Thermal Degradation of Natural Rubber Male Condoms

Maria Cristina Bó,[*1] Léa Lopes,[2] Leila Lea Yuan Visconte,[2] Regina Célia Reis Nunes[2]*

Summary: Condoms play an important role in the prevention of human immunodeficiency virus transmission. The prediction of condom shelf life became a high priority for the international and national committees responsible for the standardization of the quality of the product. In this work, two sets of batches of natural rubber condoms from three manufactures were compared to investigate the effect of the total sulphur, in their formulations, on the thermal degradation of the products. One set was manufactured in 1999–2000, and the other was manufactured in 2004–2005. The techniques used were differential scanning calorimetry (DSC) and thermogravimetry (TGA) in different atmospheres, as well as elemental analysis in the determination of the total sulphur present in the condoms. The results show that the profile of the thermal behavior is very similar to all condoms. No clear correlation between the amount of sulphur in the formulations and the thermal behavior of the products was found. This study intended to contribute to the development of a method for predicting shelf life of natural rubber male condoms.

Keywords: condoms; degradation; DSC; natural rubber; TGA/DTGA

Introduction

Natural rubber (NR) male condoms have played a decisive role in human immunodeficiency virus (HIV) prevention efforts in many countries.[1,2] An increasing number of programmes is distributing condoms for the prevention of sexually transmitted infections, including adquired immune deficiency syndrome (AIDS).[3,4]

The development of the international standard on condoms, and the knowledge that the condom was a life saving device pressured manufacturers and regulatory authorities to take much greater interest in the quality of the product. The shelf life claimed by manufacturers is generally five years, but in some tropical climates local regulations limit it to 3 years. Currently there is no method that predicts the shelf life of condoms. Generally, standards and specifications for condoms relied on the properties at the time of manufacture, plus a short period of oven conditioning, as the means of determining quality. Early condom standards used arbitrary periods of oven-conditioning at 70 °C as means of implicitly predicting shelf life. Eventually, ISO TC 157 included some requirements of shelf life in ISO 4074:2002,[5] but none of the predictive tests suggested in that standard has been shown to work adequately. ISO 4074:2002 places requirements on manufacturers if they make "significant" changes to the formulation, manufacturing process and individual sealed containers. But it is very difficult for purchasers and regulatory authorities to detect and control modifications to the condom design, and to decide what is significant and what is not.

It became clear, particularly in connection with United States Agency for International Development and other non-profit

[1] Instituto Nacional de Tecnologia, INT, Av. Venezuela 82, Caís do Porto, 20081-312 Rio de Janeiro, RJ, Brazil
Fax: (+55) 21 2123-1224
E-mail: crisbo@int.gov.br
[2] Instituto de Macromoléculas Professora Eloisa Mano, IMA - Universidade Federal do Rio de Janeiro, Brazil

supplies to Africa, that condoms being distributed there did not always meet the requirements of the standards to which they were supposed to be manufactured. Approximately 2 billion condoms are distributed by non-profit organizations each year, largely as a means of limiting the spread of HIV.[6] The distribution pipelines are long and complex, involving sea voyages through the tropics, storage on open wharves, truck transport and storage in sub-optimal warehouses. It can take several years from the time of manufacture for a condom to reach the end user.

The failure of the condom to work at the time of use has a double impact[7]. First, it may cause someone to be infected with a deadly disease, and second, if that happens, then the reputation of the method will suffer, and people will be less inclined to use condoms, thus further increasing the rate of disease transmission. It is therefore a major public health goal to make available reliable condoms to those who would benefit from their use. So, the need for a reliable indicator for shelf life is great. In order to achieve this, it is necessary to be able to predict how long a particular brand of condom will last under the conditions it encounters in distribution and storage, so that the shelf life can be correctly marked, the storage conditions can be managed as best possible, and the distribution chain can be set up to minimize risk to the quality.

Natural rubber, *cis*-1,4-polyisoprene, obtained from *Hevea brasiliensis* has long been known as an excellent elastomer with wide applications. However one of the limitations of NR is its low resistance to ageing. The high level of unsaturated bonds in natural rubber molecules makes it very susceptible oxidative degradation. Several agents like radiation, heating, ozone, weathering and mechanical strain accelerate the oxidation process.[8,9] Frequently, the products are exposed simultaneously to different conditions in storage, generating a complex structure, as a consequence of different mechanisms of degradation, involving chain-scission (depolymerization) and cross-linkage formation (recombination). It is also possible that the existing cross-links may break and a more stable type of cross-link can be formed. It can be considered that chain-scissions lead to a decrease in viscosity, while cross-linking increases the material rigidity, resulting in the formation of micro-cracks in the products due to a combination of the phenomena.[10,11]

Thermal analysis techniques such as differential scanning calorimetry (DSC), thermogravimetry (TGA) and derivative thermogravimetric (DTGA) can provide information about the nature and extent of degradation of materials.[12] In this study those techniques were used to investigate the effect of the total sulphur, in the formulations of the condoms, on the thermal degradation of the products.

Experimental

Two sets of batches of natural rubber condoms from three manufactures were used. The first set was manufactured in 2004–2005 were coded as $\mathbf{A_0}$, $\mathbf{E_0}$, $\mathbf{F_0}$. The second was manufactured in 1999–2000, coded as $\mathbf{A_5}$, $\mathbf{E_5}$, $\mathbf{F_5}$. Those condoms were stored during five years under typical local conditions in Rio de Janeiro, Brazil. The formulation and process of production of samples from the same manufacturer were reported to be the same. The condoms were parallel sided, naturally coloured condoms with a width of approximately 52 mm, packed in aluminium-foil laminates and lubricated with silicone oil. All lots complied with prevailing international standard - ISO 4074 - Natural latex rubber condoms – requirements and test methods.[5]

During the period of storage, the temperature was monitored 3 times a day. The mean storage temperature was 27 °C, with extremes of 17 °C in winter and 42 °C in summer. For all analyses the lubricant was removed from the condoms with isopropan2ol before testing.

DSC measurements were obtained in a thermal analyser TA Instruments MDSC 2920. The samples weighed about 11 ± 2 mg and scanned from -100 °C to 400 °C, at a heating rate of 10 °C min^{-1}, under a nitrogen atmosphere.

TGA/DTGA curves were carried out using a thermogravimetric analyser Shimadzu TGA-51, with vertical geometry. Samples weighing about 12 ± 2 mg were scanned from 10–700 °C at a heating rate of 10 °C min^{-1}. The analysis was done in three atmospheres: nitrogen, air and oxygen.

The total sulphur content in the samples was determined in accordance to ASTM D 4239,[13] Method C. The relative precision of this method for the determination of total sulphur covers the concentration range from 0.5 to 6.0%. It was used an elemental analyzer LECO SC 32, with sensitivity of 0,001 percent. This analysis was done in duplicate.

Results and Discussion

The glass transition temperature (T_g) was taken as the midpoint of the step in the DSC trace. DSC scans (Table 1) showed T_g values for all samples in the range of −68 °C to −64 °C. Those results are in accordance with is expected for vulcanized natural rubber.[14–16]

Taking in account the equipment error (±2 °C), there is no difference between the T_g results for condoms from the same brand, suggesting that the T_g measured from the DSC technique did not detect modifications in the polymer structures. It is well known that the ageing of vulcanized natural rubber at environmental temperature occurs mainly through oxidative reactions in the unsaturated bonds of the polyisoprene polymeric skeleton.[17,18] Silicone lubricant, impermeable packaging, and inclusion of antioxidants in the condoms formulations can prevent or minimize aerobic breakdown of latex condoms.[19]

Table 1.
T_g values.

Condom	A_0	A_5	E_0	E_5	F_0	F_5
T_g (°C)	−66.6	−68.4	−65.2	−64.7	−64.1	−65.3

The thermogravimetry study was done in three atmospheres – nitrogen, air and oxygen. TGA in nitrogen shows the same profile for all condoms, independent of storage time and brands. Figure 1(a) illustrates a typical DTGA for condoms (**A_0** and **A_5**) and Figure 1(b) shows the mass loss for different brands of condoms, and same time of storage (**A_5**, **E_5**, **F_5**). The curves are similar for all condoms and they overlap.

Table 2 presents the initial degradation temperature (onset), the mass loss and the amount of residue for each sample, obtained from the mass loss curves and the maximum temperature peak, from the DTGA curves.

The results obtained were in accordance with the literature.[20–24] Natural rubber degradation, in N_2, occurs in the region between 250–450 °C, in one stage, where the mass loss and volatilization of degradation products take place rapidly. It was also observed that time storage and differences in formulations are not significant variables for measuring the mass loss versus temperature, in nitrogen. At temperatures lower than 250 °C and in the absence of oxygen, NR remains practically stable and no loss in mass is observed.[22] Nevertheless, ingredients present in the vulcanized natural rubber, as accelerators, antioxidants, zinc oxide, stearic acid, among others, begin to degrade below 200 °C.[20] In general, the TGA results of natural rubber condoms do not show any loss until 250 °C, because the additives in the dispersion are present in very small quantities - less than 9% of the formulation. The dispersion consists of colloidal sulphur (as vulcanizing agent); zinc oxide (as vulcanizing activator); one or more accelerators; one or more stabilizers, antioxidants, dispersant, and a pigment, if the condoms are to be colored. Other additives can be used depending on the manufacturer.[25]

The type of vulcanization system for condom production is a conventional one, where the amount of sulfur is higher than the quantity of accelerators. Depending on the formulation the level of sulphur can

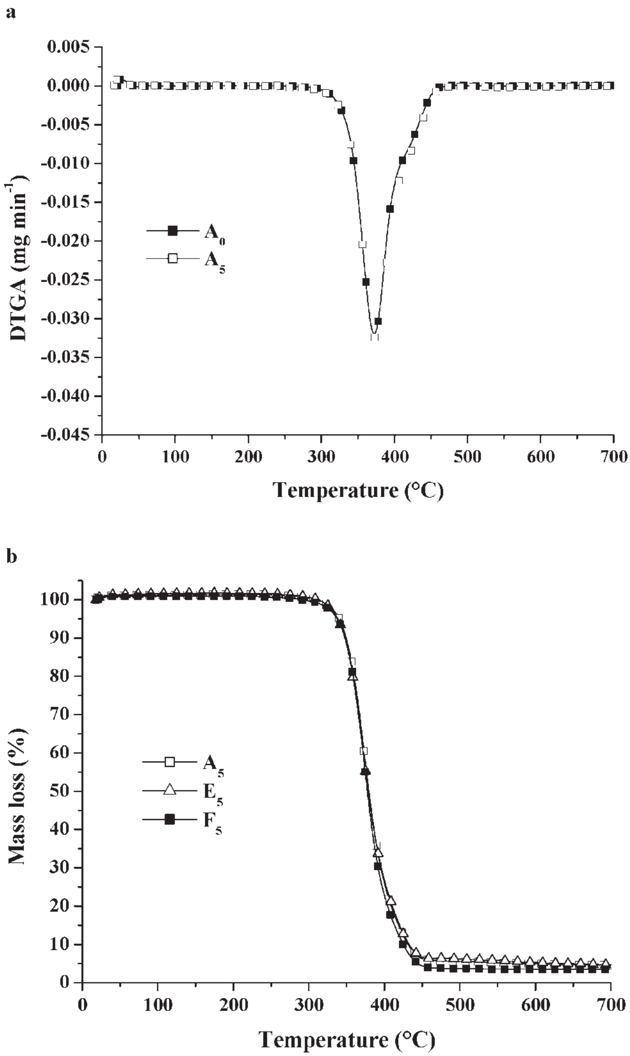

Figure 1.
In N_2, 10 °C min^{-1}: (a) DTGA $\mathbf{A_0}$, $\mathbf{A_5}$, (b) TGA $\mathbf{A_5}$, $\mathbf{E_5}$, $\mathbf{F_5}$.

vary between 0.5 to 2.0%. The typical bridging structures found are complex, containing a mixture of inter- and intramolecular cross-links, as monosulfide, disulfide and polysulfide, parallel vicinal, cross-links attached to common or adjacent carbon atoms, intra-chain cyclic monosulfide and others.[26,27]

Table 2.
TGA in nitrogen, at 10 °C min^{-1}.

Condom	Onset (°C)	Peak (°C)	Total mass loss (±1%)	Residue (±1%)
$\mathbf{A_0}$	349.0	372.3	96.2	3.8
$\mathbf{A_5}$	348.5	374.1	96.6	3.4
$\mathbf{E_0}$	349.9	373.6	97.7	2.3
$\mathbf{E_5}$	348.5	372.0	97.1	2.9
$\mathbf{F_0}$	349.9	374.4	97.8	2.6
$\mathbf{F_5}$	350.0	373.5	97.4	2.7

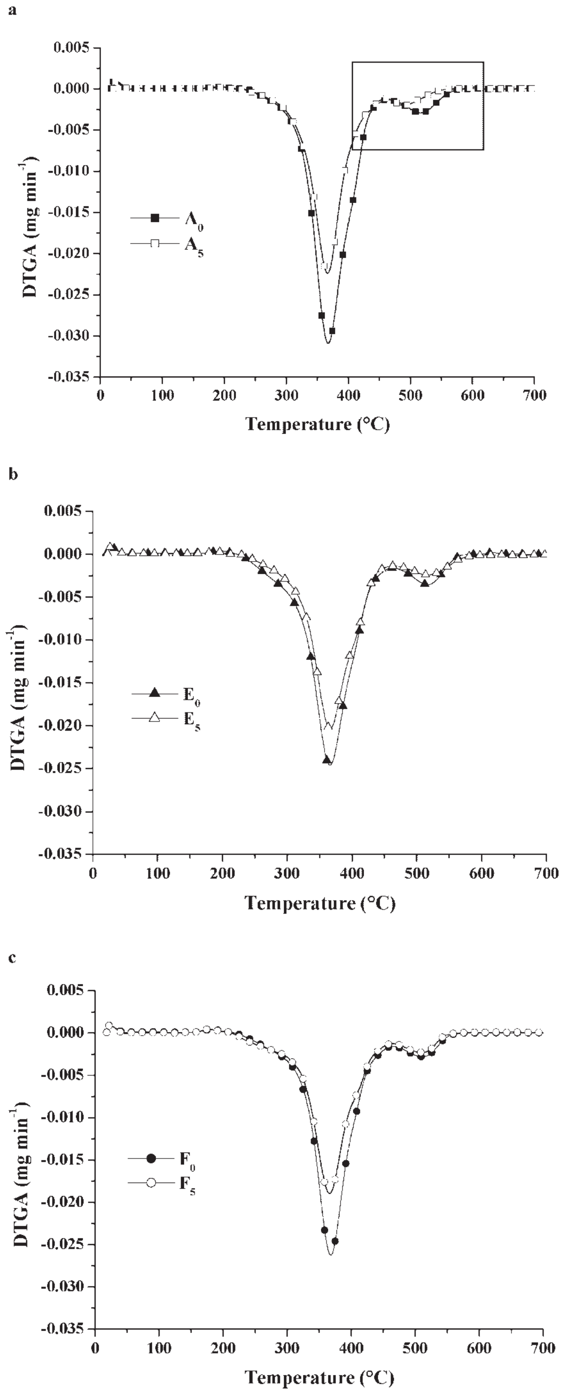

Figure 2.
DTGA in air, 10 °C min^{-1}: (a) $\mathbf{A_0}$, $\mathbf{A_5}$ (b) $\mathbf{E_0}$, $\mathbf{E_5}$ (c) $\mathbf{F_0}$, $\mathbf{F_5}$.

Table 3.
TGA in air, 10 °C min^{-1}.

Condom	First Step			Second step		
	Onset (°C)	Peak (°C)	Total mass loss (±1%)	Onset (°C)	Peak (°C)	Total mass loss (±1%)
A_0	335.0	367.4	89.2	490.1	515.9	7.8
A_5	330.0	366.5	89.9	477.0	489.3	6.8
E_0	324.0	366.2	86.8	489.9	516.4	9.8
E_5	322.0	366.1	88.4	485.0	517.0	10.6
F_0	329.8	368.3	88.2	480.5	510.9	8.4
F_5	325.0	366.4	89.5	480.1	511.6	8.4

TGA results in air shows the degradation of the samples in two stages, the first in the region between 250–450 °C and a second one, weaker, between 450–600 °C. Figure 2 illustrates the DTGA: (a) **A_0**, **A_5** (b) **E_0**, **E_5** (c) **F_0**, **F_5**.

Table 3 shows the onset peak, mass loss and residue of these samples, in atmospheric air for step 1 and 2. The first step in the degradation corresponds to the decomposition of vulcanized natural rubber. For the older samples (**A_5**, **E_5**, **F_5**), the degradation occurs at slight lower temperatures (onsets) than for the newer ones (**A_0**, **E_0**, **F_0**), which can be related to a more labile structure for the older condoms.

In the 2nd step, it is observed an evident difference between **A_0** and **A_5**. As shown in Table 2, the difference in the temperature onsets for those samples is around 13 °C, with the older condom having a lower temperature (477 °C) and the difference between the **A_0** and **A_5** maximum temperature peaks is even larger, almost 27 °C. This difference is signalized in Figure 2(a).

The results obtained in air, in the region 450–600 °C, suggest the occurrence of reactions in the vulcanized system where sub-products are degraded and others are generated. It has been reported that some polysulfide cross-links, at elevated temperatures, transform into sulfenic or thiosulpoxylic acid groups, which prevent autocatalytic thermo-oxidative decomposition.[22,28] The lack of a second step in the degradation in an inert atmosphere indicates the absence of thermally stable intermediate products, as opposed to what happens in the air. The residue at temperatures above 600 °C, normally around 3%, reflects the inorganic yield in the material. This residue amount is larger than the one normally found for synthetic polyisoprene in air[29] but in the case of natural rubber latex condoms, the value reflects the mineral content *in Hevea* dispersions.

Figure 3 shows the DTGA results of the condoms in oxygen. The degradation process is basically in four stages, with the third stage being very difficult to visualize for the older condoms (**A_5**, **E_5**, **F_5**). This difference is highlight with a square in the figure.

The first step occurs between 200–300 °C, with mass loss about 11% for all condoms, probably due the decomposition of small labile molecules. The 2nd, 3rd and 4th stages correspond to the degradation of vulcanized natural rubber. For all condoms the highest amount of mass is degraded in the second and the third step. As already said, for old condoms (**A_5**, **E_5**, **F_5**), the third step is not clear configured. After 450 °C, one peak is clearly observed for all condoms. The mass loss in this step can be related to the degradation of rubber sub-products as monomer (isoprenes), dimmers (dipentene), with other oligomers up to hexamer in significant concentration, as well as cyclized rubber.[30,31]

Table 4 shows the onsets, the peaks and the mass loss for the 2nd, 3rd and 4th steps. As said before, the third stage was very subtle, so its onset could not be calculated; besides the peaks can be visible in the graphs of the derivate. The mass loss on the 3rd stage for the older samples could not be discriminated from the mass loss in the second stage.

The results for elemental analysis for the determination of total sulphur in the

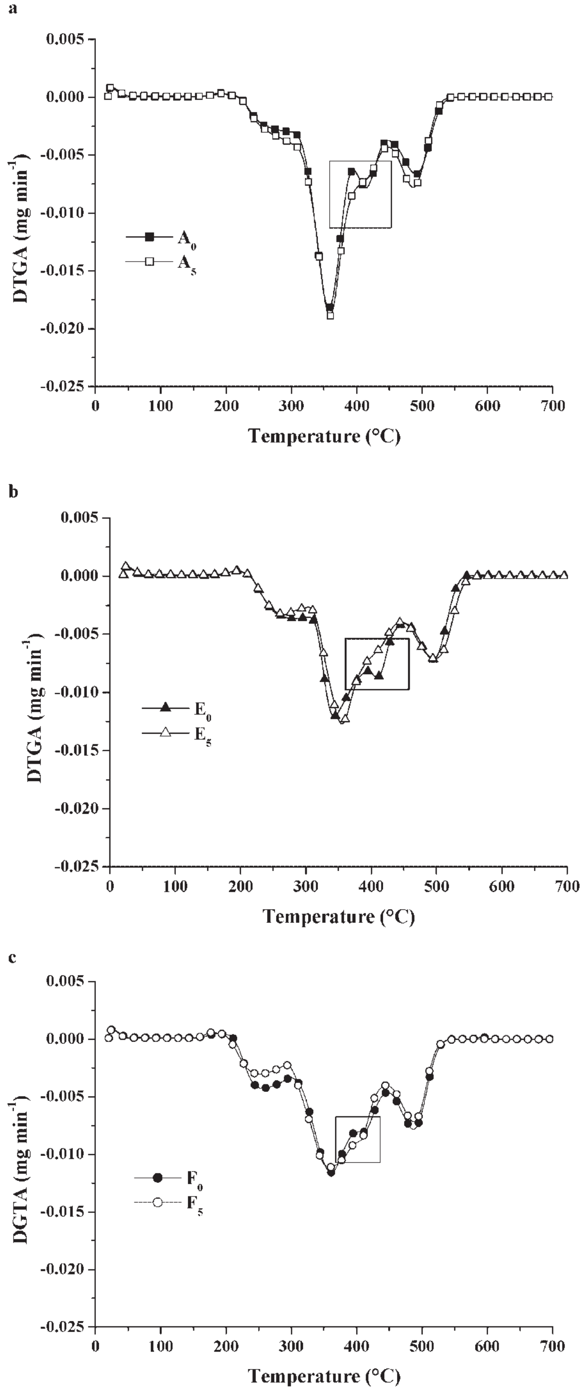

Figure 3.
DTGA, in oxygen, 10 °C min^{-1}: (a) **A_0**, **A_5** (b) **E_0**, **E_5** (c) **F_0**, **F_5**.

Table 4.
TGA in oxygen, 10 °C min^{-1} heating rate.

Condom	Second step			Third step			Fourth step		
	Onset (°C)	Peak (°C)	Mass loss (±1%)	Onset (°C)	Peak (°C)	Mass loss (±1%)	Onset (°C)	Peak (°C)	Mass loss (±1%)
A_0	327.5	357.3	49.3	–	414.2	17.74	464.6	490.6	19.7
A_5	330.7	358.8	64.8*	–	418.3	*	464.8	486.6	19.7
E_0	327.5	343.2	42.5	–	409.0	20.95	470.0	494.4	21.6
E_5	324.8	355.4	58.3*	–	412.9	*	469.8	497.7	27.0
F_0	330.2	360.6	42.5	–	409.2	17.05	465.2	487.0	22.7
F_5	325.1	358.1	65.1*	–	406.6	*	463.2	487.4	21.7

* Mass loss in the 3rd step is included in the mass loss of the 2nd step.

condoms are presented in Table 5. For condoms **A** and **E** were observed that the sulphur content was altered in the formulations at some point during the 5 years. The difference in the total sulphur is quite significant for condoms **A_0** and **A_5**. Currently, manufacturers are able to assume that such changes are minor in terms of the requirements of the international standard, and thus neither report them nor conduct additional shelf life studies on the new formulation. The sulphur content for **F_0** and **F_5** are equivalent.

The relative amount of sulphur and accelerators determine not only the vulcanization process, but also influence the physical, chemical, mechanical and service properties of latex products.[32] The presence of residual sulphur will allow additional vulcanisation to continue until it is used up. The amount of sulphur, from the cross-linking agent and the accelerators, has a fundamental role in the oxidative degradation process of the polyisoprene backbone. The decomposition profile seems to be defined by the presence of polysulfides cross-links, and plays an important role in determining the physical properties of NR.[33,34]

Table 5.
Total sulphur (ASTM D 4239).[13]

Sulphur (% w/w)					
A_0	1.14 ± 0.03	**E_0**	1.16 ± 0.01	**F_0**	0.69 ± 0.03
A_5	0.79 ± 0.02	**E_5**	1.05 ± 0.01	**F_5**	0.71 ± 0.01

Conclusion

The profile of the thermal behavior (DSC and TGA) for all condoms was very similar, undependably of formulations. Some minor difference, for the new and old condoms, in the air and O_2 atmospheres were observed.

The amount of sulphur determined by elemental analysis can be used to show changes in formulation. In this case, it has shown that two out of the three manufacturers had changed the sulphur level in their formulations. The differences in sulphur content identify by elemental analysis were not clear correlated with the thermal behavior.

Acknowledgements: The authors are grateful to PETROFLEX Indústria e Comércio S.A. and Pólo de Xistoquímica, UFRJ.

[1] S. D. Pinkerton, P. R. Abramson, *Soc. Set Med.* **1997**, *44*, 9, 1303.
[2] C. G. Levi, M. A. A. Vitória, *AIDS* **2002**, *16*, 2373.
[3] Ministério da Saúde. Plano Estratégico do Programa Nacional de DST e Aids 2005. Brasília. Available at: www.aids.gov.br/documentos e publicacoes.
[4] World Health Organization, Joint United Nations Programme on HIV/AIDS, United Nations Population Fund. Position statement on condoms and HIV prevention, July 2004. 2p. Available at: http://www.who.int/publications/en.
[5] International Organization for Standardization. **ISO 4074**: Natural latex rubber condoms – requirements and test methods. Switzerland, 2002.
[6] ONUSIDA. Informe sobre la epidemia mundial de SIDA 2006. Available at: www.unaids.org.
[7] M. Steiner, R. Foldesy, D. Cole, E. Carter, *Contraception* **1992**, *46*, 279.

[8] P. Lucas, M. Baba, J. Lacoste, J. L. Gardette, *Polym. Degrad. Stab.* **2002**, *76*, 449.
[9] H. Varghese, S. S. Bhagawan, S. Thomas, *J. Therm. Anal. Ca.* **2001**, *63*, 749.
[10] L. R. Barker, *J. Nat. Rubber Res.* **1990**, *5*, 266.
[11] N. M. Mathew, S. K. De, *Polymer* **1983**, *24*, 1042.
[12] T. Hatakeyama, F. X. Quinn, in: "Thermal Analysis - Fundamentals and Applications to Polymer Science". John Wiley & Sons. England, 1994.
[13] American Society for Testing and Materials. **ASTM D 4239**: Standard test methods for sulphur in the analysis sample of coal and coke using high temperature tube furnace combustion methods. Philadelphia, 2005.
[14] R. J. Andrews, E. A. Grulke, in: "Polymer Handbook", 4^{th} ed., J. Brandrup, E. H. Immergut, Eds., J. Wiley & Sons, New York 1999. p. VI–208.
[15] A. Hoffmann, T. Koch, B. Stühn, *Macromolecules* **1993**, *26*, 7288.
[16] R. F. Boyer, *Macromolecules* **1992**, *25*, 5326.
[17] V. S. Vinod, S. Varghese, B. Kuriakose, *Polym. Degrad. Stab.* **2002**, *75*, 405.
[18] I. R. Goodchild, T. J. Pond, *J. Natural Rubber Res.* **1997**, *12*, 1.
[19] M. J. Free, V. Srisamang, J. Vail, D. Mercer, R. Kotz, D. E. Marlowe, *Contraception* **1996**, *53*, 221.
[20] M. T. Ramesan, *J. React. Funct. Polym.* **2004**, *59*, 267.
[21] A. P. Matheus, S. Packirisamy, S. Thomas, *Polym. Degrad. Stab.* **2001**, *72*, 423.
[22] A. R. R. Menon, C. K. S. Pillai, G. B. Nando, *Polym. Degrad. Stab.* **1996**, *52*, 265.
[23] R. Asaletha, M. G. Kumaran, S. Thomas, *Polym. Degrad. Stab.* **1998**, *61*, 431.
[24] A. K. Sircar, T. G. Lamond, *Rubber Chem. Tech.* **1972**, *45*, 329.
[25] J. Gerofi, in: "Condoms", A. Mindel, BMJ Books, London **2000**.
[26] A. V. Chapman, M. Porter, in: "Chemistry Natural Rubber Science Technology", Robert AD. Sulphur Vulcanization, Hertfordshire: Malaysian Rubber Producers' Research Association, **1990**.
[27] J. A. Brydson, in: "Rubbery Material and Their Compounds". New York, **1985**. p. 70.
[28] L. Slusarski, G. Janowska, *J. Thermal Analysis* **1984**, *29*, 95.
[29] D. D. Jiang, G. F. Levchik, S. V. Levchik, C. Dick, J. J. Liggat, C. E. Snape, C. A. Wilkie, *Polym. Degrad. Stab.* **2000**, *68*, 75.
[30] B. S. T. Boonstra, G. J. Van Amerongen, *Ind. Eng. Chem.* **1949**, *41*: 161.
[31] S. Groves, R. Lehrle, *Eur. Polym. J.* **1992**, *28*: 373.
[32] J. Maret, N. M. Mathew, D. J. Francis, J. Sahayadasan, Kottayam, Cochim, Trivandrum, *KGK* **1999**, *5*: 316.
[33] M. Nasir, G. K. Teh, *Eur. Polym. J.* **1988**, *24*: 733.
[34] E. M. Bevilacqua, *Rub. Chem. Tech.* **1960**, *33*: 51.

