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AGEING MONITORING OF PLASTICS USED IN NUCLEAR POWER PLANTS BY DSC

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Abstract

Degradation of polymeric materials used in nuclear power plants (NPP), especially polymeric cable insulation materials, in the course of their service can be monitored by measuring their properties by DSC, mainly oxidative induction time – OIT. The studied materials were in-laboratory aged by applying main stressors that act in NPP – ionising radiation and temperature. The dependence of OIT on radiation and thermal degradation of polymeric material was determined. The OIT values have been compared to elongation at break as a property that directly reflects the functionality of the studied material. The comparison of monitored OIT of real cable samples taken from NPP with dependencies on how the OIT values change with the elongation at break, makes possible to establish the extent of cable degradation. This method can be considered as a suitable and effective technique for lifetime assessment not only of cable insulations but also of many other plastics.

Keywords: cable, differential scanning calorimetry, lifetime, plastics, qualification

Introduction

The plastics used in nuclear power plants (NPP) are exposed to a high number of various deteriorative environmental effects during their operational life. The dominant stressors causing age-related degradation of plastics materials in the presence of oxygen are temperature and radiation dose. The real service conditions usually involve synergistic effects between two or more stressors. For many of the polymers of interest, oxidation is the dominant ageing mechanism and is initiated both thermally and by radiation. The result of oxidation is the embrittlement of materials, increasing the probability of cracking under mechanical stresses [1–3].

To perform the functionality under long-term service conditions, the materials (and the equipment as well) must be qualified. The procedure used for the qualification includes in-laboratory accelerated ageing at enhanced temperatures and dose rates of radiation, which should simulate ageing in long-term service condition. For safety-related cables, their large majority are qualified for 40 years – usually the original licensed term of plants [3–5].

The service ageing of polymeric materials in NPP environment is a complex and long-term process. To simulate this process, a number of approximations as well as

1418–2874/2001/ \$ 5.00 © 2001 Akadémiai Kiadó, Budapest Akadémiai Kiadó, Budapest Kluwer Academic Publishers, Dordrecht large acceleration factors have to be used. This results in the fact, that the predicted service lifetime need not be fully justified. Therefore, an additional subsequent ageing monitoring (on-going qualification) of the selected materials and equipment is now recommended [4, 5].

The principle of on-going qualification is to start repetitive testing after a certain installed time e.g. 10 years, and subsequently demonstrate continued qualification by repeated measurement (monitoring) of the actual state of the material [3–5]. The determination of the actual state of a material is based on measuring a property, which is joined with the equipment (item) functionality and which changes with the advanced degradation. The general method used for plastics consists in measuring their mechanical properties (e.g. elongation at break for cables, compression-test characteristics of sealings, etc.). But all these methods need large samples and they are destructive. Hence, in the NPP containment, where no cutting out of any samples is allowed, such a method is not applicable. If there is not a sample deposit, where the samples age under the same (or as close as possible) conditions as the real samples, a non-destructive method should be used. Among the methods proposed for monitoring of plastics ageing [6], the use of differential scanning calorimetry (DSC) is one of the best solutions. Selected material property determined by DSC is compared to a property, which is directly proportional to the material degradation and its functionality.

Experimental

Instruments

DSC measurements have been evaluated according to the standards [7, 8] by DSC 7 – Perkin Elmer and DSC910/2100TA – DuPont/TA Instruments. For mechanical testing the tensile testing machine INSTRON 4301 has been used. Irradiation has been carried out in ⁶⁰Co gamma ray source. Simulation of thermal ageing has been done in thermal chambers Heraus with forced air circulation.

Electrical cables

Polymeric insulated electrical cables (mainly on the basis of XPE, EPR/EVA, EPR, PVC, etc.) are used to provide instrumentation signals, power or control over virtually all remotely operated power plant equipment. Their replacement due to failure or expiration of qualified life is prohibitively expensive [3]. Hence, the cables should be subjected to the on-going qualification programme to check that real ageing during NPP service has not degraded the insulation systems as much as was predicted by the qualification test. The best method for cable condition monitoring would be the removal of a sample to determine the mechanical properties. Since it is generally not possible, a non-destructive method for cable condition monitoring has to be used. Electrical properties, which demonstrate the cable functionality at best and are non-destructive as well, usually do not change unambiguously with the advanced

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degradation. Therefore, the electrical properties are generally not suitable for cable lifetime assessment [4].

Polymers age predominantly by means of chemical reaction with oxygen. Antioxidants are chemicals added to polymers in order to inhibit oxidative reaction. As long as antioxidants remain in an insulation polymer, the properties of cable insulation do not degrade significantly. Since the OIT is related to the content of antioxidants, it has been chosen as the parameter for monitoring of cable insulation degradation [9, 10]. With the advanced degradation its content decrease and the OIT is shorter. The OIT measurement does not give absolute values. This means that there is no time limit, the exceeding of which would announce that the cable is at the end of its service life and must be changed. Therefore for all cables, which have been subjected to ageing monitoring (and to assessment of rest service lifetime) the OIT values have been correlated to elongation at break.

To assess the lifetime of a particular cable, a correlation curve showing the dependence of OIT *vs.* elongation at break has to be plotted at first. Several samples of the cable materials are subjected to the accelerated ageing, which should simulate different times of ageing under service conditions. The procedure of simulation of ageing is a complicated and long-term process and consists in the simulation of main stressors that act in NPP containment (they are usually radiation, enhanced temperature and accident simulation). This process is, together with the method of calculations, described e.g. in [3, 4, 11]. The elongation at break and OIT are determined with aged samples of both core insulations and cable jacket. The data obtained are used for plotting so-called 'correlation curves' (Figs 1 and 2). It is assumed, that each cable needs its own correlation curve.

The actual state (actual value of elongation at break) of an already installed cable can be now assessed by DSC data (OIT values) coming from the microsamples cut directly in NPP containment, and using correlation curves (Figs 1 and 2). If it is known how the elongation at break changes with the simulated time of NPP operation

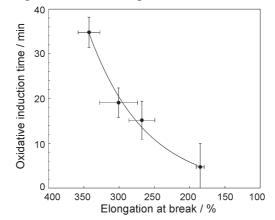


Fig. 1 The OIT as a function of the absolute elongation at break for a PVC based sheath

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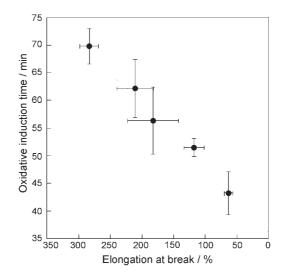


Fig. 2 Dependence of the OIT on the elongation at break for an EPR/EVA cable insulation material

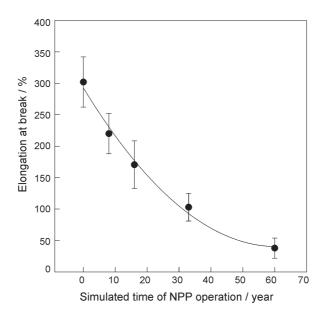


Fig. 3 Dependence of the elongation at break on the simulated service time of a cable material from Fig. 2. It has been simulated the operation temperature 55°C at the dose rate 1 kGy/year

(Fig. 3), then it is possible to predict the residual service lifetime (the time to reach the end-point criterion). In the case of cables with polymeric insulations, 50% absolute elongation at break of insulation materials is usually applied as an end-point cri-

terion [4, 5, 12] under condition, that a LOCA (loss-of-coolant accident) survivability of the cable was proved [3, 4, 11].

Within NRI Ře Testing laboratory, there have been qualified about 30 types of cables in Czech and Slovak NPPs by using DSC method.

This method is applicable not only for cables, but also for many other plastics. From NPP materials of interest DSC method can be used for seals, gaskets, cable splices, paints, plastic radioactive waste disposal containers, etc. One only has to find a property (like OIT [10], shift of T_g , change of heat or temperature of fusion [13] etc.) that changes with the advanced degradation and can be correlated to any suitable functional property.

The whole procedure of sampling and DSC testing has to be well standardized and all experimental effect, that can influence the results have to be taken into consideration [14, 15]. Once the correlation curve is plotted, only the samples from NPP are measured in specific intervals. The interval between two measurements is from 1 to 10 years. It depends on the extent of degradation and no change has been observed for several years.

Despite of many advantages (like easy-to-apply, non-destructive, the cable can even be energized during sampling), the non-destructive methods are only seldom applied. Two main reasons are as follows: in many countries even microsamples are not allowed to cut out from actually installed cables; additionally, the whole procedure is time exhausting and the analysis may be highly site specific. In order to prepare the correlation plots, the materials have to be accelerately aged by applying radiation and thermal ageing and testing of LOCA survivability. All these tests need very special equipment and take relatively long time, which is expensive. Hence, the use of DSC for ageing monitoring makes sense only for materials where the information of their degradation state and their residual service life are of major consequence. Those are materials important for safety-related systems of NPP or materials expensive owing to their quantity in NPP. This is the case of cables, which are hundreds of kilometres in NPP but it is not possible to remove samples for functional testing.

Conclusions

DSC method can be considered to be essentially a non-destructive test. At present, there are only few methods in-plant applicable that have been used for on-going qualification and assessment of material service lifetime. Using differential scanning calorimetry has been demonstrated to be useful for degradation monitoring many insulation and jacket materials used for cables in Czech and Slovak NPPs. On the basis of this technique, the extent of degradation of other polymeric materials can be assessed.

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