DOI: 10.5028/jatm.2009.0102223229

Juliano Libardi*
State University of Campinas
Campinas-Brazil
j_libardi@yahoo.com.br

Sérgio P. Ravagnani
State University of Campinas
Campinas-Brazil
ravag@feq.unicamp.br

Ana Marlene F. Morais
Institute of Aeronautics and Space
São José dos Campos- Brazil
ana.morais@iae.cta.br

Antonio Roque Cardoso
Institute of Aeronautics and Space
São José dos Campos- Brazil
a-roque@uol.com.br

* author for correspondence

Study of plasticizer diffusion in a solid rocket motor´s bondline

Abstract: *This work aims to determine the diffusion coefficient of the plasticizers dibutyl phthalate (DBP), dioctyl phthalate (DOP) and dioctyl azelate (DOZ) on the internal insulating layer of solid rocket motors. These plasticizers are originally present in the layers of rubber, liner and propellant, respectively. This species are not chemically bonded and tend to diffuse from propellant to insulating and vice versa. A computer program based on the mathematical model of Fick's second Law of diffusion was developed to perform the calculus from the concentration data obtained by gas chromatographic (GC) analyses. The samples were prepared with two different adhesive liners; one conventional (LHNA) and the other with barrier properties (LHNT). A common feature of both liners was that they were synthesized by the reaction of hydroxyl-terminated polybutadiene (HTPB) and diisocyanates. However, a bond promoter was used to increase the crosslink density of the LHNT liner and to improve its performance as barrier against the diffusion. The effects of the diffusion of the plasticizers were also investigated by hardness analyses, which were executed on samples aged at room temperature and at 80ºC. The results showed an increase trend for the samples aged at room temperature and an opposite behavior for the tests carried out at 80ºC.*

Keywords*: Fick's Law, Diffusion, Bondline, Solid rocket propellant, Thermal insulation, Liner, Plasticizer, Hardness, Gas chromatograph.*

NOMENCLATURE

Al	Aluminum powder
AP	Ammonium perchlorate
ASTM	American Society For Testing And Materials
C	Mass concentration
M_{eq}	Mass concentration at the equilibrium
M_1	Final mass concentration
C_0	Initial mass concentration
C_t	Mass concentration in a time t
CG	Gas Cromatograph
D	Diffusion coefficient
DBP	Dibutyl phthalate
DOP	Dioctyl phthalate
DOZ	Dioctyl azelate
HTPB	Hydroxyl terminated polybutadiene
IAE	Institute of Aeronautics and Space
IPDI	Isophorone diisocyanate
l	Thickness
LHNA	Conventional adhesive liner
LHNT	Adhesive liner with barrier properties
MAPO	Trimethylaziridinylphosphine oxide
MS	Mass spectography
NB 7113	Thermal insulation based on Nitrilic Rubber
R1	Propellant layer at 3 mm from interface
R2	Propellant layer at 25 mm from interface
R3	Propellant layer at 55 mm from interface
t	Time
TDI	2.4-toluene diisocyanate
x	Normal coordinate to cross section
z	Plane region of a sample

Received: 04/09/09
Accepted: 06/10/09

INTRODUCTION

The solid rocket motor is comprised of a combustion chamber filled with a solid composite propellant. To protect the interior of the chamber against the high temperatures generated during the combustion an insulating rubber is bonded to the internal wall of the vessel. The propellant is casted into the motor and bonded to the rubber by a thin layer of adhesive liner thus forming a "sandwich" system containing the layers of propellant, liner and rubber (Marsh, 1970; Sutton and Bilblarz, 1986; Rezende, 2001).

The term bondline is referred here to the interfaces of propellant/liner/insulator. The thin layer of liner prevents the separation of the bond system and can also act as a barrier to control the diffusion of mobile species in solid rocket motors (Byrd and Guy, 1985; Gercel et al., 2000).

Most of the solid composite propellant composition contains approximately 15 weight percent of a polymeric resin of hydroxyl terminated polybutadiene (HTPB), 80 weight percent of the solids: ammonium perchlorate (AP) and aluminum powder (Al) and five weight percent of additives as cure agents, burn catalysts, stabilizers, plasticizers and etc. The amount of each ingredient can vary according to the application desired. The concentration of the plasticizers can represent up to 60% of the total additives (Paniker and Ninan, 1997; Bandgar et al., 2001; Folly and Mäder, 2004; Lourenço et al., 2006).

The plasticizers are used to act as a lubricant and to increase the flexibility of the polymeric chains, to improve the rheological properties during processing and to reduce the viscosity of the system. Otherwise, the plasticizer is not chemically bonded and can diffuse between the interfaces of the bondline formed in the "sandwich" system due to its concentration differences. In general, other free species which are not bounded to the matrix, such as burn agent catalysts and cure agent can also diffuse (Pröbster and Schmuker, 1986; Paniker and Ninan, 1997; Belhaneche-Bensemra et al., 2002; Gottlieb and Bar, 2003; Marcilla et al., 2004; Grythe and Hansen, 2007).

During the storage period the propellant suffers a natural process of deterioration defined as aging. The main mechanisms that govern the aging process are the diffusion and oxidation of the polymeric matrix which can occur at room temperature or can be accelerated by the increase of the temperature during storage (Celina et al., 2000; Hocaoğlu et al., 2001; Judge, 2003; Dilsiz and Ünver, 2006).

The diffusion process of the plasticizers can cause degradation of the adhesion in the interfacial layers, change the mechanical properties of the propellant and can affect the performance of the rocket motor (Byrd and Guy, 1985; Pröbster and Schmuker, 1986, Gottlieb and Bar, 2003).

In this work two different types of adhesives are used to bond the propellant to the rubber. The compositions of both liners are based on the HTPB binder. The liner identified as LHNA contains the plasticizer dibutyl phthalate (DBP) in its chemical formulation and is cured with the 2.4-toluene diisocyanate (TDI). The liner identified as LHNT has a higher crosslink density than LHNA due to the addition of a bond promoter, is cured with the isophorone diisocyanate (IPDI) and does not have any plasticizer in its composition.

The purpose of this study is to calculate the diffusion coefficients of the plasticizers in the insulation layer of samples prepared with LHNT and LHNA liners using the mathematical model of Fick. We also report the results of the hardness tests of samples submitted to natural and accelerated aging.

EXPERIMENTAL

The LHNT adhesive was developed in the Chemistry Division of the Institute of Aeronautics and Space (IAE). The bond promoter trimethylaziridinylphosphine oxide (MAPO) was used to increase the crosslink density of this liner to prevent the diffusion of the mobile species between the insulation and propellant and vice versa (Gercel et al., 2000).

The plasticizers dioctyl azelate (DOZ), dioctyl phthalate (DOP) and dibutyl phthalate are, respectively, present in the composition of the propellant, rubber and liner. The determination of the diffusion coefficients of this species in the insulation layer of samples prepared with the LHNT and LHNA was executed by a computer program based on Fick's second law. The software, developed for this work, used the concentration data from chromatographic analyses obtained up to 31 days after the curing period from samples aged at 80°C.

This interval was established based on previous observations carried out with samples aged at 50ºC, at which time the results obtained showed that the diffusion process reached the equilibrium at approximately 50 days after the curing period. Moreover, the softening of the propellant near to the interface was also verified. Then, based on previous observations the hardness tests were performed on different regions of the propellant to confirm the occurrence of the softening.

The diffusion phenomenon on propellant/liner/insulation rubber layers occurs due to the concentration differences between these regions. The diffusion system can be described by Fick's second law of diffusion (Crank, 1957), represented by the following equation

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{1}$$

Considering the diffusion in one direction *z* of a plane sheet:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} \tag{2}$$

Considering the region $-l < z < l$ of one plane sample with $2l$ of thickness, assuming on (t=0) a constant concentration (C_0) and on the surface area the concentration (C_1). Thus, observing the following conditions:

(a) Initial condition:

to t = 0 and $\forall\ -l < z < l \rightarrow C(l,0) = C_0$

(b) Boundary conditions:

to $t > 0$ and $z = 0 \rightarrow \partial C/\partial z = 0$

And to $t > 0$ and $z = l \rightarrow C(l,t) = C_1$.

Appling the conditions above and using the method of separation of variables and denominating the mass concentrations as ***M*** we obtained the following equation:

$$\frac{M_t}{M_{eq}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp(-D(2n+1)^2 \pi^2 t / 4l^2) \quad (3)$$

Where M_t is the mass concentration on test layer in a period t of time, M_{eq} is the mass concentration at equilibrium and D is the diffusion coefficient.

Equation (3) combined with Minimum Square, Newton Raphson and Gauss elimination methods were used to calculate the diffusion coefficient through the computational program in Fortran language developed for this work (Libardi, 2009).

Sample preparation

Metallic boxes with internal dimensions 130 x 130 x 65 mm (length x height x thickness) were used to prepare the samples. Firstly, the insulation rubber (NB7113) was placed into the box and, in sequence, an adhesive liner (LHNA), was applied over its surface. In the next stage, the box was filled with the propellant forming the interfaces of interest to this work and was submitted to the curing process at 50°C for seven days. The same procedure was executed for samples prepared with the LHNT liner. The sample block formed is shown in Fig. 1. The insulating layer is formed by both layers of rubber and liner. The HTPB-based propellant is cured with isophorone diisocyanate (IPDI) and its composition contains 84 weight percent of solids (aluminum and perchlorate ammonium) immersed in 15 weight percent of HTPB and 3.1 ± 0.04 weight percent of the plasticizer DOZ. The rubber contains 6.9 ± 0.13 weight percent of DOP and the liner 1.3 ± 0.03 weight percent of DBP.

Plasticizer extraction

Immediately, at the end of the curing process the block of the sample containing the layers of propellant/liner/rubber was removed from the metallic box. The sample was sliced into six pieces of 10 mm thickness each one, as Figure 2 shows, and aged at 80°C for 31 days. On days 1, 3, 7, 12, 20 and 31 one slice was removed from the oven and cooled up to room temperature, which in this work is referred to as the range of temperature between 24 and 27ºC. Then, the insulating layer (rubber and liner) were separated from the propellant. In sequence, this layer was fragmented into small squared pieces of approximately 5 x 5 mm in dimension. From these portions, 1g of the material was separated and transferred to the filter paper. In next step, this paper was placed into the Soxhlet extractor and filled with 150 mL of ethyl acetate. The process of extraction was carried out at 75ºC for 16 hours. The whole process was achieved in triplicate and for each replicate were executed ten extractions.

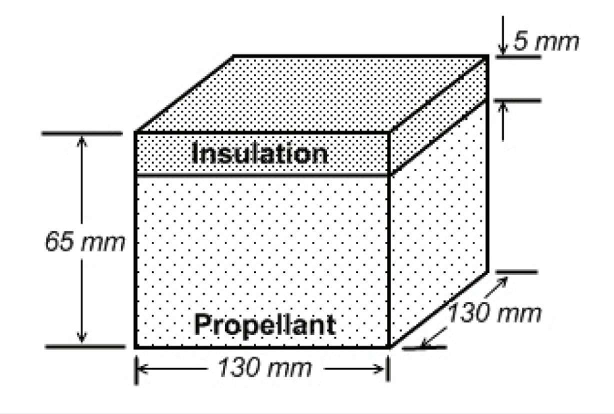

Figure 1: Dimensions of the block of the propellant sample containing the propellant and insulation (rubber and liner) layers.

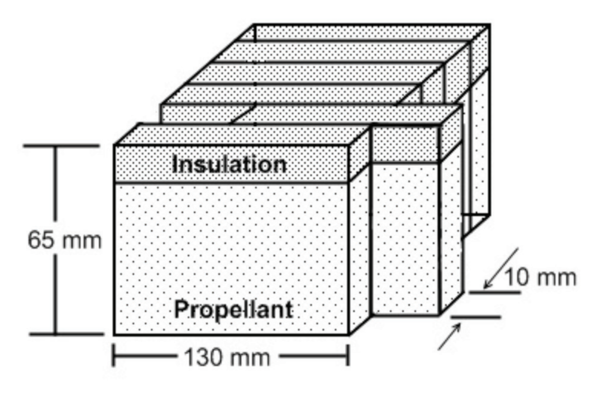

Figure 2: Scheme of the partition of the block of propellant sample.

After the extraction the chromatographic analysis was conducted to determine the plasticizer mass concentration.

Gas Chromatograph

The chromatographic analyzes were performed using a Varian Gas Chromatograph (CG) with an ionization flame detector and a Finningan Mass Spectroscopy (MS). The column utilized was a DB5 (5% phenyl methyl silicon) with diameter of 0.25 mm, 0.25 μm of porosity and 30 m in length. To execute the analyses, 1mL/min flow rate of nitrogen was used and 1μL of the sample was injected.

Shore A Hardness

The hardness tests were executed simultaneously in two identical groups of samples. One group was aged at 80ºC in commercial air-circulating oven with controlled temperature (± 1ºC) under ambient atmospheric conditions (~712 mm Hg). The other group was aged at room temperature (24 – 27ºC). The samples were not submitted to moisture control. On days 20, 27, 40 and 54 after the curing period, both groups were submitted to the *Shore A* analyzes.

The indentations were performed in three different regions of the propellant as shown in Figure 3. These regions were designated as R1, R2 and R3, and are located at 3 mm, 25 mm and 55 mm, respectively, measured from the composite interface with the liner.

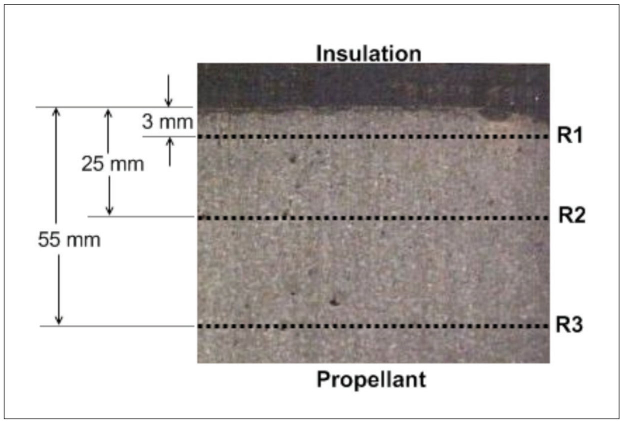

Figure 3: Image of the propellant (gray layer) and the insulation (black layer). The dotted line indicates the regions R1, R2 and R3 submitted to the hardness tests.

A durometer with Shore A digital scale was used according to ASTM D 2240 – 05 (1995). Five indentations were executed in order to have consistent results

RESULTS AND DISCUSSIONS

Figures 4 and 5 shows the mass concentration data versus time of the plasticizer DOZ, DOP and DBP obtained by chromatographic analyses in the insulating layer at 80ºC.

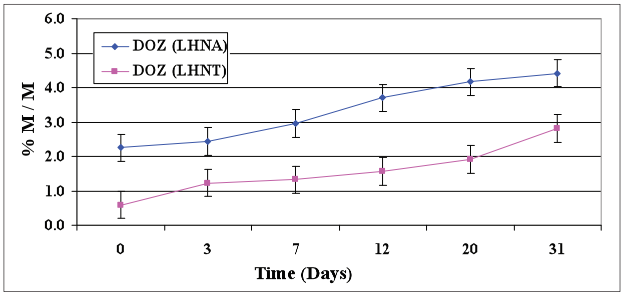

Figure 4: DOZ mass concentration vs time at 80°C on the insulating layer for the samples prepared with the LHNA and LHNT.

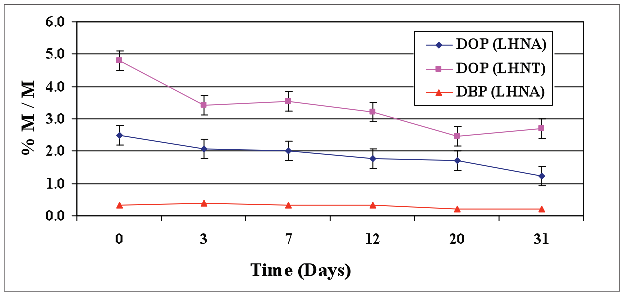

Figure 5: DOP and DBP mass concentration vs time at 80°C on the insulating layer for the sample prepared with the LHNA and LHNT.

Figure 4 shows that the DOZ plasticizer diffused from the propellant into the insulation layer. Otherwise, the DOP and DBP exhibited opposite behavior (Fig. 5) since they diffused from insulating to propellant. The values found for all plasticizers in the first period (end of the cure) analyzed indicate that the diffusion of these species occurred during the cure of the propellant. The mass concentrations of the plasticizers determined in the samples prepared with the LHNT liner are smaller than the concentrations of the plasticizers determined in the samples prepared with the LHNA liner, as can be seen in both Figures 4 and 5. These results suggest the LHNT liner acts as a barrier against the diffusion of the plasticizers.

The diffusion coefficients of the plasticizers DOZ, DOP and DBP calculated by Fick's mathematical model are exhibited in Tab.1. The values were determined from the concentration data obtained from the gas chromatographic analyses executed in the insulating layer of the samples aged up to 31 days after the curing period at 80ºC and prepared with both liners LHNA and LNHT.

Table 1: Diffusion coefficients of DOP, DOZ and DBP determined on the insulating layer at 80ºC.

Liner	**Diffusion coefficient *D x* 10^7 (cm^2/s)**		
	DOP	**DOZ**	**DBP**
LHNA	1.54	2.01	0.456
LHNT	0.603	0.703	-

As observed in Table 1, the diffusion coefficient of the plasticizer DOZ on the insulating layer obtained from the samples prepared with the LHNT liner is lower than the coefficient obtained from the samples prepared with the LHNA liner in the same region. Firstly, this result shows that the DOZ diffused from the propellant into the rubber due to the concentration differences. The lower coefficient can be explained by the higher crosslink density of the liner LNHT that caused the reduction of the free volume between its molecules, thus diminishing the displacement of the plasticizers across the interface and consequently its diffusion coefficient.

It can be also observed in Table 1 that the diffusion coefficient of the DOP obtained with the samples prepared with the LHNT liner is lower than the coefficient obtained with the samples prepared with the LHNA liner. In this case, the DOP is originally present in the composition of the rubber and the barrier effect of the LHNT, due to its higher crosslinking density, prevented its diffusion into the propellant layer more effectively than the LHNA liner, as confirmed by the coefficients found. The plasticizer DBP is only present in the composition of the LHNA liner and its diffusion coefficient is lower than the DOZ and DOP on the insulating layer.

The experimental and simulated curves of diffusion of the DOZ, DOP and DBP are exhibited in Fig. 6 - 10. From these figures it is possible to verify good agreement between the theoretical and experimental curves, which validates the mathematical model of Fick applied to this study (Gottlieb and Bar, 2003).

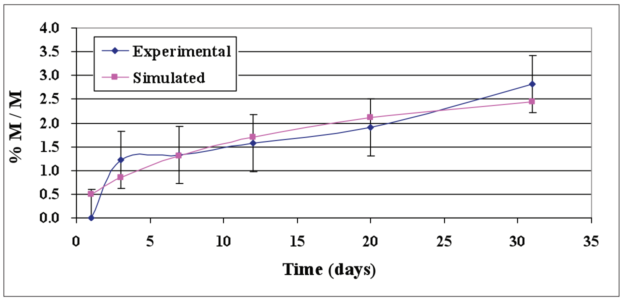

Figure 6: Experimental and simulated diffusion curves vs time for DOZ on the insulating layer at 80°C (LHNT).

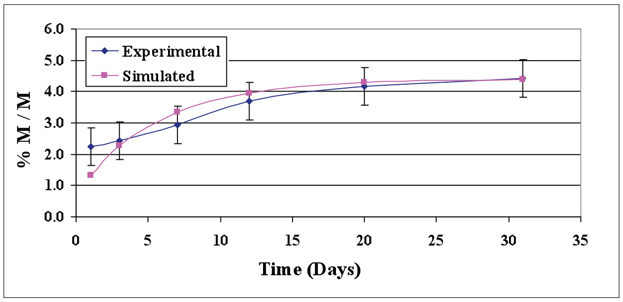

Figure 7: Experimental and simulated diffusion curves vs time for DOZ on the insulating layer at 80°C (LHNA).

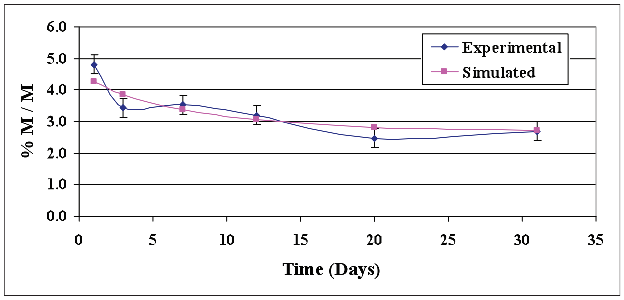

Figure 8: Experimental and simulated diffusion curves vs time for DOP on the insulating layer at 80°C (LHNT).

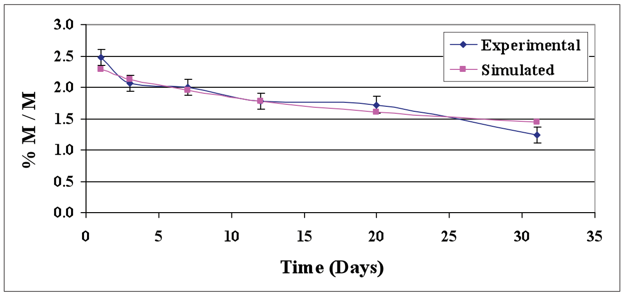

Figure 9: Experimental and simulated diffusion curves vs time for DOP on the insulating layer at 80°C (LHNA).

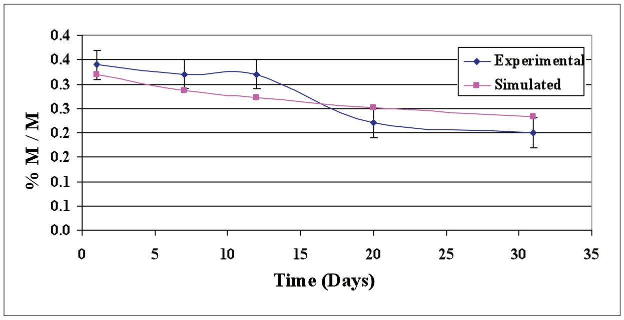

Figure 10: Experimental and simulated diffusion curves vs time for DBP on the insulating layer at 80°C (LHNA).

The curves in Fig 11 and 12 were build from the results obtained of the indentations executed in regions R1, R2 and R3 of the propellant layer located, respectively, at 3 mm, 25 mm and 55 mm measured from an interfacial layer.

The results of the hardness analyses of the samples aged at room temperature are exhibited in Fig. 11 where is possible to verify an increase trend of the hardness with aging period for the three regions analyzed. The loss of the plasticizer to the insulation layer due to the process of diffusion predominantly causes the hardening of the propellant and influences the layer adhesion (Hocauğlu et al., 2001). The hardening of the HTPB based propellants during aging was attributed by Celina et al. (2000) as a consequence of an oxidative crosslinking of the binder due to considerable unsaturation in the polymer structure and easy access of atmospheric oxygen.

It is also possible to observe in Fig. 11 that the values of the hardness determined in the regions R2 and R3 are both similar and higher than the values found in the region R1. The lower values in this region indicate the softening in the first 3 mm of the propellant. According to Byrd and Guy (1985), the diffusion of various substances can interfere with the propellant cure, producing a soft layer, hence resulting in a weak bond. The cure agent itself may diffuse out of the propellant before the crosslinking is complete. This phenomenon usually occurs within the first 5 mm of the propellant.

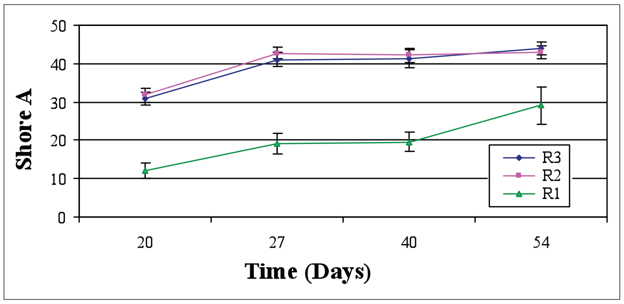

Figure 11: Hardness Shore A versus time for different regions of the propellant determined at room temperature.

The results of the hardness analyses of the samples aged at 80ºC are exhibited in Fig. 12. In this condition, lower values of the hardness in the region nearest to the interface than the values determined in the regions R2 and R3 were also found.

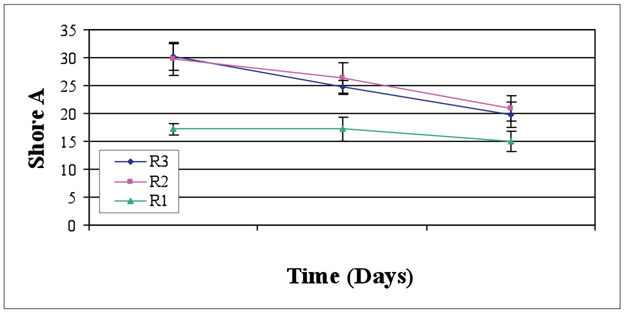

Figure 12: Hardness Shore A versus time for different regions of the propellant at 80°C.

The decreasing trend of the hardness in all extension of the sample at higher temperatures (Fig. 12) was not expected since the polymeric matrix was already formed in the period analyzed and its natural trend is to suffer hardening due to the loss of plasticizer and due to the oxidation process (Celina et al.,2000; Dilsiz and Ünver, 2006).

According to Kishore (1984) the moisture can reduce the tensile strength and the hardness of the propellant. Also according to Iqbal and Liang (2006) the water molecules do not react with the ingredients of the HTPB based propellant, however, at higher temperature the interaction between the polymer and the solid particles can degrade its mechanical properties.

The plasticizer diffusion in the bondline was observed in this work, which might explain the changes in the hardness at room temperature but it seems that at a higher temperature the effect of the moisture is more significant. In order to better understand this behavior, more specific studies are necessary.

CONCLUSION

The mathematical model of Fick applied in this work calculated the diffusion coefficients of the DOZ, DOP and DBP plasticizers with success. According to the concentration data it is possible to conclude that the diffusion process begins at the early stages of curing. The agreement between the simulated and experimental values validates this model.

The barrier effect of the LHNT liner, due to its higher crosslink density, was confirmed by the results of the diffusion coefficients of the plasticizers on the insulating layer.

The results of the hardness tests carried out with samples aged at room temperature and at 80ºC showed the softening of the propellant on the layer located at 3 mm from the bondline. During the aging an increasing trend of the hardness for the samples aged at room temperature and for the samples aged at 80ºC was observed and an opposite behavior was verified. The changes can cause damages mainly to the bondline, thereby affecting the performance and security of the rocket motor.

ACKNOWLEDGMENTS

The authors acknowledge the Brazilian Agency CNPq for financial support and the Division of Chemistry of the Institute of Aeronautics and Space (IAE).

REFERENCES

American Society For Testing And Materials, 1995, ASTM D 2240 - 05: “Standard Test Method for Rubber Property: Durometer Hardness,1-13 p.

Byrd, J. D., Guy, C. A., 1985, “Destructive Effects of Diffusing Species in Propellant Bond Systems”, Proceedings of AIAA/SAE/ASME/ASEE- 21st Joint Propulsion Conference, Monterey, July, pp.1438.

Bandgar, B. M., Krishnamurthy, V. N., Mukudan, T., Sharma, K. C., 2001, " Mathematical Modeling of Rheological Properties of Hydroxyl-Terminated Polybutadiene Binder and Dioctyl Adipate Plasticizer", Journal of Applied Polymer Science, Vol.85, pp. 1002-1007.

Belhaneche-Bensemra, N., Seddam C., Ouahmed S., 2002, "Study of the Migration of Additivies from Plasticized PVC", Macromol. Symp. Vol. 180, pp. 191-201.

Crank, J., 1957, "Mathematics in Diffusion", Claredon, Oxforf, 85 p.

Celina, M., Graham, A. C., Gillen, K, T., Assink, R, A., Minier, L. M., 2000, "Thermal Degradation Studies of a Polyurethane Propellant Binder", Rubber Chemistry and Technology, Vol.73, pp. 779-797.

Dilsiz, N., Ünver, A., 2006, "Characterization Studies on Aging Properties of Acetyl Ferrocene Containing HTPB-Based Elastomers", Journal of Polymer Science, Vol. 101, pp. 2538-2545.

Folly, P., Mäder, P., 2004, "Propellant Chemistry", Chimia, Vol. 58, pp.374-382.

Gercel, B. O., Üner, D.O., Pekel, F., Özkar, S., 2001, "Improved Adhesive Properties and Bonding Performance of HTPB-Based Polyurethane Elastomer by Using Aziridine Type Bond Promoter" J. of Applied Polymer Science, Vol. 80, pp. 806-814.

Grythe, K. F., Hansen, F. K., 2007, "Diffusion Rates and the Role of Diffusion in Solid Rocket Motor Adhesion", Journal of Applied Polymer Science, Vol. 103, pp. 1529-1538.

Gottlieb, L., Bar, S., 2003, "Analyzes of DOA Migration in HTPB/AP Composite Propellants", Propellants, Explosives, Pyrotechnics, Vol.28, pp.12-17.

Haska, S. B., Bayramli, E., Pekel, F., Özkar, S., 1998, "Mechanical Properties of HTPB-IPDI-Based Elastomers", J. Appl. Polym. Sci., Vol. 64, pp.2347-2354.

Kishore, K., Pai Verneker, V. R., Varghese, G., 1984, "DTA Studies on the Thermal Oxidation and Crosslinking Reactions of Carboxyl-Terminated Polybutadiene", Polymer Science, Vol. 22, pp. 1481-1486.

Hocaoğlu, Ö., Özbelge, T., Pekel, F., Özkar, S., 2001, "Aging of HTPB/AP-Based Composite Solid Propellants, Depending on the NCO/OH and Triol/Diol Ratios, Vol. 79, pp. 959-964.

Iqbal, M. M., Liang, W., 2006, "Modeling the Moisture Effects of Solid Ingredients on Composite Propellant Properties", Aerospace Science Technology, Vol.10, pp. 695-699.

Judge, M. D., 2004, "The Application of Near-Infrared Spectroscopy for the Quality Control Analysis of Rocket Propellant Fuel Pre-Mixes", Talanta, Vol. 62, pp. 675-679.

Libardi, J., 2009, "Estudo do Fenômeno de Difusão de Plastificantes em Propelente Compósito Sólido à base de Polibutadieno Hidroxilado Utilizado em Motores Foguete" Tese Doutorado, Universidade Estadual de Campinas, S.P., Brazil, 45p.

Lourenço, V. L., et al., 2006, "Determinação da Distribuição de Funcionalidade de HTPB e Verificação de sua Influência no Comportamento Mecânico de Poliuretano Utilizado em Motor-Foguete", Polímeros, Vol.16, No.1, pp. 66-70.

Marsh JR, H. E.,1970, " Polymers in Space Research", Ed. Marcel Dekker, New York, 365 p.

Marcilla, A., García, A., García-Quesada, J. C., 2004, "Study of the migation of PVC plasticizers", J. Anal. Appl. Pyrolysis, Vol. 71, pp. 457-463.

Paniker, S. S., Ninan, K. N., 1997, "Influence of Molecular Weight on the Thermal Decomposition of Hydroxyl-Terminated Polybutadiene", Termochimica Acta, Vol.290, pp.191-197.

Pröbster, M., Schmucker, R. M., 1986, "Ballistic Anomalies in Solid Rocket Motors Due to Migration Effects", Acta Astronautica, Vol. 13, pp.599-605.

Rezende, L. C., 2001, "Envelhecimento de Propelente Compósito à Base de Polibutadieno Hidroxilado", Tese Doutorado, Universidade Estadual de Campinas, S.P., Brazil, pp. 3-8.

Sutton,G. P., Biblarz, O., 1986, "Rocket Propulsion Elements", Ed. John Wiley, New York, 231 p.