Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 525–528

ASSESSMENT OF PARAMETERS FOR SIMULATION OF THERMAL AGEING OF MATERIALS IN NUCLEAR POWER PLANTS USING DSC

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Simulation of thermal ageing is an important part of qualification of materials designed for the use in nuclear power plants (NPP). According to standards, the simulation of long-term service thermal ageing is performed isothermally at elevated temperature using Arrhenius methodology. The samples or equipment are aged in thermal chamber, to bring them to the same state as after long-term service time. To proceed a reliable simulation, the testing parameters should be taken very carefully and the accelerator factors should not be too high. The testing temperature and time and the activation energy are the most important parameters. Determination of these factors and the limitations of their use in practice are discussed.

Keywords: *activation energy, DSC, lifetime, plastics, thermal ageing*

Introduction

Fundamental to the safe operation of commercial nuclear power plants (NPP) and to the protection of public health and safety through regulation is the need to ensure that safety systems and equipment can perform their intended functions during normal operation, earthquakes, and postulated accidents. Demonstration that safety systems and equipment can perform as required is called 'equipment qualification' [1]. The equipment can be qualified using one or a combination of the following methods: testing, analysis or operating experience.

Testing refers to a sequence of tests all performed on the same sample [1, 2]. The tests are designed to simulate in service ageing to predict condition at the end of the service life. The other series of test is intended to simulate the service conditions encountered during extreme design base events (both seismic and accident events).

The basic goal of the qualification is to demonstrate that the material is capable to fulfill its functions toward at the end of its planned service life. Therefore, the equipment (cable, motor, valve, sealing, etc.) is exposed to accelerated environments to bring them to the same condition as after long time service ageing.

One part of the qualification process is simulation of thermal ageing. The Arrhenius methodology (isothermal ageing at elevated temperature) has been considered an acceptable method of addressing accelerated ageing. It must be mentioned, that the ageing need to be performed with the whole equipment (e.g. at least 5 m of cable), because at the end of the testing the aged samples are subjected to the diagnostic measurement.

Experimental

Instruments

The DSC measurements have been performed with Perkin-Elmer DSC7 and with TA Instruments Q-100. The experiments have been carried out in pure oxygen both in the isothermal and in the dynamic mode. In the experiments the sample mass was 1.5 to 2.5 mg and the sample geometry was in all cases the same.

The mechanical properties have been evaluated by using the INSTRON 4301 testing machine at a test speed of 200 mm min^{-1} at the room temperature.

Long-term ageing experiments have been carried out in thermal chambers Heraus and/or Binder with forced air circulation (10 air changes per hour) and temperature unhomogeneity ±1.5°C.

Methods

The whole qualification procedure is under surveillance of National Nuclear Regulatory Body and/or International Atomic Energy Agency. Therefore, only standardized and overall accepted methods can be used. For simulation of thermal ageing such a method is the Arrhenius one. The Arrhenius equation is here used in the form [1–3], which enables to calculate the time to equivalent damage at different temperatures (Eq. (1)).

$$t_1 = t_2 \mathrm{e}^{\frac{E_a (T_2 - T_1)}{R T_1 T_2}} \quad (1)$$

where t_1 – time of accelerated ageing, t_2 – required service life, E_a – activation energy in J mol^{-1},

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1388–6150/$20.00

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T_1 – temperature of accelerated ageing, T_2 – service temperature and R – gas constant.

Applying Eq. (1) we assume that the short-term simulation of thermal ageing at higher temperature causes the same degradation as the service long-term ageing at lower temperature. This means, we assume, that the chemical mechanisms leading to ageing do not change with temperature and thus, the E_a does not change in the extrapolated region.

The test time (t_1) in thermal chamber at elevated temperature depends on the service temperature, required service life, testing temperature and activation energy.

The service conditions are given in the project. The testing temperature and the activation energy must be usually set by the testing laboratory.

Results and discussion

Testing temperature

For reliable simulation of long-term thermal ageing, the temperature of accelerated ageing should not be too far from the service temperature. The standards [4, 5] recommend using not more the 25°C difference. But to simulate 40 years of service ageing, such a small difference would lead to very long testing time. Hence, the test temperature is usually higher.

The maximum allowed ageing temperature is limited by the range of chemical stability (the temperature range in which for specific time no chemical changes are detected) or by any thermodynamical transition in the material, like glass transition (T_g), softening or melting point [6, 7]. If between the test and service temperature such a phenomena occurs, it is very difficult, if not impossible, to extrapolate the data from higher to lower temperature. The testing would be in this case not very reliable. An excellent tool, which can easy and fast find out if such a process appears in the temperature of interest is differential scanning calorimeter (DSC). A typical example is given in Fig. 1. The DSC curve of a XPE based sample suggests, that the temperature of the simulation of thermal ageing should not exceed 105°C.

Possibility of heterogeneous ageing throughout the sample is another important reason for using not too high temperatures. For such a phenomenon can be responsible the migration and evaporation of additives (mainly plasticizers) [3, 8, 9], or the diffusion limited oxidation (DLO). DLO becomes significant whenever the rate of oxygen consumption in a material is greater than the rate at which oxygen can be resupplied from the surrounding air atmosphere. DLO effect was found for number of polymers at the temperature higher than 80°C [9].

Activation energy

The thermal ageing simulation procedure requires single value of activation energy (E_a). The E_a is a value, which is determined from the overall rate of often very complicated thermooxidative degradation. An established and generally acceptable method [4] for E_a estimating consists in accelerated ageing of material in thermal chambers at various temperatures for different times and subsequent determination of its functional properties. From the ageing curves, which show the plot of measured property *vs*. time of ageing, usually the points of 50% change for different temperatures are determined. The E_a is then calculated using these points and Eq. (1). But very long testing time (~5000 h), together with high material consumption are limiting factors of this method.

Therefore, it is advisable to accelerate the process of E_a determination, e.g. by using thermogravimetry or DSC [1, 3, 10–14]. Using these methods, the E_a can be estimated very fast and with small material requirements. Following NPP accepted methods of E_a estimation by using DSC have been tested:

- According to ASTM E 698 [10]: unaged samples were heated in oxygen environment with up to 7 different heating rates from 1 to 15 K min^{-1}.
- Measuring in isothermal mode at various temperatures: these experiments have been carried out with new samples in isothermal mode at 5 to 7 different temperatures between 180 and 250°C. The oxidation inductive time (OIT) has been evaluated. The E_a has been calculated according to Arrhenius equation from the slope of the plot of the logarithm of OIT as a function of reciprocal absolute temperature.
- Modified conventional (IEC 216) method: at first, small samples had been aged in a thermal chamber at the temperatures of 120, 150 and 180°C for the time

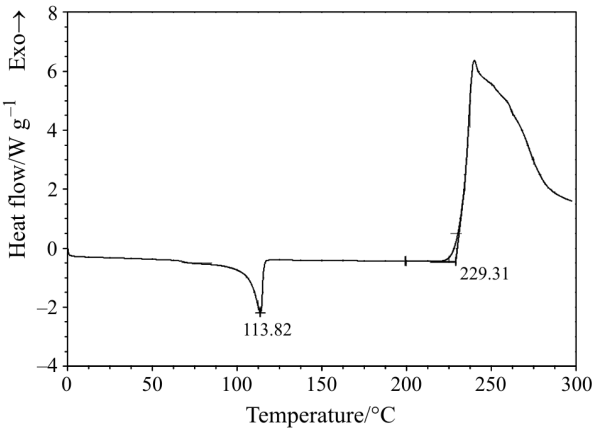

Fig. 1 DSC curve of a XPE based cable used in NPP. The sample was heated 10 K min^{-1} in oxygen environment. From the curve follows, that the testing temperature during the simulation of thermal ageing should not exceed 105°C

up to 76 days, at least for 5 different times at each ageing temperature. Then OIT has been measured. For each temperature, the points corresponding to the time of 50% OIT decrease have been evaluated from the plot of OIT *vs*. ageing time in the thermal chamber. These points have been used for E_a calculation.

Some measured values of activation energies of cables used in NPPs are presented in Table 1. The results show an expected fact, different test methods give different values. The reason for such a behavior was discussed earlier in [13]. Moreover, when measured real cable samples, often very high scatter of experimental results are obtained due to the material unhomogeneity. Such a scatter negatively influences the standard deviation, which is in our case up to 20%. These facts evoke a question: which value should be used for testing? In the case of electrical cable, where the most important end-point criterion is the absolute value of 50% of elongation at break, E_a determined from the change of mechanical properties should be preferably used (Table 1).

The very last possibility, but sometimes the only one remaining, is to find the E_a value in an appropriate database [e.g. 1, 15]. But it must be taken into account that estimation of E_a depends on many factors, like material composition (additives, colors, antioxidants, etc.), method of E_a estimation, monitored criterion, experimental factors etc. Hence, the use of literature data can insert a mistake, which could subsequently result in unrealistic optimistic or pessimistic data.

The degradation process of commercial polymers is usually a sum of several multistage, overlapped reactions that involve several compounds in the material – antioxidants, stabilizators, fillers, pigments etc.; and these reactions have several different activation energies. Besides, the chemical reactions of solids are often complicated by physical processes (diffusion, sublimation, adsorption–desorption, etc.), which are also characterized by their own activation energies. The relative contributions of these individual steps to the overall reaction rate tend to vary with temperature and extent of conversion. Therefore, the effective E_a, which is determined from the overall data and is generally a function of these variables, can vary with the testing conditions and methods of evaluation [9, 14, 16–18].

If the service conditions are known and the E_a with the maximum allowed testing temperature are determined, the testing time can be calculated from Eq. (1). For example for the XPE1 cable (Table 1), which is planned to be in operation for 40 years at 60°C were determined following parameters: E_a=104 kJ mol^{-1} and testing temperature 105°C (Fig. 1). From Eq. (1) it follows, that the cable

Table 1 A comparison of activation energies of some cables used in nuclear power plants. The results have been obtained by using various test methods and various end-point criteria. The standard deviations are not shown (because of better survey), but they are about 10–20% of measured values for all methods and for all samples. All results are given in kJ mol^{-1}. This table was partially published in [13]

Cable		E_a determined using new, unaged samples		E_a calculated from the points of 50% change of below mentioned properties of already aged samples***					
		DSC* ASTM (meth. 1)	DSC** isotherm. (meth. 2)	DSC (meth. 3)	Strain at break	Tensile strength	Stiffness change	Color change	Break at bending
					convent. method				
PVC 1	sheath	129	128	111	114	107	103	113	
XPE 1	sheath	123	123	97	104		119	130	93
PVC 2	sheath	125		116	104		119	146	
PVC 3	sheath	114		121			116		93
XPE 2	sheath	154	151	82				81	
XPE 3	sheath	164		119			127	113	97
XPE 1	core	124		76			152		136
PVC 4	sheath	109	130	104			90		81
PVC 5	sheath			91			117	109	100
PVC 1	core			95			103	119	112
PVC 6	sheath			125			105	115	91
PVC 2	core	96	118		113	113			
PVC 7	sheath			139	115	107	103		
EPR/EVA	core	194	143	91	104	87			
	sheath		153		113	87			

*according to the ASTM E 698 (different heating rates); ** measurement in isothermal mode at various temperatures; *** according to IEC 216

(about 10 m long sample) should be aged at 105°C for 166 days to bring it to the same condition as after 40 years at 60°C. At the end of the simulation the functional properties are measured. (The qualification for NPP continues simultaneously or in the next step with the simulation of radiation ageing and postulated accidents. During and at the end of the testing the sample is subjected to the diagnostic measurements.)

Safe margin

Because there exists many uncertainties in simulation of thermal ageing, it is used to employ a safe margin. This safe margin can be covered by an increase of the test temperature or more often by prolonged test time. Besides, the on-going program [3], which is able to assess the actual state of the cable through cable condition monitoring at real NPP positions has been implemented in many NPPs. An additional method, how to increase the reliability of lifetime prediction is to use the 'deposit methodology' [1–3]. Some testing samples are placed at the location in NPP, where temperature and radiation are higher than at the other positions. At such a place (deposit), the testing samples age a little bit faster than at the real positions and it is possible to assess how the in-service material will behave in the near future.

Conclusions

For simulation of long term thermal ageing of materials used in NPP only approved methods must be used. These methods are set by the legislation and/or by the international standards. They do not give many possibilities how to proceed the qualification. In the case of thermal ageing the Arrhenius approach is most often used. The samples are aged at elevated temperature to accelerate the long-term process in service. DSC is very useful tool to propose the ageing temperature because it can very fast and easy find out the processes that influence the reliability of the simulation (melting, T_g point, etc.). For the calculation of the ageing time, the activation energy must be known. Because the suppliers usually do not know E_a value, it must be determined by the testing laboratory. This is often done by DSC, because it is very fast with small material consumption.

After the ageing in thermal chamber, the samples are subjected to the diagnostic measurement procedure to test if the material fulfill all beforehand defined criteria. These are usually criteria, i.e. limit values of a property beyond which value the degree of deterioration is considered to reduce the ability of material to withstand a stress encountered in actual service.

Several approximations and limitations associated with using of such a method cause, that the predicted service lifetime need not be fully justified. Therefore, the additional subsequent on-going monitoring of the material degradation state is recommended [2]. On-going monitoring is performed on real samples (e.g. cable in service) and/or on deposit sample. For monitoring of ageing of plastics used in NPP, the DSC has been established also as a very useful tool [19, 20].

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