Adhesion of an HTPB–IPDI-Based Liner Elastomer to Composite Matrix and Metal Case

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ABSTRACT: Adhesional characteristics of an elastomeric liner composition toward a highly filled composite matrix and metal case were investigated. The system is composed of an excess isocyanate functionality in the elastomer compared to an excess hydroxyl functionality in the composite matrix. Both phases essentially contain the same binder (HTPB) and curing agent (IPDI). A bifunctional aziridine (MAPO) is used as a bond (adhesion) promoter. The effects of the R value, triol/diol ratio, and MAPO concentration on the adhesive nature of the metal–elastomer-matrix system were investigated by tensile and peel test methods. Maximum T-peel values were obtained for the NCO/OH ratio of $R = 1.15$ and for the triol/diol ratio of 0.054. The optimum MAPO concentration was found to be around 1–2% for the elastomer. As a result of this investigation, three candidate compositions were selected to be employed as an elastomeric material. On these compositions, metal–elastomer–composite (MEC) tensile, MEC-shear, lap-shear, elastomer–composite (EC) peel, and T-peel tests were applied. These compositions reflect acceptable combinations of strength and elasticity as well as good adhesive values required for a liner material. In particular, one of the compositions tested seems to be a good candidate when all the required characteristics of an elastomeric liner material are considered. It has a large enough elasticity with the required modulus to withstand the compressive and shearing forces in applications together with good adhesive properties toward the composite matrix and the metal. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2355–2362, 1997

Key words: elastomer; liner; adhesion; composite; HTPB; diisocyanate; bond promoter; tensile; shear; peel

INTRODUCTION

In the previous article,[1] we reported on the results of a parametric study based on the mechanical behavior of an elastomeric liner composition at various triol/diol and NCO/OH ratios. In this study, the adhesional characteristics of the same elastomer toward a highly filled composite matrix and metal cases were investigated. The system is composed of an excess isocyanate functionality in the elastomer compared to an excess hydroxyl functionality in the composite matrix which creates a reactive interface between the two polymeric phases. Both phases essentially contain the same binder (hydroxyl-terminated polybutadiene [HTPB]) and the same curing agent (isophoron diisocyanate [IPDI]). A bifunctional aziridine [tris(methylaziridinyl)phosphine oxide (MAPO)] is used as a bond (adhesion) promoter. For metal surfaces, a trifunctional isocyanate primer (Desmodur-RE) is applied before casting the elastomer that forms strong chemical bonds with the liner and the metal surface.

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Apart from the adhesional strength due to the reactive moieties at the interface, adhesion between miscible polymers and self-adhesion are thought to be operative for the system under investigation, in particular, above the glass transition temperature (T_g) of the polymer by a reptation mechanism.[2] In recent years, there has been large numbers of theoretical and experimental studies on the mechanism of adhesion by chain diffusion at the interface and its effect on the toughness and the strength of an interfacial bonding.[3] Among the methods to improve adhesion is that of partial curing of one of the components to increase interdiffusion.[4] The solvent-swelling techniques have been found to give only modest increases in adhesion.[5] If one or both phases are elastomeric, the viscoelastic deformation processes are profoundly altered.[6,7] The experimental results are qualitatively consistent with the theories proposed.[8,9]

All the phenomena mentioned above are relevant to the interactions observed at the interfaces that we studied. In a highly complex system such as used in this study, the preparation of an effective liner requires extensive tests to find the optimum conditions with regards to mechanical, adhesive, and processing parameters. This report outlines the effects of the triol/diol ratio, the *R* value, and the amount of the bond promoter on the adhesive behavior of the elastomeric liner toward the composite matrix and the metal case.

EXPERIMENTAL

Materials

HTPB (R45-M, number-average molecular weight of 2700, ARCO Chemical Co., Philadelphia, PA), isophoron diisocyanate (IPDI, Fluka AG, Leverkusen, Germany), 4,4′,4″-triphenylmethane triisocyanate (Desmodur-RE, Bayer, Leverkusen, Germany), triethanolamine (TEA, Merck, Darmstadt, Germany), carbon black (25 nm particle diameter, 98% carbon content, 0.7% sulfur content, 110 m^2/g surface area, pH 4, Printex-U, Degussa A.G., Frankfurt, Germany), dioctyladipate (DOA, Kimtaş, Istanbul, Turkey), and tris[1-(2-methyl)aziridinyl]phosphine oxide (MAPO, ARSYNCO, Germany) were used as purchased.

Elastomer Matrix and Composite Matrix Preparation

Elastomer matrices are prepared as described before.[1] The composite matrix is prepared under similar conditions in a sigma blade mixer and then cast onto a partially cured liner and cured together at 65°C for 7 days. The composite matrix is essentially composed of 10% prepolymer, TEA, and IPDI, 5% plasticizer, antioxidant, and burning rate modifier, and 85% aluminum and ammonium perchlorate.

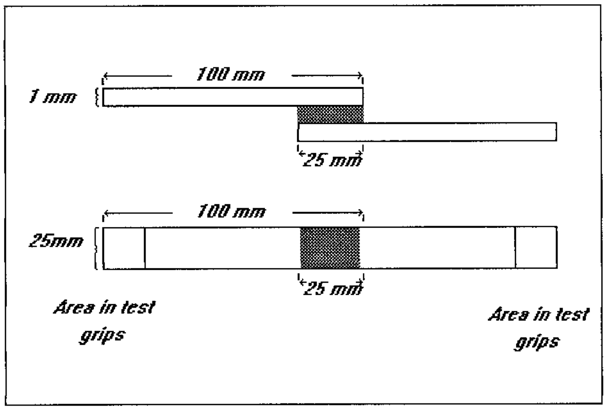

Figure 1 A schematic illustration of lap-shear tensile test specimen.

Surface Preparation of Metal for the Liner Applications

Before application of the primer (Desmodur-RE), sandblasting and degreasing are performed to the metal surface. Degreasing is done with trichlorethane. The primer is a trifunctional isocyanate and is able to react with both with the liner and metal surface to form strong chemical bonds. A freshly prepared liner is applied to the metal surface in all cases.

Lap-shear Tensile Test

In this method, comparative shear strengths between the liner and the metals are determined on a standard specimen under specified conditions of preparation and testing.[10] The aim of the shear tests is to find the adhesive power of the liner to the metal case. The test specimen is illustrated in Figure 1. The test is performed at a constant crosshead speed of 1 mm/min. The maximum shear stress is calculated from eq. (1):

$$\text{Shear stress} = \frac{\text{max load (kg)}}{\text{shear area (cm}^2)} \qquad (1)$$

T-peel Test

This method is primarily intended to determine the relative peel strength of the adhesive bonds

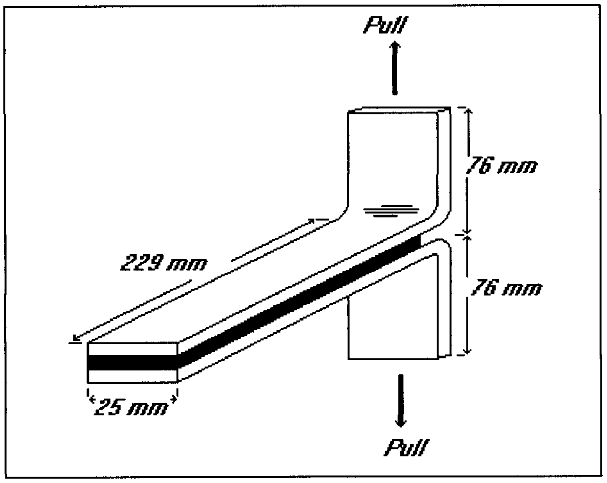

Figure 2 A schematic illustration of T-peel test specimen.

between the flexible adherents using a T-type specimen (Fig. 2).[11] As a support material in the T-peel tests, flexible aluminum shims of 0.4 mm thickness are used. After depositing the freshly prepared liner, two panels are squeezed and allowed to cure 7 days at 65°C. The test is performed at a constant crosshead speed of 200 mm/min and the peel strength is expressed in g/cm.

Metal–Elastomer–Composite Tensile Test (MEC-Tensile)

The adhesive or cohesive nature of failure is tested in the metal–elastomer–composite system with a specimen as shown in Figure 3. The load applied is perpendicular to the adhesion plane of the liner, metal, and composite. The composite matrix is cast onto a partially cured elastomer and the whole system is cocured at 65°C. The test is performed with a crosshead speed of 1 mm/min. The maximum load per unit area and the mode of failure are recorded.

Multiaxial Shear Test (MEC-Shear)

This test describes the mechanical behavior of the metal–elastomer–composite system under shear. The load is applied parallel to the adhesion plane (Fig. 4). The shear value is calculated from eq. (1). The test specimens are prepared similar to the MEC-tensile specimens. The test is performed at a constant crosshead speed of 50 mm/min. The maximum load at failure and mode of failure are recorded.

Elastomer–Composite Peel Test (EC-Peel)

The aim of the experiment is to observe the failure type between the composite and elastomer matrices when peel forces are applied. In this method, the metal substrate that is used as the adherent to the elastomer in the T-peel test is replaced by the composite propellant. The peel force is applied to the elastomeric part as shown in Figure 5. The function of the flexible aluminum shim is to transfer the stresses directly to the composite–elastomer interface without complications caused by the

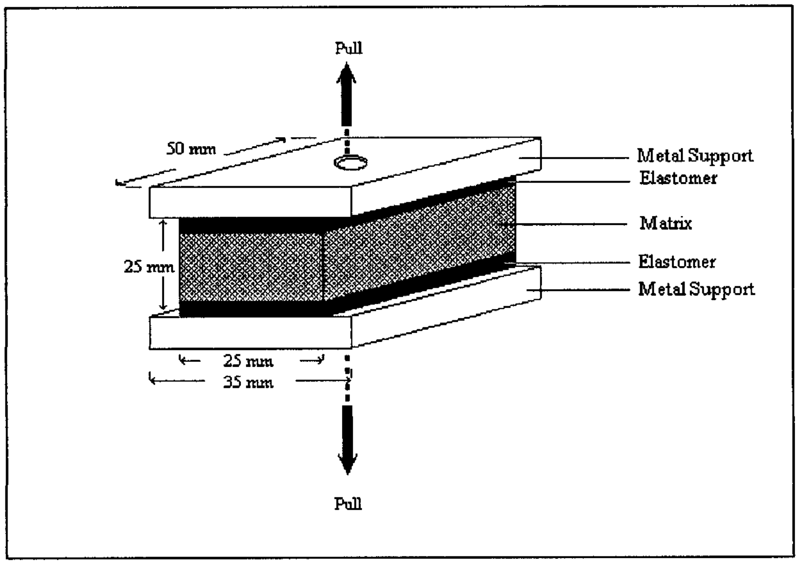

Figure 3 A schematic illustration of metal–elastomer–composite tensile test specimen.

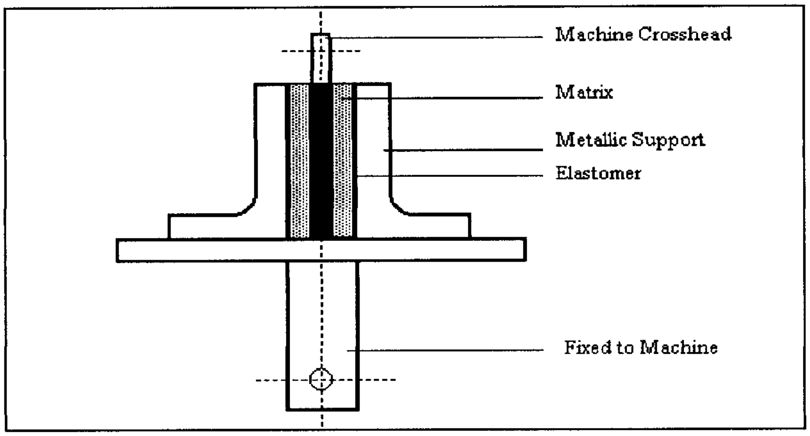

Figure 4 A schematic illustration of multiaxial shear test specimen.

elasticity of the liner. The EC-peel test is performed at a constant crosshead speed of 50 mm/min. Metal shims are prepared as in the T-peel test. The sample preparation and test procedures are the same as in the MEC-tensile and MEC-shear tests.

RESULTS AND DISCUSSION

First, the effects of the NCO/OH ratio, triol/diol ratio, and MAPO concentration on the adhesive nature of the metal–elastomer–matrix system are investigated, which are given below.

Effect of NCO/OH Ratio

In these experiments, the ratio of triol/diol is maintained constant and no bond promoter (MAPO) is used. The influence of the NCO index (R value) on the adhesive properties of the liner is evaluated. Tensile properties of the liner elastomers were given in the previous study.[1] Elastomer–matrix adhesion tests are carried out on the EC-peel test specimens. Adhesive properties of the liner compositions are given in Figure 6. From visual observation, the mode of failure is found to be adhesive in nature for low R values (Table I). The same type of adhesive failure is also observed for the highest NCO/OH ratio ($R = 1.3$). The remaining NCO/OH ratios ($R = 1.05–1.20$) show cohesive failure in the composite matrix, which is indicative of strong adhesive bonding. Figure 6 illustrates that the maximum peel value is obtained around $R = 1.15$, which seems to strike the best balance between the excess functionalities at the interface and other adhesive mechanisms at work.

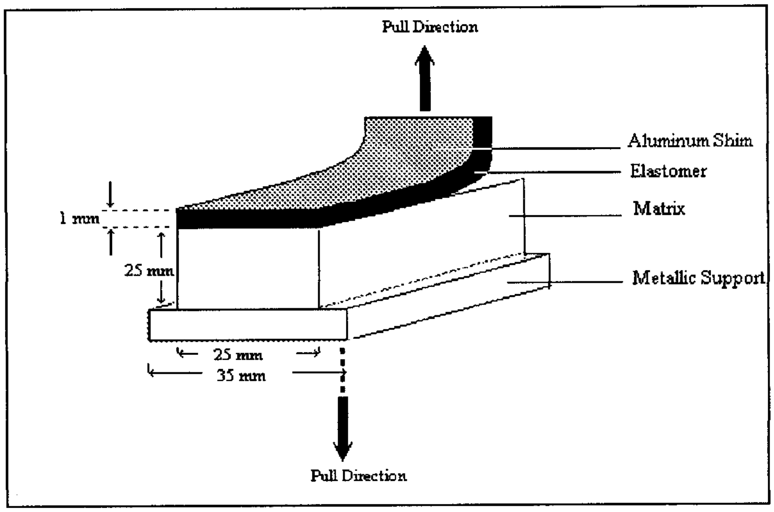

Figure 5 A schematic illustration of elastomer–composite peel test specimen.

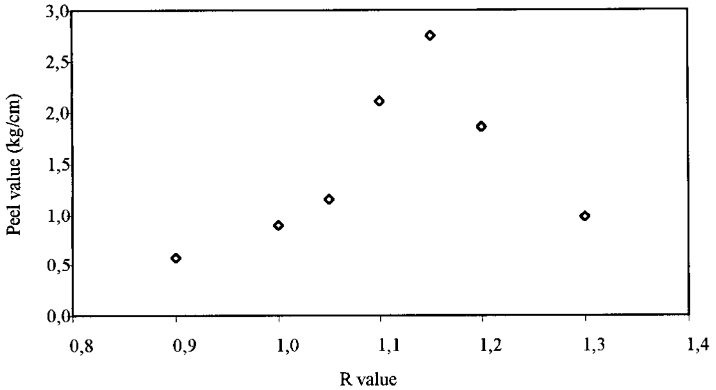

Figure 6 Effect of *R* value on the adhesion of elastomer to matrix (EC-peel test).

Effect of Triol/Diol Ratio

The effect of triol/diol ratio on the tensile properties of the elastomer was reported in the previous publication.[1] The total concentration of the hydroxyl groups is kept constant; therefore, the main interest in this study was the behavior of the elastomer under shearing forces, which is inspected by the T-peel test. The results of the tests are listed in Table II. All samples show a cohesive failure in the elastomer and the maximum T-peel value (2253 g/cm) is obtained at a triol/diol ratio of 0.054. This ratio seems to be the optimum value in terms of shear strength and, therefore, is used in the subsequent formulations.

Similar phenomena were observed on a matrix consisting of an HTPB resin with low hydroxyl functionality (smaller than 2) which requires a high triol content to achieve a tensile strength of 6–7 kg/cm^2 and 50–60% elongation at break.[12,13] As the *R* value increases, a lower amount of triol is required to crosslink the polymer. Thus, for the liner system used in this study, a relatively small amount of triol suffices. Again, the results of the T-peel tests are of operational significance and reflect a balance among the crosslink density, molecular weight, and number of polyurethane linkages.

Table I Adhesive Properties of Elastomer as a Function of NCO/OH Ratio (*R* Value) at a Constant Triol/Diol Ratio of 0.054

R Value	Peel Value (g/cm)	Mode of Failure
0.90	572	AF
1.00	902	AF
1.05	1160	CFP
1.10	2110	CFP
1.15	2748	CFP
1.20	1856	CFP
1.30	986	AF

CFP: cohesive failure in the propellant; AF: adhesive failure at the interface.

Effect of MAPO Concentration

Compounds containing the aziridine group such as MAPO have been extensively employed as bonding agents in HTPB propellants and as bond promoters in liner formulations. Despite the widespread use of these reagents, surprisingly few studies have been reported concerning the mode of action and the reactivity of this class of compounds in the HTPB propellant and liner environments. The reaction of aziridines with alcohols and isocyanates was studied by Broline.[14] The pot life extension of propellants with aziridines was studied by Cuksee.[15] However, there are no adhesion test data on elastomers containing aziridine-type bond promoters.

It is assumed that aziridine molecules at the liner surface interact with the ammonium per-

Table II Adhesive Properties of Elastomer as a Function of Triol/Diol Ratio at a Constant NCO/OH Ratio of *R* = 1.10

Triol/Diol	T-peel Value (g/cm)	Mode of Failure
0.000	1450	CF
0.031	1385	CF
0.054	2253	CF
0.130	905	CF
0.500	1062	CF

CF: cohesive failure in the elastomer.

Table III Adhesive Properties of Elastomer as a Function of MAPO Concentration at a Constant NCO/OH Ratio of $R = 1.10$ and Triol/Diol Ratio of 0.054

% MAPO	Peel Value (g/cm)	Mode of Failure
0.00	1050 ± 43	AF
0.50	2700 ± 36	AF
1.00	4070 ± 137	AF
1.50	3560 ± 110	CFI
2.00	3530 ± 22	CFP
2.50	2880 ± 32	AF
3.00	2630 ± 7	AF
4.00	2570 ± 25	AF

AF: Adhesive failure; CFI: cohesive failure at the interface; CFP: cohesive failure in propellant.

chlorate particles at the propellant surface. In other words, the interaction occurs at the liner–propellant interface. The addition of MAPO to the liner up to an optimum amount increases the adhesive strength of the liner–propellant system and, thus, the bond reliability of the system. To determine the effect of MAPO concentration on adhesion, elastomer–composite (EC-peel) tests were performed. The effect of MAPO on the adhesion of the elastomer toward the matrix is studied at a constant NCO/OH ratio of $R = 1.10$ and a triol/diol ratio of 0.054 by varying the MAPO percentage in the range of 0.00–4.00. The results of these tests are given in Table III and Figure 7. The peel values of the elastomer samples containing 1.0, 1.5, and 2.0% MAPO are quite high and very close to each other. Another important criterion in the liner composition selection is the mode of failure. Although the sample containing 1.0% MAPO has the highest EC-peel adhesive strength, the mode of failure is somehow adhesive. In an acceptable liner–matrix system, the failure has to be cohesive in the matrix or the elastomer surface should pick up some particles from the matrix during the failure. The latter is described as cohesive failure at the interface (denoted as CFI in Table III). The optimum MAPO concentration is found to be around 1–2% for the elastomer.

Tests Performed on Selected Compositions

From the results discussed so far in this report, three liner compositions are selected for applications and the tests that follow are applied. The liner compositions selected are given in Table IV. These formulations reflect the optimum combinations of strength and elasticity as well as good adhesive values required of a liner material. The mechanical properties of three selected formulations are given in Table V. Inspection of Table V reveals that increasing the MAPO content and triol/diol ratio enormously increase the modulus and decrease the elasticity of the liner. The effect of both parameters can be explained by the formation of crosslinks via triols and aziridinyl groups with isocyanate.

MEC-Shear Test

The maximum shear stress values for the metal–elastomer–composite specimen obtained from the multiaxial shear tests are given in Table VI. Failure is assumed to occur when the strength of the joint is exceeded. The failure in these tests always occurs cohesively in the propellant as expected. It is interesting to note that the F-3 composition which gives the highest lap-shear stress values

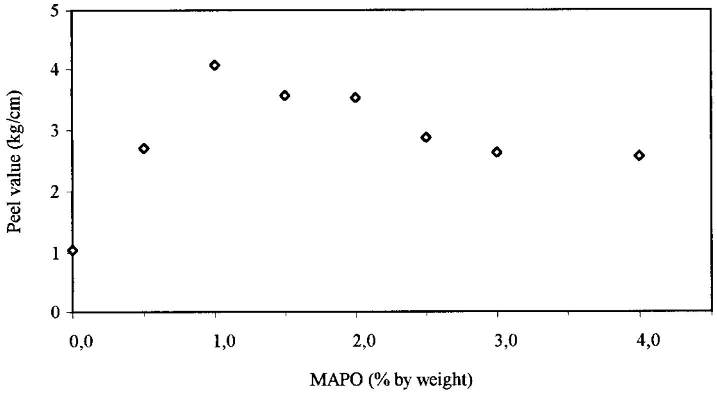

Figure 7 Effect of MAPO concentration on adhesive strength of elastomer to matrix.

Table IV The Liner Compositions Tested (Values are Weight Percentages)

Material	Composition F-1	Composition F-2	Composition F-3
HTPB	75	74	73
IPDI	6.9	6.8	8.8
Bond promoter	0.5	2.0	0.5
Carbon black	10	10	10
DOA	6	6	6
R value	1.1	1.1	1.1
Triol/diol	0.054	0.054	0.388

with respect to aluminum is the least effective composition in protecting the propellant from cohesive failure. It can be said that F-3 is inferior in shock-absorption capacity and transfers the stress applied more or less directly into the propellant. In MEC-shear tests, F-1 exhibits higher values relative to F-2 and F-3. Due to its elastomeric nature, it should withstand high shear stresses during dynamic tests, e.g., in rocket applications.

MEC-Tensile Test

This method is applied to decide the type of failure between the elastomer and the matrix.[16] The liner should have enough internal cohesive strength and adhesive capability both to the propellant and to metal case for the reliability. The average values of stress at failure are 6.3 ± 1.0, 5.9 ± 1.4, and 5.5 ± 0.8 kg/cm^2 for F-1, F-2, and F-3, respectively. The failure is either cohesive in the matrix or cohesive at the interface (CFI). Again, the more elastomeric liner composition F-1 functions better than do the F-2 and F-3 compositions during dynamic tests. F-3 has a lower value than those of the F-1 and F-2 compositions. The shear strength of the metal–elastomer–composite system is weaker than the tensile strength of the system. The MEC tensile strength of the metal–elastomer–composite system is around 1 MPa; however, the MEC shear strength of the system is around 0.3 MPa, which is more relevant in motor applications. The shear forces are more effective in dynamic tests, because the rocket motor leaves the launcher approximately at 40 times the gravitational force. Thus, the adhesion of liner to the case and to the propellant is a critical parameter.

Lap-shear Test

The results of the lap-shear tensile tests are also given in Table VI. In general, the shear stress value between the liner and the aluminum substrate is lower for F-2. However, for the F-1 and F-3 systems, the values are superior. The values for the lap-shear tensile test are the averages of a minimum of 20 tests. The F-1 and F-3 compositions have an extremely good failure behavior which is always cohesive in the liner. When the lap-shear tests with and without the primer application are compared, it is observed that the primer-applied metals have a 1.5 times higher adhesive strength than that of the samples without the primer application.

T-peel Test

The 90° peel test carried out between 0.4 mm aluminum sheets gave a load of 6800 ± 350, 6200 ± 500, and 4700 ± 350 g/cm for F-1, F-2, and F-3, respectively. These values are the average of a minimum of 10 tests for each liner formulation. In a typical test, the load fluctuates around an

Table V Average Stress, Strain, and Initial Modulus Values for the Selected Liner Compositions

Liner Composition	Maximum Stress (kg/cm^2)	Strain at Break (%)	Initial Modulus (kg/cm^2)
F-1	8.3 ± 0.2	860 ± 17	0.9 ± 0.2
F-2	11.7 ± 1.6	330 ± 89	6.0 ± 0.6
F-3	15.9 ± 3.3	220 ± 35	11.2 ± 1.7

Table VI Various Test Method Results Applied to Selected Compositions

Test Method	Unit	F-1	F-2	F-3
MEC-shear	kg/cm^2	5.56	4.29	3.22
MEC-tensile	kg/cm^2	6.30	5.92	5.51
Lap-shear	kg/cm^2	11.82	7.97	13.97
T-peel	g/cm	6800	6200	4700

average value, signifying the tearing action of stresses and the resultant accumulation when the stresses are relieved. Again, in the more rigid formulation, F-3, the propagation of cracks occurs at lower values of load compared to F-1 and F-2. The stress distributions in the peel test are quite complex, and the force required to initiate and maintain stripping is influenced by width of the specimen and the mechanical properties of the layer. The force required to initiate the peeling process or crack propagation is higher than the normal peeling strength of the specimen. A small variation of adhesive strength or thickness of the adherent will result in a large variation of the peel force. For this reason, the average force of over 12–15 cm length is taken as an indicator of the peel strength.

CONCLUSION

The effects of the R value, triol/diol ratio, and MAPO concentration on the adhesive properties of an elastomeric liner toward a composite propellant and a metal case were investigated and optimum conditions with regards to each parameter were determined. On selected compositions, more extensive tests were carried out to find the liner system that is promising on operational grounds. For all parameters, feasible values in terms of good adhesion, strength, elasticity, and toughness were determined. One important point arising from this investigation is that MAPO, which, in general, is used to increase adhesion at the elastomer–matrix interphase, is also instrumental in increasing the crosslink density of the elastomer—hence, its concentration in the composition has to be thought of together with the triol/diol ratio. Among the compositions tested, F-2 seems to be a good candidate when all the required characteristics of an elastomeric liner material are visualized. It has a large enough elasticity with the required modulus to withstand the compressive and shearing forces in applications. At the same time, the adhesive properties of the F-2 composition toward the composite matrix and the metal are within the acceptable limits.

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