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UNDERSTANDING AND OPTIMIZATION OF LONG TERM AGEING IN CABLE INDUSTRY

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ABSTRACT

In this paper we present an approach to new and improved methods to understand the ageing of polymer materials used in cables in order to be able to better predict their lifetime. EPDM compounds (filled and unfilled) were aged by exposure to gamma radiation. The evolution of the mechanical properties was investigated, the principal reactions in the polymer matrix due to the irradiation elucidated and the influence of the filler on the ageing process was followed. The results are: At low dose of irradiation the EPDM material is cross-linked. At higher doses the material degrades (chain scission).The presence of a filler can strongly influence the evolution of the mechanical behavior after ageing.

KEYWORDS

Ageing, EPDM, cable, irradiation, degradation.

INTRODUCTION

Polymer materials in cables and accessories are exposed to severe environmental conditions. An example would be cables in nuclear power plants where the cables might be exposed to elevated temperatures and gamma irradiation. These conditions are known to cause their ageing and consequently their degradation over the time. Once this degradation has progressed long enough the cable loses the mechanical and/or electrical properties that are required from the customer.

Figure 1: Cables in nuclear power plants may be exposed to irradiation.

The correct choice of polymer materials and additives used for cable insulation and sheath can improve the resistance of the cable against this ageing process. Since many years semi-empirical methods are used in order to predict the lifetime of polymer materials under certain conditions, most often for the ageing at elevated temperatures. In general these methods are based on the well known equation of van't Hoff and Arrhenius:

$$\ln(k) = \frac{-E_a}{R}\frac{1}{T} + \ln(A) \qquad [1]$$

This equation dates back to 1884 and tells us that when a chemical reaction has a rate constant k which obeys the Arrhenius equation, a plot of ln(k) versus T^{-1} gives a straight line (T = temperature). The slope of this line allows to calculate the activation energy E_a of the reaction.

Considering the fact that this equation was developed to describe a simple and well defined chemical reaction it works astonishingly well for complex systems such as polymer compounds where neither the exact chemical degradation reactions are known nor the reaction rate constant k, which in general is approached by the evolution of a mechanical property such as the loss of 50% of elongation at break or something like that.

However in many cases, the Arrhenius equation does not allow to predict the evolution of the degradation of polymer materials as precisely as we want it. Examples are nuclear cables where the ageing of the polymers in the cables is due to elevated temperature and gamma irradiation, and to make things even more complicated where the irradiation dose can vary over a wide range, from the "usual' low level of irradiation to high doses which can occur in case of an incident. In such a complex situation where different degradation mechanisms interfere we need to understand the different chemical reactions, their interaction and in which way different materials used in polymer compounds will accelerate or not these chemical reactions.

Several industrial and academic partners have therefore started a research program for the better understanding of the long term ageing of polymers: the mechanisms of degradation under the influence of irradiation and elevated temperatures, the influence of different materials used in polymer compounds on the ageing process, mathematical models which would allow to calculate the influence of the ageing of polymer materials on their mechanical properties and hence to predict their lifetime.

In this paper we present the first results of this study: the influence of gamma irradiation on the mechanical properties of filled and unfilled EPDM.

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MAIN PART

EFFECTS OF IRRADIATION

It is known that irradiation can cause cross-linking as well as chain scission reactions[1]. Both reactions will have an inverse effect on mechanical properties: additional cross-linking will increase and chain scission will decrease the mechanical strength. The competition between these two reactions is schematised in Figure 2:

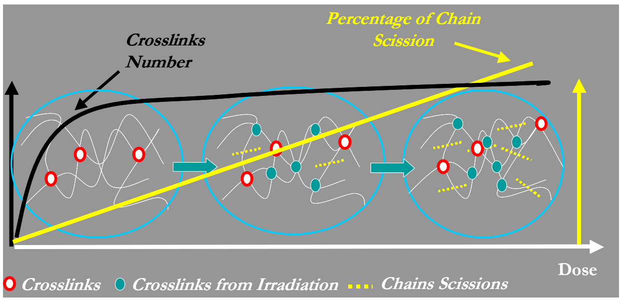

Figure 2: Chain scission and additional cross-linking caused by irradiation of a cross-linked EPDM.

EVOLUTION OF MECHANICAL PROPERTIES

Thus it can be explained that the unfilled and peroxide cross-linked EPDM increases slightly in strain and stress at break after exposure to a low dose of gamma irradiation (50 kGy), but then shows a sharp drop in mechanical properties as the chain scission reaction prevails at higher irradiation doses (Figure 3).

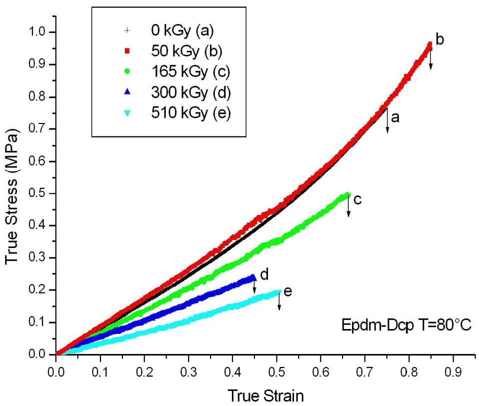

Figure 3: Evolution of mechanical properties of unfilled EPDM (peroxide cross-linked) after irradiation ageing.

Once the EPDM is filled (in this case with 150 phr ATH = Aluminium-tri-hydrate, $Al(OH)_3$), the evolution of the mechanical properties with the dose of gamma irradiation changes dramatically: While the tensile stress at break remains almost constant, the strain at break increases with increasing irradiation dose (Figure 4).

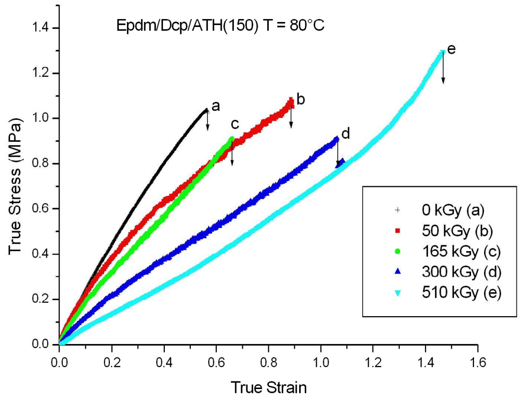

Figure 4: Evolution of mechanical properties of filled EPDM (peroxide cross-linked, filled with 150 phr ATH) after irradiation ageing.

INFLUENCE OF THE FILLER ON AGEING

The results of the evolution of the mechanical properties show that the presence of a filler has an important impact. An intermediary filler concentration (50 phr) was hence tested. A summary of the evolution of the mechanical properties with increasing irradiation dose is shown in Figure 5 (for the tensile stress at break) and in Figure 6 (for the tensile strain at break):

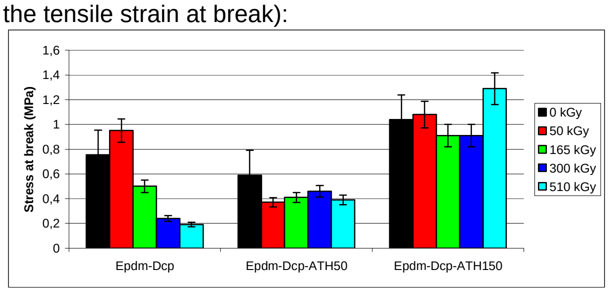

Figure 5: Tensile stress at break (in MPa, at 80°C) after irradiation ageing (50 to 510 kGy) for cross-linked EPDM, unfilled and filled (with 50 and 150 phr ATH).

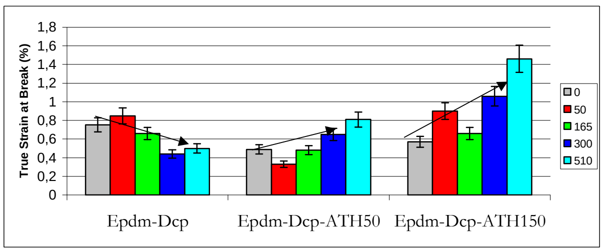

Figure 6: Tensile strain at break (in %, at 80°C) after irradiation ageing (50 to 510 kGy) for cross-linked EPDM, unfilled and filled (with 50 and 150 phr ATH).

The graphs show that already a low concentration of filler (50 phr ATH) changes the evolution of the mechanical properties during ageing if compared to the unfilled material: The elongation (strain) at break shows an increase instead of a decrease during irradiation. The dramatic decrease of the tensile stress at break which appears for the unfilled EPDM is strongly reduced.

POSSIBLE EXPLANATIONS

The filled EPDM represents in fact three distinct zones: the EPDM polymer matrix, the filler (which can be considered as inert to the ageing) and the interface filler/EPDM. The latter one can have a major influence on the mechanical properties of the filled compound, its ageing properties are not well known.
At high filler concentration the particles may come so close to each other that a "filler-network" is created.
Apart from that, the filler can of course also have a catalytic influence on the ageing of the polymer.
To complicate things: the EPDM investigated is semi-crystalline. The crystallinity strongly influences the mechanical properties. Therefore all mechanical tests were done at 80℃ in order to eliminate this factor.

MODELING OF THE AGEING OF EPDM

A first approach has been undertaken to do modeling on the ageing of unfilled EPDM. The number of active chains has been obtained by swelling measures on the samples.
A chain scission has for consequence the disappearance of an active chain and each cross-linking reaction the formation of two active chains. Since for the already peroxide cross-linked EPDM the major reaction is chain scission, we assume that the total density of active chains is:

o $\nu = \nu_0 - A \cdot t$ [2]

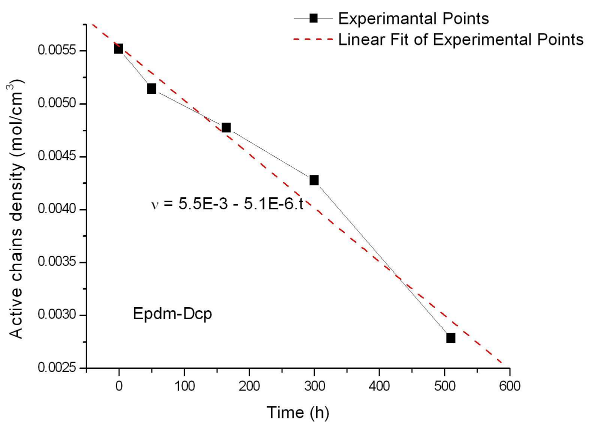

Figure 7: Calculation of the evolution of active chains in cross-linked EPDM during irradiation ageing.

The slope of the curve gives the constant A, allowing the calculation of the disappearance of active chains due to chain scission during irradiation ageing.
The not cross-linked and unfilled EPDM material will be cross-linked by irradiation and at the same time loses active chains due to chain scission. It can be assumed that full cross-linking by irradiation without interference of chain scission would lead to the same maximum density of active chains as observed for the peroxide cross-linked material: ν_0. Hence using the constant A and ν_0 as determined for the peroxide cross-linked material for the determination of the active chain density of initially not cross-linked EPDM gives:

- o Density of active chains formed by cross-linking : $\nu_{cross\text{-}linking} = \nu_0 \cdot (1\text{- } \exp(-t/\tau)^x)$ [3]
- o Density of active chains destroyed by chain scission: $\nu_{Chain\ scission} = - A \cdot t$ [4]
- o Density of all active chains in the material : $\nu = \nu_{cross\text{-}linking} + \nu_{chain\ scission}$ [5]

Using the above formulae the two competing reactions of chain scission and cross-linking in unfilled EPDM can be quantified in terms of the resulting active chains (Figure 8).

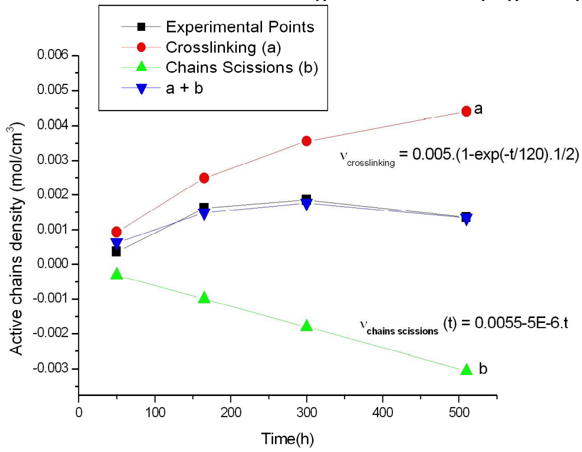

Figure 8: Calculation of the evolution of active chains in not cross-linked and unfilled EPDM during irradiation ageing.

Using the parameters obtained for unfilled EPDM and applying them to filled and cross-linked EPDM results in a curve fit which superposes well with the experimental results when the calculated curve is shifted upwards by adding a coefficient (Figure 9).

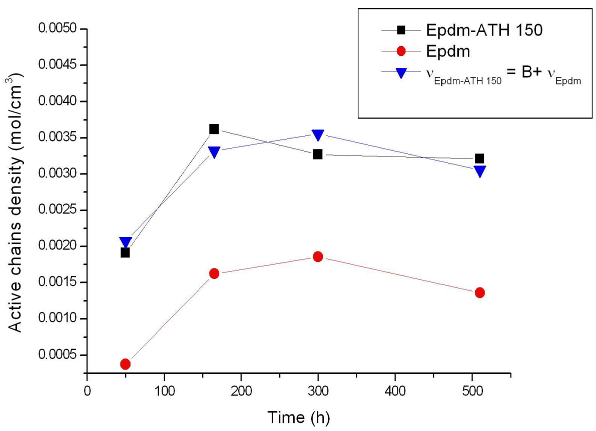

Figure 9: Modelling of the evolution of the number of active chains in filled EPDM during irradiation ageing and comparison with experimental results.

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SUMMARY AND OUTLOOK

The first results of this study show that irradiation of an EPDM causes cross-linking as well as chain scission. The latter reaction prevails at higher irradiation doses and naturally is more important for an already cross-linked material compared to a not cross-linked material.
If the EPDM is filled with ATH in principle the same reactions are observed. The presence of ATH as filler changes dramatically the evolution of the mechanical behaviour during irradiation ageing compared to an unfilled material:

- for the cross-linked but unfilled EPDM the elongation at break and the tensile stress at break decrease with increasing irradiation dose
- a different evolution of the mechanical properties is noted for the cross-linked elastomer filled with ATH: the elongation at break increases with increasing irradiation dose, the tensile stress at break remains almost constant.

First attempts of modelling the ageing based on the calculation of the active chains were successful and are applicable to not cross-linked, cross-linked and filled EPDM.

Two key points which will be investigated in the further study are:

- the role of the interface between the filler and the polymer matrix in the ageing process
- the effects of thermal ageing in comparison to the irradiation ageing

ACKNOWLEDGEMENTS
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GLOSSARY

EPDM: Ethylene Propylene Diene Monomer