relation between the tensile mechanical properties and the dynamic mechanical properties. Even the reduced curves for the three samples before aging do not show any marked differences (Fig. 4), indicating that the increase of R only shifts the dynamic mechanical properties along the time axis as expected for variations in crosslinking.

TABLE XI
Influence of Various PAZ/PAM Ratios on Tensile Mechanical Properties

Sample	Aging, days	σ_m, MPa	ϵ_m, %	ϵ_m/ϵ_r at 228° K	E, MPa
1.2 PAZ/0.2 PAM	0	0.88	30	41/43	6.76
	28	0.89	29	—	6.77
	56	1.00	31	41/42	7.18
0.9 PAZ/0.3 PAM(–Fe_2O_3)	0	0.74	33	53/54	6.71
	14	0.71	35	—	5.63
	28	0.76	38	58/59	6.01
	56	0.73	37	55/56	6.65
0.6 PAZ/0.4 PAM (–Fe_2O_3)	0	0.67	41	59/61	4.86
	14	0.65	39	—	5.21
	28	0.72	40	59/60	5.58
	56	0.68	35	44/56	6.15
0.9 PAZ/0.2 PAM	0	0.79	37	59/60	4.04
	14	0.82	36	—	4.33
	28	0.79	36	53/54	4.10
	56	0.79	36	49/50	4.13
0.6 PAZ/0.2 PAM	0	0.63	38	66/68	3.58
	14	0.75	38	61/62	4.08
	28	0.73	39	63/64	3.85
	56	0.52	38	59/61	2.77
0.1 PAZ/0.2 PAM	0	0.51	23	14/29	3.30
	28	0.52	21	—	3.49
	56	0.56	19	15/20	4.32

Effect of the Curing Temperature

The effect of two curing temperatures, 60° and 71°C, on the dynamic mechanical properties can be seen in Table VII. Only these two temperatures could be studied because of limitations in processing arising from the viscosity and the stability of the various components.

Sample 0.9 PAZ/0.2 PAM cured at 60°C gave tan δ(max) and E''(max) values which were almost stable at different aging period. However, sample 0.9 PAZ/0.2 PAM (344°K) showed a decrease of both values which is especially obvious after 56 days of aging.

The tensile mechanical properties (Table VIII), on the other hand, show identical behavior for both samples, indicating that this change in curing temperature does not have any effect on the mechanical properties.

Effect of Changes in Prepolymer Batch

Dynamic and tensile mechanical properties for two samples having similar formulations, but with two different prepolymer batches, give very close values following a similar trend. The only difference is a slightly better aging behavior of sample 0.9 PAZ/0.2 PAM(Prep) after 56 days at 60°C. The possibilities of reproducing fixed mechanical properties has been proven to be very good.

Effect of Various PAZ/PAM Ratios on Aging

Various samples were formulated to study any possible effect of the PAZ/PAM ratio on the aging behavior of those composites. First, the tensile mechanical

TABLE XII
Influence of Various PAZ/PAM Ratios on Dynamic Mechanical Properties

Sample	Aging, days	tan δ(max)		E''(max)	
		T, °K	—	T, °K	Pa × 10^{-8}
1.2 PAZ/0.2 PAM	0	225	0.14	212	1.2
	28	213	0.20	213	1.5
	56	223	0.18	213	1.5
0.9 PAZ/0.3 PAM(–Fe_2O_3)	0	229	0.13	219	0.8
	14	235	0.15	217	0.9
	28	235	0.12	222	0.9
	56	241	0.15	222	0.9
0.6 PAZ/0.4 PAM(–Fe_2O_3)	0	233	0.18	220	0.85
	14	233	0.16	221	0.9
	28	236	0.11	220	0.8
	56	230	0.15	220	0.9
0.9 PAZ/0.2 PAM	0	220	0.23	209	1.9
	14	220	0.22	208	1.9
	28	221	0.20	209	1.8
	56	227	0.18	209	1.1
0.6 PAZ/0.2 PAM	0	219	0.21	206	1.6
	14	220	0.20	209	1.1
	28	215	0.23	209	1.3
	56	218	0.21	207	1.2
0.1 PAZ/0.2 PAM	0	230	0.31	205	1.1

properties in Table XI show that all those composites have satisfactory mechanical properties, excepting sample 0.1 PAZ/0.2 PAM, where all the values are too low indicating the necessity of incorporating sufficient amount of PAZ. All the other samples do not show any definite aging trend.

The summary of dynamic mechanical properties in Table XII leads to the same conclusion that aging does not affect the surface agents using tan δ(max) or E''(max) values. There are some variations that appear to be more or less at random.

The reduced curves show three different sets of curves: a highest one for the two samples without Fe_2O_3, an average one for samples 1.2 PAZ/0.2 PAM, 0.9 PAZ/0.2 PAM, and 0.6 PAZ/0.2 PAM, and a lowest one for sample 0.1 PAZ/0.2 PAM.

All the measurements on the Rheovibrometer were expertly taken by Mr. Yvon Boucher.

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