

## Influence of Crosslinking and Plasticizing on the Viscoelasticity of Highly Filled Elastomers

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**ABSTRACT:** Solid propellants, like all highly filled elastomers, exhibit a complex nonlinear viscoelastic behavior. The aim of this study was to establish the relationships between the structure and properties, which is needed to construct a robust constitutive law for these materials. An extensive design of experiments approach allowed us to quantify the influence of the curing agents and plasticizer molecules on the microstructure of the propellant and its viscoelastic properties. Swelling and gel permeation chromatography measurements described the microstructure of the propellant and prestrained dynamic mechanical analysis (PDMA) characterized the viscoelastic behavior. The curing agents reacted with polymer chain ends participating in the network, in the sol fraction, or in filler–binder links. Consequently, the polymer network was incomplete even in stoichiometric conditions, and a minimum of 10% of the polymer was free in the microstructure. In addition, preswelling the polymer with plasticizer molecules before curing modified the obtained network by decreasing the crosslink density in the binder and increasing it in the vicinity of the filler surface. This study provided new insight into the local deformation mechanisms controlling nonlinearity as measured by PDMA. The nonlinear behavior appeared between 0 and 1.7% prestrain in both the elastic and viscous parts of the behavior. The network reached its maximum extensibility in the elastic part and constrained the sol fraction in this extended mesh for the viscous part. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40392.

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### INTRODUCTION

Solid propellants are highly filled elastomers used for the propulsion of rockets and launchers. Their filler volume fraction reaches 80%. The remaining constituent of the material is a binder, which holds the particles together and ensures the viscoelastic properties of the composite up to large strains. Because of the high filler-to-binder ratio, the material exhibits a complex nonlinear mechanical behavior, and predictive material models are needed to design the structure of the launchers.

The modeling of the nonlinear viscoelastic mechanical behavior exhibited by propellants is a current research challenge. Phenomenological models<sup>1–5</sup> currently lead to inaccurate predictions of the material behavior under complex loadings or extreme environmental conditions, whereas homogenization theories<sup>6–9</sup> are usually predictive only up to filler fractions of 30–50%.

The difficulty of determining models based on the physics of the material arises from the complexity of the microscopic structure and the induced local deformation mechanisms in the

binder. An additional obstacle arises from the involved binder–filler and filler–filler interactions. The aim of this study was to understand the links between the solid propellant microstructure and its macroscopic mechanical properties.

A design of experiments (DoE) method was implemented to consider the influence of four factors, namely, the filler fraction, the bonding agents, the NCO/OH ratio, and the plasticizer content. The influences of the filler fraction and the filler–binder bonding agents (FBBAs) were discussed in Azoug et al.<sup>10</sup> (AZ1). In this article, the results quantifying the influence of the NCO/OH ratio, and the plasticizer content were discussed.

Crosslinking in hydroxyl-terminated polybutadiene (HTPB) based propellants is controlled through the ratio of the number of isocyanate functional ends of the curing agents (NCO) and the number of hydroxyl groups of the polymer chains (OH). Solid propellants are voluntarily undercrosslinked; that is, the NCO/OH ratio is lower than 1. Consequently, a part of the polymer chains remains unlinked to the network and

constitutes a free assembly of polymer chains denoted as the sol polymer.

The *sol fraction* is defined as the microstructural phase that can be extracted by swelling in a good solvent, i.e. the fraction of the binder unlinked to the global polymer network and not contributing to the elastic response. The sol fraction in propellants is mainly composed of the sol polymer and plasticizer molecules.

The plasticizer is an additive that masks polar groups of polymer chains and, as a consequence, enables the polymer chains to move freely past each other. Therefore, its microscopic role has an impact on the macroscopic viscoelastic behavior. The incorporation of plasticizers before curing, denoted as preswelling, must be distinguished from the swelling of the cured polymer with plasticizers or diluents, denoted as postswelling.<sup>11</sup> The effect of postswelling on solid propellants was considered in a previous study.<sup>12</sup> The results show that the macroscopic viscoelastic behavior was modified according to the swelling or contraction of the network independently of the viscosity of the introduced liquid. This study focused on the effect of preswelling with plasticizer molecules.

The added plasticizers facilitated the manufacturing process and targeted specific mechanical properties in the final material. The propellants could be considered to be preswelled materials because a high quantity of plasticizers was introduced into the premix before we cured the polymer. The incorporation of diluents or plasticizers before the creation of a three-dimensional polymer network generated networks with a different topology. These topological changes persisted after the removal of the diluents and led to notable changes in the mechanical properties.<sup>11</sup> For example, the addition of plasticizers before curing in the filled elastomers decreased the viscoelastic storage and loss moduli.<sup>13,14</sup>

## EXPERIMENTAL

As described in AZ1,<sup>10</sup> a D-optimal DoE was built. The details of the formulation of the materials were given in AZ1. The main elements are described as follows. The DoE factors were the formulation ingredients that influenced the mechanical behavior the most. Four factors were chosen:

- Filler fractions between 86 and 90 wt %.
- NCO/OH ratios between 0.8 and 1.1.
- Plasticizer contents between 10 and 30% of the binder.
- The presence or absence of FBBA (categorical).

The fillers were ammonium perchlorate and aluminum particles.

The exact synthesis of the FBBA molecules cannot be described because of confidentiality restrictions. Their mechanism was described in AZ1.<sup>10</sup>

The binder was based on an HTPB prepolymer cured with a methylene diisocyanate. The prepolymer had a molar mass of 2900 g/mol and a mean functionality of around 2.3. The ratio of the quantity of the curing agent methylene diisocyanate with respect to the quantity of hydroxyl

functions in the introduced prepolymer was the NCO/OH ratio. The NCO/OH ratio evolved between 0.8 and 1.1. At values lower than 1, a part of the prepolymer was not linked to the global network and was, therefore, extractable. As a result, it constituted a part of the sol fraction and was named the sol polymer.

The introduced plasticizer was dioctyl azelate. A plasticizer content of at least 10 wt % of the binder was necessary to manufacture the material. The percentage range of plasticizer explored in the DoE was 10–30 wt % of the binder. The molecules of plasticizer did not bind with the network or the fillers and were located only in the sol fraction.<sup>15</sup>

The materials were thermally cured for 2 weeks at 50°C. The levels of the factors for each of the 22 manufactured materials are given in Table I.

Macroscopic and microscopic experiments were performed on the materials. The microscopic structure was characterized by swelling experiments, which determined the sol polymer fraction ( $F_{solpol}$ ) and the crosslink densities of the propellant and the binder ( $D_p$  and  $D_b$ , respectively). The experimental procedure was described in AZ1.<sup>10</sup>

In addition to the experiments described in AZ1, the relative molecular weights [number-average molecular weight ( $M_n$ ) and

**Table I.** Materials Manufactured According to the DoE Method

Material	Filler (wt %)	FBBA	NCO/OH ratio	Plasticizer (wt % binder)	GPC
0	86	–	1.1	10	X
1	90	–	0.8	30	X
2	86	×	1.1	20	
3	90	×	0.8	20	
4	86	–	1.1	30	X
5	90	×	1.1	30	
6	90	–	0.8	10	
7	86	×	0.8	10	
8	86	–	0.8	20	X
9	86	×	0.8	30	
10	90	–	0.95	20	
11	88	–	1.1	20	X
12	90	×	1.1	10	
13	88	×	0.95	30	
14	88	×	0.95	15	
15	88	–	0.88	25	X
16	88	–	0.95	10	X
17	90	×	0.8	10	
18	86	–	0.8	10	X
19	86	×	1.1	10	
20	89	–	1.1	20	
21	89	–	0.8	10	

The absence and presence of FBBA are indicated with – and ×, respectively. X indicates the materials of the DoE on which a GPC test was performed.

weight-average molecular weight ( $M_w$ ) and the polydispersity index ( $M_w/M_n$ ) of the sol fraction were measured by gel permeation chromatography (GPC) for eight materials of the DoE (see Table I). The sol fraction was extracted by swelling in toluene. For each material, 40 mg of the sol fraction was diluted in 20 mL of tetrahydrofuran. The mix was agitated for 2 h and then injected at 35°C. The device was equipped with three PLgel mixed columns, and polypropylene glycol was used for calibration. The molecular weights of the pure plasticizer and HTPB prepolymer molecules were also determined with the same procedure.

The macroscopic mechanical viscoelastic response was determined by prestrained dynamic mechanical analysis (PDMA), as detailed in AZ1.<sup>10</sup> We recall that the evolution of the storage and loss moduli according to prestrain is characterized by three variables: the plateau value ( $P$ ) in the linear region, the threshold of the onset of nonlinearity ( $T$ ), and the slope of the curve in the nonlinear region ( $S$ ). For each variable, the symbols  $(\bullet)'$  and  $(\bullet)''$  indicate correspondence with the storage modulus and the loss modulus, respectively.

The DoE analysis procedure determined models quantifying the influence of each factor on the chosen response, as described in AZ1.<sup>10</sup>

## RESULTS AND DISCUSSION

### Fit of the Models

The fit of the models was quantified by the optimal adjusted correlation coefficients ( $R_{adj}^2$ ).<sup>16</sup> This value should be equal to 1 when the response of the material is perfectly represented by the mathematical model, depending on the composition of the material, that is, the four factors. The optimal  $R_{adj}^2$  values were 0.99 for  $F_{solpol}$ , 0.96 for  $D_p$ , and 0.97 for  $D_b$ .

As expected, the correlation coefficients for the microscopic quantities were extremely high. The values measured for  $F_{solpol}$  and the crosslink densities were directly dependent on the composition of the material.

Table II shows the  $R_{adj}^2$  values characterizing the fit of the models obtained for the PDMA responses.

The PDMA coefficients indicated that the models fit the  $P$ s of both the storage and loss moduli very precisely (Figure 1). Hence, the evolution of these responses was the direct result of the influence of the chosen factors. The coefficients obtained for the  $S$  values were slightly lower but were still satisfying, especially when the experimental error was taken into account. The measurements at high prestrain tended to be more scattered than the one obtained in the linear domain.

The correlation coefficients of the models for the  $T$ s were the smallest (Figure 2). When the strain amplitude ( $\epsilon_a$ ) was 0.5%,

the coefficients were too weak to allow us to study the influence of the factors. As a result, the values of  $T$  at  $\epsilon_a = 0.5\%$  were excluded from the analysis. Figure 2 shows the values predicted by the DoE model as a function of the measured values for the parameters  $T'$  and  $T''$ .

The weak correlation for  $T'$  and  $T''$  originated from both the scattering of the experimental data and modeling errors. The measured  $T$  values were determined by optimization of the phenomenological model on the experimental data and depended on initial values and user-chosen constraints. Therefore, the solution was not unique, and  $T$  was a weak point in the phenomenological model proposed here.<sup>12</sup> In addition, the DoE model may not have been able to distinguish each of the complex influence of the factors and their interactions on this aspect of the behavior.

### Characterization of the Microstructure

$D_p$  and  $D_b$  increased with the NCO/OH ratio (Figure 3). As this factor controlled the amount of available curing agents, it directly influenced  $D_p$  and  $D_b$  by themselves.

Because the binder was assumed to be composed mainly of plasticizer and polymer molecules, the percentage of polymer (sol or participating in the network) in the binder depended primarily on the introduced plasticizer content.  $F_{solpol}$  was defined as the volume percentage of the total quantity of the polymer in the binder to remove the influence of the plasticizer content.  $F_{solpol}$  measures the ratio between the volume of the sol polymer and the total volume of polymer chains in the binder.

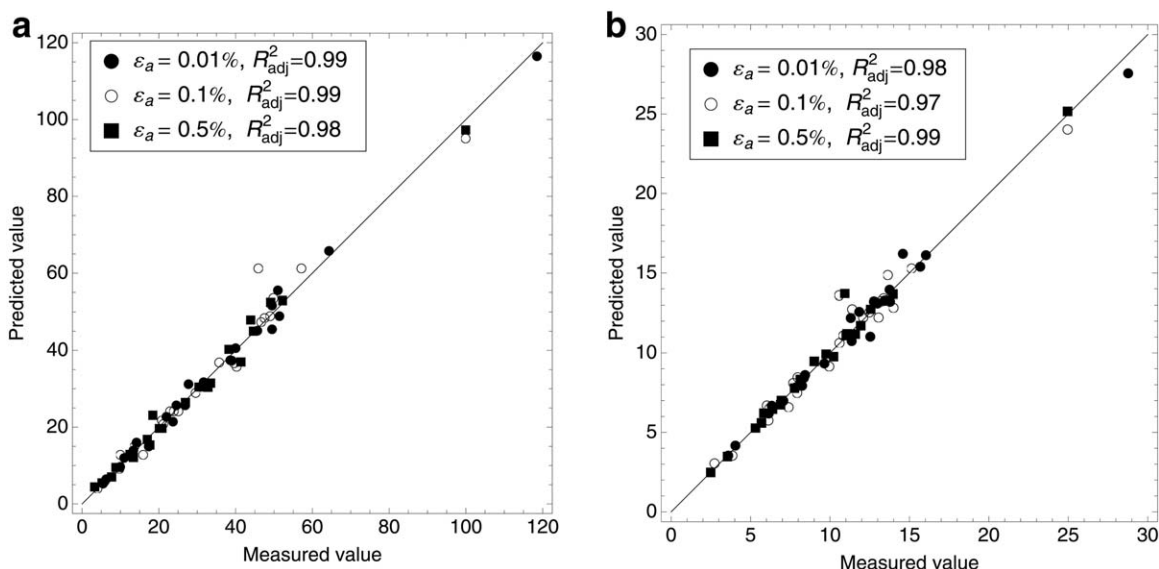
Increasing the NCO/OH ratio not only increased the crosslink density but equally changed the quantity of the sol and network polymer chains (Figure 4).  $F_{solpol}$  decreased with the NCO/OH ratio. As expected, increasing the relative amount of curing agents in the material permitted a larger amount of polymer chains to be linked to the network.

For large NCO/OH ratios ( $>1$ ), where a complete network could be built,  $F_{solpol}$  formed at least 10% of the polymer. Moreover,  $F_{solpol}$  seemed to reach a minimum, whose value depended on the plasticizer content (Figure 4). The presence of  $F_{solpol}$  at a high NCO/OH ratio proved that the curing agents not only built the three-dimensional network by linking the polymer chains to each other but also reacted to other molecules. This corroborated the results in AZ1,<sup>10</sup> where it was proven that the reaction of molecule X on the filler surface consumed the curing agents.

For small NCO/OH ratios ( $<1$ ),  $F_{solpol}$  reached extremely high values, between 50 and 70% of the polymer (Figure 4). This was an astonishing observation as it seemed unlikely that a

**Table II.**  $R_{adj}^2$  Values for the Models of the PDMA Responses

$\epsilon_a$ (%)	$P'$	$P''$	$T'$	$T''$	$S'$	$S''$
0.01	0.99	0.98	0.71	0.54	0.75	0.80
0.1	0.99	0.97	0.83	0.58	0.94	0.77
0.5	0.98	0.99	0.22	0.33	0.87	0.79



**Figure 1.** Correlation between the  $P_s$  predicted by the DoE model and the measured  $P_s$ : (a)  $P'$  and (b)  $P''$ .

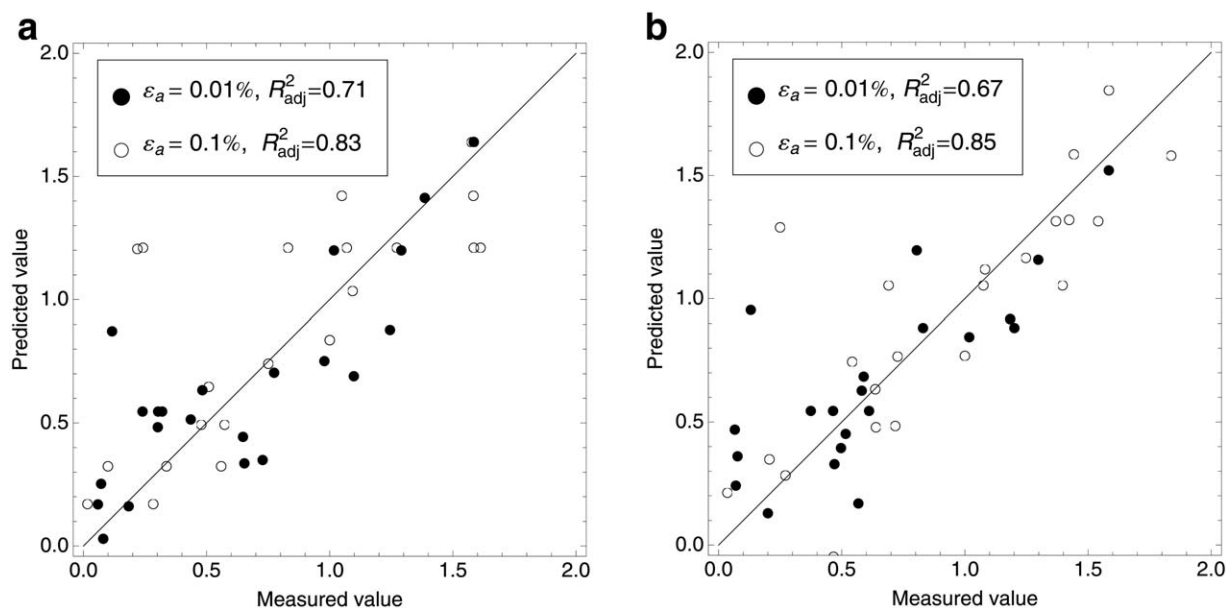
polymer composite could remain solid while presenting 70% of its polymer chains as soluble, even when the large filler fraction and the weak binder–filler links created by molecule X were taken into account. Further insight into this question was given by the measurements of the molecular weights in the sol fraction.

The molecular weights of the molecules in the sol fraction are represented on Figure 5 with respect to  $F_{solpol}$ . The mean value  $M_n$  is represented in plain lines, whereas the dashed lines indicate the minimum and maximum molecular weights of the distribution according to  $M_w/M_n$ . Several low-molecular-weight peaks were observed for all of the compositions and represent the additives included in all industrial materials, such as antiox-

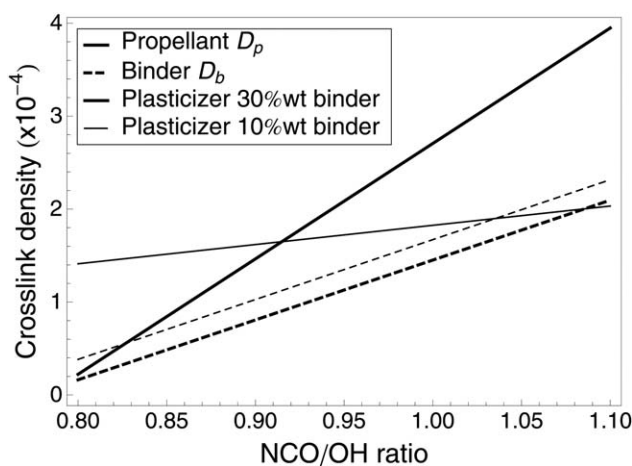
idants. As these molecules had little influence on the mechanical behavior, they are not represented in Figure 5 and are neglected in the following discussion.

By definition, plasticizer molecules are low-molecular-weight components compared to polymer chains. Thus, the molecular weight of the plasticizer molecules in the sol fraction was easily distinguished from the HTPB molecular weights.

In materials containing little  $F_{solpol}$ , the HTPB molecular weights were distributed around one mean value, which was equal to about twice the molecular weight of the HTPB prepolymer. However, the width of the molecular weights distribution was large. Hence, this phase of the microstructure already



**Figure 2.** Correlation between the  $T$  values predicted by the DoE model and the measured  $T$  values: (a)  $T'$  and (b)  $T''$ .



**Figure 3.**  $D_b$  and  $D_p$  versus the NCO/OH ratio and the plasticizer content (filler fraction = 88 wt %, no FBBAs).

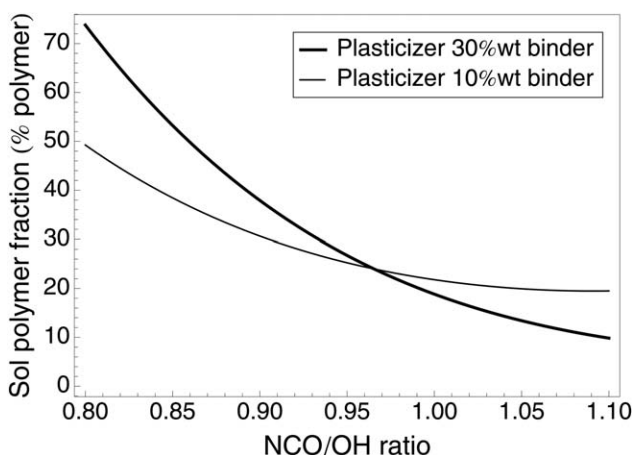
consumed some curing agents to link a few chains to each other without building a network.

As  $F_{\text{solpol}}$  increased,  $M_w/M_n$  increased up to 2.03 for a  $F_{\text{solpol}}$  of 30 wt % of the polymer. This showed the transition between a  $F_{\text{solpol}}$  centered around one value and the microstructure of undercrosslinked materials described in the next paragraph.

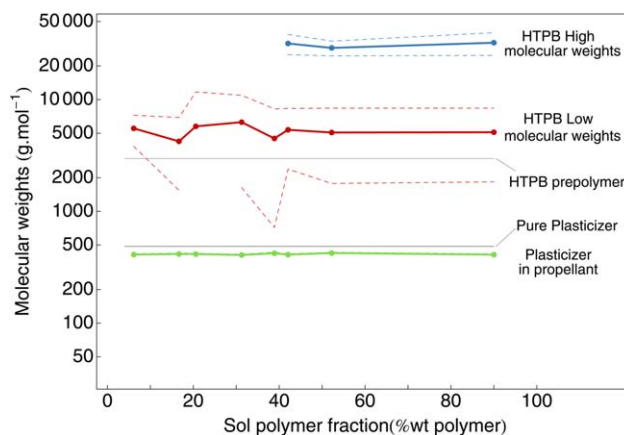
At high  $F_{\text{solpol}}$ 's, a new phase appeared, which contained molecular weights larger than 30,000 g/mol. This phase represented parts of the network that lacked curing agents to be linked to the global network. These parts empowered the solid to display the high  $F_{\text{solpol}}$  measured by swelling.

To complete the study of the microstructure, the influence of the plasticizer content on the crosslink density and  $F_{\text{solpol}}$  were examined.

$D_b$  decreased when the plasticizer content increased (Figure 3). This decrease proved that the addition of plasticizers before curing (preswelling) modified the resulting network. More precisely, the preswelling increased the weight between crosslinks.



**Figure 4.**  $F_{\text{solpol}}$  according to the NCO/OH ratio and the plasticizer content (filler fraction = 88 wt %, no FBBAs).



**Figure 5.**  $M_n$  and  $M_w/M_n$  values for the sol fraction measured by GPC for the eight materials of the DoE. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The influence of the plasticizer content on  $D_p$  (Figure 3) and  $F_{\text{solpol}}$  (Figure 4) strongly depended on the NCO/OH ratio. The behavior could be divided into two domains with NCO/OH thresholds at 0.91 and 0.96 for  $D_p$  and  $F_{\text{solpol}}$ , respectively. When the NCO/OH ratio was lower than this threshold,  $D_p$  decreased, and  $F_{\text{solpol}}$  increased with increasing plasticizer content. When the NCO/OH ratio was higher than this threshold,  $D_p$  increased, and  $F_{\text{solpol}}$  decreased when the plasticizer content increased.

As this effect was not measured on  $D_b$ , we concluded that the change in  $D_p$  and in  $F_{\text{solpol}}$  due to plasticizers was eliminated by the dissolution of the fillers. Thus, the influence of the plasticizer content was associated with the increase in crosslinks in the neighborhood of fillers attributed to the reaction of the FBBA molecule X. As presented in AZ1,<sup>10</sup> the molecule X reacted with the filler surface and with the polymer chains and consumed curing agents. It appeared that the plasticizers facilitated this reaction. One possible explanation was that the plasticizers facilitated the movements of the curing agents toward the surface of the fillers where they reacted with molecule X and a polymer chain, either part of the network or of the sol fraction.

In the presence of an adequate quantity of curing agents,  $D_p$  increased and  $F_{\text{solpol}}$  decreased with increasing plasticizer content. The fact that the influence of the filler fraction on both  $D_p$  and  $F_{\text{solpol}}$  was strongly connected to the plasticizer content (Figure 6) was further support for the preceding argument. More precisely, the reaction of molecule X was facilitated by the plasticizer molecules; therefore, the influence of the filler fraction was larger for larger contents of plasticizer.

The reaction of molecule X was, however, annihilated by the dissolution of the fillers in the second part of the swelling experiment (see AZ1), and hence, it did not participate in the measurement of  $D_b$ .

An additional effect arose from the preswelling of the network by plasticizers; that is, the amount of chains participating in the network increased for the same quantity of curing agents introduced. At NCO/OH ratios larger than 1, the outcome was an

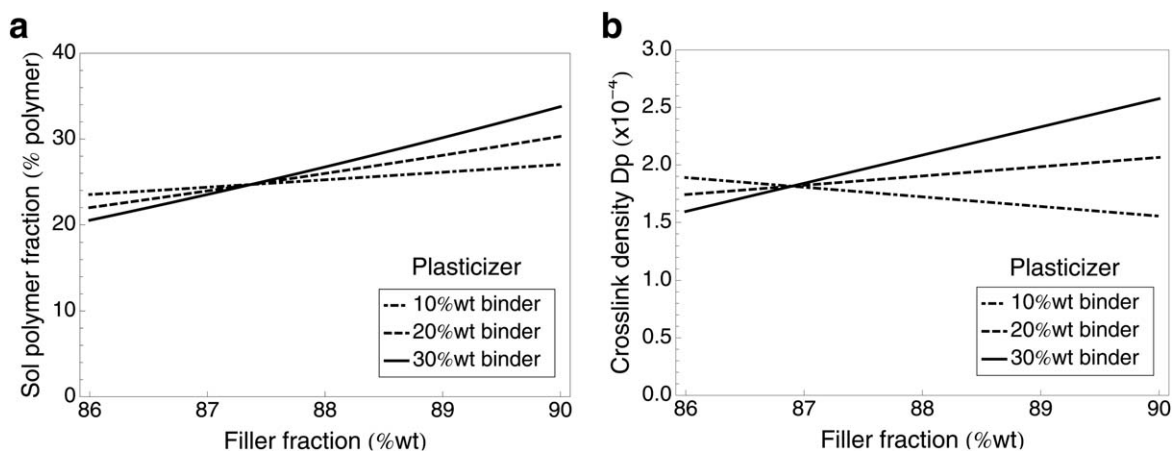


Figure 6. Interaction of the filler fraction and the plasticizer content influencing the microstructure (NCO/OH = 0.95, no FBBA).

almost complete network and a sol fraction that decreased with increasing plasticizer content.

When the quantity of curing agents was not large enough to generate a complete network, the plasticizers facilitated the movements of small molecules into the microstructure. In this configuration, the presence of molecule X further deprived the network of essential curing agents. Consequently,  $F_{\text{solpol}}$  increased and  $D_p$  decreased with increasing plasticizer content.

To summarize, the microstructure was schematically composed of fillers and binder. The influence of the fillers and binder–filler links was studied previously by AZ1.<sup>10</sup> This study focused on the influence of the NCO/OH ratio and the plasticizer content on the binder. The binder itself was seen as a polymer chain network and a sol fraction.

The NCO/OH ratio quantified the quantity of curing agents available to chemically link the HTPB chains and create a network. Consequently, this factor strongly controlled the crosslink density of the material. In addition, when NCO/OH was less than 1, that is, when the amount of curing agents was not sufficient to form a complete network, a new phase appeared in the sol fraction and was composed of portions of the network not linked to the global network. Finally, some of these curing agents were actually used by the FBBA molecule X to react with the filler surface and form binder–filler weak links.

The plasticizers played a double role in the formation of the microstructure. First, they preswelled the network, and this led to a decrease in the crosslink density in the presence of high quantities of plasticizers. Second, the plasticizers molecules seemed to facilitate the movements of small molecules, such as curing agents or molecule X, into the microstructure and toward the filler surface. This part of the study showed that the plasticizers increased the crosslink density in the vicinity of fillers when the NCO/OH ratio was higher than 1.

#### Deformation Mechanisms

In this section, we discuss the results of the characterization of the macroscopic viscoelastic behavior. First, the influences of the NCO/OH ratio and the plasticizer content on the linear

behavior at low prestrain are discussed. Second, the deformation mechanisms leading to the nonlinear behavior are identified.

The measurements show that  $P'$  increased with the NCO/OH ratio (Figure 7). This could be explained by the fact that an increase in the NCO/OH ratio had a double effect. On one hand, it increased  $D_p$ . On the other hand, it decreased  $F_{\text{solpol}}$  and, hence, increased the quantity of elastically effective chains. Both effects led to an increase in the storage modulus, as observed in other elastomers and elastomer composites.<sup>17–19</sup>

$P''$  increased with the NCO/OH ratio (Figure 8). A limit value in  $P''$  was obtained for NCO/OH  $\cong$  1. When we scrutinized the outcome of the increase in the NCO/OH ratio at the polymer chain level, we noticed a decrease in  $F_{\text{solpol}}$ ; this was assumed to be mainly responsible for the dissipations by intermolecular frictions. A decrease in  $P''$  would then be expected. However, the study of the microstructure also showed that at low NCO/OH ratios, a portion of  $F_{\text{solpol}}$  was actually composed of parts of network that had a low mobility in the global network and that did not produce increased dissipations. Moreover, an increase in the NCO/OH ratio also increased the crosslink density, and this led to a decrease in the mesh size. The sol polymer

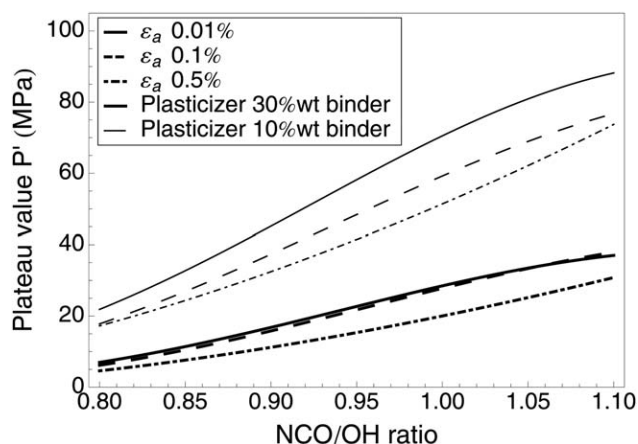
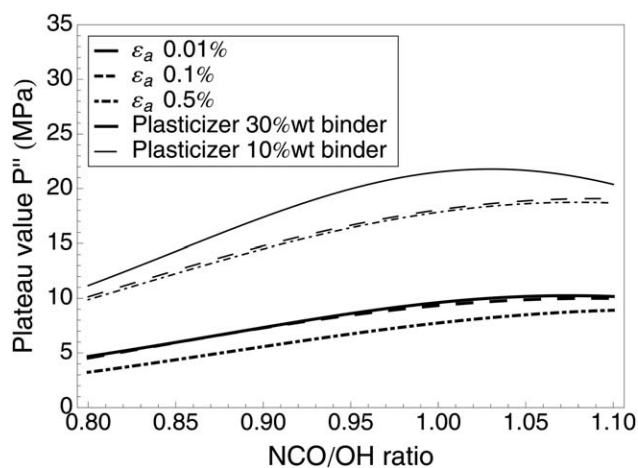


Figure 7.  $P'$  according to the NCO/OH ratio and the plasticizer content (filler fraction = 88 wt %, no FBBA).



**Figure 8.**  $P''$  according to the NCO/OH ratio and the plasticizer content (filler fraction = 88 wt %, no FBBAs).

chains placed themselves in the network and, then, were further constrained by a denser network.

Noticeably, the NCO/OH ratio influenced the linear mechanical behavior more strongly at lower plasticizer contents, whereas its influence on the microstructure was larger for larger plasticizer contents. The previous section showed that depending on the plasticizer content, part of the curing agents was used to create crosslinks in the proximity of the fillers. Because this reaction depended on the filler fraction and increased the effective filler volume, the model probably merged this phenomenon with the influence of the filler fraction.

The decrease in  $P'$  with increasing plasticizer content was stronger for a high NCO/OH ratio (Figure 7). The introduction of plasticizer molecules and a high quantity of curing agents led to a concentration of crosslinks around the fillers, which in turn, deprived the network of curing agents.  $P'$  measured the elasticity of the binder and, hence, decreased with increasing plasticizer content.

For a low NCO/OH ratio, the decrease in  $D_p$  and the increase in  $F_{\text{solpol}}$  led to a decrease in  $P'$  when the plasticizer content increased.

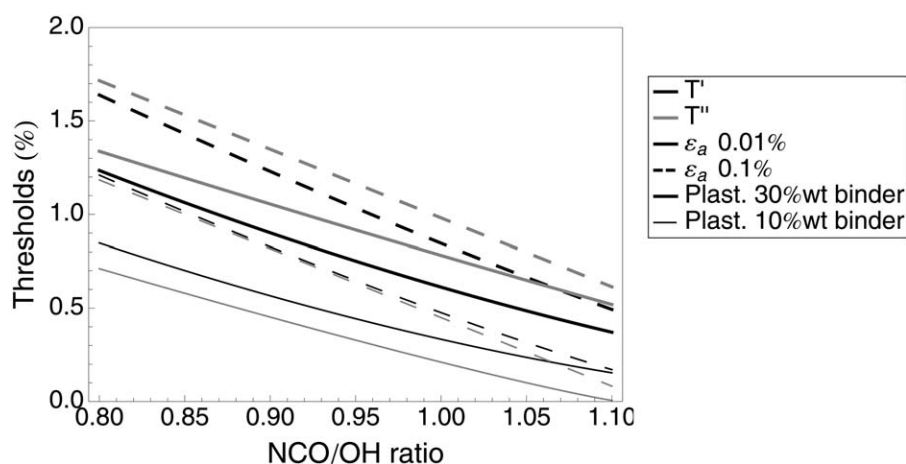
$P''$  strongly decreased with increasing plasticizer content (Figure 8). This could be explained by the fact that the plasticizer molecules facilitated the movements of the polymer chains through a decrease in the molecular friction. As expected, the dissipations measured by  $P''$  in the linear domain were reduced when the plasticizing effect was increased.

$T'$  and  $T''$  decreased strongly with the NCO/OH ratio and presented similar values (Figure 9).  $T'$  and  $T''$  could be interpreted as the levels of prestrain at which the elastic and viscous nonlinearities started.

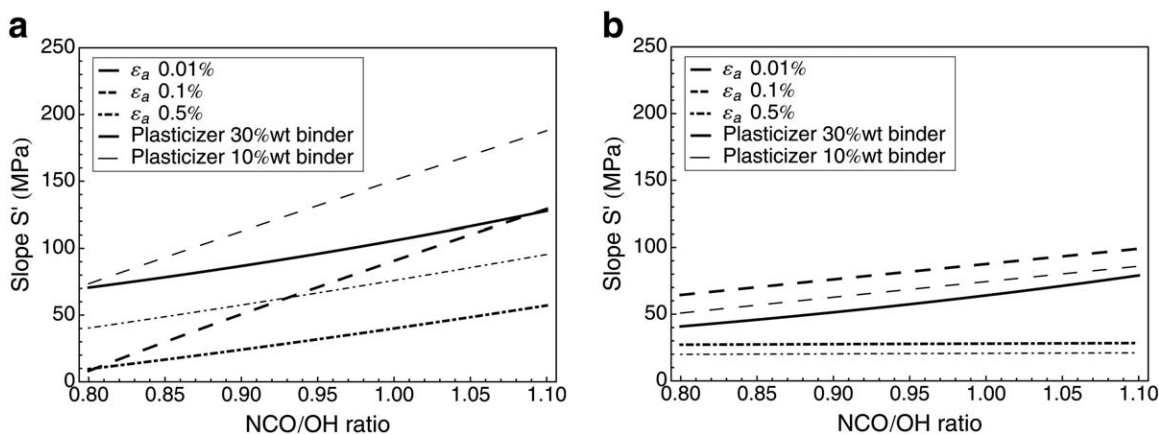
It is well known that the presence of a high filler fraction induces a highly heterogeneous strain and stress fields. Strain localization and stress transmission bands are formed whenever the distance between the fillers is close enough. As a result, only a part of the binder reached a highly nonlinear material behavior at a given prestrain.  $T'$  corresponded to the configuration where part of the binder reached its maximum extensibility. As the increase in plasticizers decreased  $D_b$ , it was equally associated with an increase in the maximum extensibility of the network and, in turn, an increase in  $T'$ .

$T''$  was higher than  $T'$  when the plasticizer content was high and was lower otherwise. Because of the complex influence of the plasticizer on the distribution of crosslinks in the microstructure,  $T''$  depended primarily on the mesh size of the network. Thus,  $T''$  was the prestrain where the sol fraction became sufficiently constrained by the network and significantly increased the inner friction. As expected,  $T''$  increased with the plasticizer content.

In the presence of FBBAs,  $S'$  increased with the NCO/OH ratio at all  $\epsilon_a$ s [Figure 10(a)]. When no FBBAs were added,  $S'$  increased less strongly with the NCO/OH ratio at small amplitudes and did not depend on the NCO/OH ratio at an  $\epsilon_a$  of 0.5% [Figure 10(b)]. A similar increase in the storage and loss moduli with prestrain was observed for the filled elastomers at higher prestrains. This was associated with the limit of extensibility of the network.<sup>20–23</sup> Consequently, the nonlinear domain at a low prestrain for highly filled elastomers were associated with the maximum extensibility of the network. As larger parts



**Figure 9.**  $T'$  and  $T''$  according to the NCO/OH ratio and the plasticizer content (filler fraction = 88 wt %).



**Figure 10.**  $S'$  versus the NCO/OH ratio and the plasticizer content (filler fraction = 88 wt %): (a) with FBBAs and (b) without FBBAs.

of the network reached the limit of extensibility, we observed a larger storage modulus.

The influence of the NCO/OH ratio on the nonlinear behavior highly depended on whether the network was linked to the filler surface or not. Indeed, when the network was not linked to the filler surface, chain sliding on the filler surface according to deformation was possible. This mechanism allowed the polymer network to rearrange and balance the imposed prestrain. As a result, the increase in the slope with the NCO/OH ratio was smaller. When the amplitude was high enough, the rearrangement of the network according to deformation was great enough to prevent the crosslink density from having an influence on the increase in the modulus with prestrain.

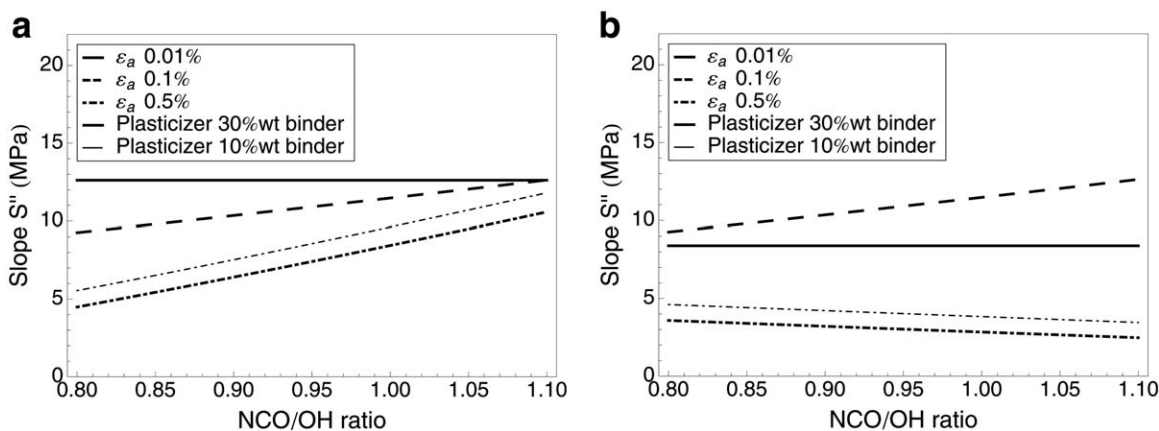
When FBBAs were present,  $S'$  increased with the NCO/OH ratio at high  $\varepsilon_a$ s and was constant at a low  $\varepsilon_a$  [Figure 11(a)]. When no FBBAs were introduced, the contrary result was obtained; that is,  $S'$  decreased with increasing NCO/OH ratio [Figure 11(b)]. (An exception was  $\varepsilon_a = 0.1\%$ ).

The influence of the NCO/OH ratio on  $S'$  was a combination of two effects. First, the crosslink density increased, which in turn, reduced the mesh size of the network and increased the dissipation. Second,  $F_{\text{solpol}}$  decreased, and the outcome was a

substantial decrease in the dissipation by intermolecular friction. The chemical connection between the fillers and the binder determined the prevailing effect. The connection itself depended on the presence of FBBAs.

When FBBAs were present, the network was linked to the filler surface and was highly deformed. The sol polymer chains inside the network represented a smaller fraction of the total polymer but were more constrained and, hence, produced larger dissipations. Consequently,  $S'$  increased with the NCO/OH ratio. In the absence of FBBAs, the network adapted with a strain mechanism, and this diminished the constraints on the sol polymer chains. Because the quantity of  $F_{\text{solpol}}$  decreased with increasing NCO/OH ratio, the macroscopic outcome was a decrease in  $S'$ . This decrease also indicated that chain sliding on the filler surface was not the main dissipation mechanism.

In the presence of FBBAs,  $S'$  decreased with the plasticizer content at amplitudes higher than 0.01% [Figure 10(a)]. Preswelling the network with plasticizers decreased  $D_b$  and facilitated the rearrangement of the polymer chains according to strain. As a result, the introduction of plasticizers decreased the amount of highly constrained networks between the fillers at a given prestrain level and, as a consequence, decreased  $S'$ .



**Figure 11.**  $S''$  according to the NCO/OH ratio and the plasticizer content (filler fraction = 88 wt %): (a) with FBBAs and (b) without FBBAs.



In the absence of FBBA,  $S'$  exhibited a small increase with increasing plasticizer content [Figure 10(b)]. Independently of the presence or absence of FBBA,  $S'$  depended only on the plasticizer content when  $\varepsilon_a$  was 0.5% (Figure 11). The complex influence of the plasticizer molecules on the microstructure justified these observations. By definition, the main role of plasticizers was to prevent friction between the polymer chains. However, they also facilitated the concentration of crosslinks on the filler surface, which in turn, increased the effective filler volume. Both mechanisms strongly influenced  $S$  but could not be distinguished from each other.

## CONCLUSIONS

In this series of experiments, we systematically studied the influence of the composition on the microstructure and mechanical behavior of a solid propellant similar to the industrial composition and containing active fillers. This allowed us to take into account the actual filler–binder interactions and the influence of additives such as FBBA without any assumptions. We implemented a DoE that took into account four factors: the filler fraction, the presence of FBBA, the NCO/OH ratio, and the plasticizer content. A previous article presented the influence of the filler particles and their interactions with the binder, that is, the influence of the filler fraction and FBBA factors. The results concerning the influence of the NCO/OH ratio and plasticizer content are discussed in this article.

The characterization of the microstructure through the swelling experiments and GPC showed the complex action of both the curing agents, quantified by the NCO/OH ratio, and the plasticizer content on the binder. The nonlinear viscoelastic behavior was determined by PDMA tests. With a phenomenological model, the nonlinearity of each material was quantified and processed in the classical frame of the DoEs. The correlation between the DoE predicted values and the experimental data was satisfying for all responses, except for  $T$ .

The curing agents had three roles: (1) the curing agents reacted with the active sites of the polymer chains to form a three-dimensional network, (2) the curing agents also linked the polymer chains in the sol fraction, and (3) the curing agents participated in the reaction of molecule X with the filler surface.

As expected, the plasticizer molecules preswelled the network and reduced the molecular friction between the polymer chains. In addition, plasticizers facilitated the movements of small molecules into the microstructure. These movements resulted in an increase in crosslinks at the proximity of fillers when the amount of curing agents was sufficient.

The results of PDMA were discussed. We took into account the influence of each factor on the microstructure, and the main deformation mechanisms were determined. The first article (AZ1) showed that the high filler packing induced a highly heterogeneous strain field between fillers. This study provided further insight into the deformation of the binder. The nonlinearity of the behavior originated when the maximum extensibility of the network for the elastic part was reached and

constrained the sol fraction in this extended network for the viscous part.

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