Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 799–804

COMPARISON OF THE ACTIVATION ENERGIES AS DETERMINED BY DSC AND BY CONVENTIONAL METHODS

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Abstract

The results of determination of activation energies (E_A) of polymeric cable insulations obtained by conventional methods (usually based on the evaluation of changes of mechanical properties of insulations after their ageing in thermal chamber at different temperatures) have been compared with results obtained by methods employing the differential scanning calorimetry (DSC). Three DSC methods have been tested: the method according the ASTM E 698; measuring of DSC characteristics in the isothermal mode at several different temperatures; and the method based on evaluation of DSC characteristics of insulations after their thermal ageing in thermal chamber. The last method – which can be called as a modified conventional method, because instead of mechanical properties, the DSC characteristics are determined – has been found as most acceptable and giving similar values of E_A as the other conventional methods.

Keywords: activation energy, cable insulation, differential scanning calorimetry, lifetime

Introduction

The electric cables play a very important role among the components performing safe and reliable operation of any nuclear power plant (NPP). Their insulations have to be made of such materials which are sufficiently resistant to the effect of aggressive environment (enhanced temperatures, radiation, humidity, attack of chemicals, etc.). These effects result, during the long-term operation, to the gradual loss of electrical and mechanical properties of their insulating materials. It is why the control of degradation of all safety-related cables and the qualification tests before their NPP installation are necessary [1, 2]. The procedure used for the cable qualification includes in-laboratory accelerated ageing using enhanced temperatures and dose rates of radiation which should simulate the cable ageing in long-term service conditions (~40 years at 60°C) [3].

Because one of the most degradative factor causing the cable ageing under NPP service conditions is the enhanced temperature the parameters for simulating the NPP thermal ageing have to be determined very carefully. The determination of appropriate temperature and time of accelerated thermal ageing of a cable polymeric material depends, among others, on activation energies (E_A) of the thermooxidative

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

degradation of individual polymeric components. Hence, a correct determination of the E_A is the basic condition for a reliable assessment of the cable service lifetime.

The conventional method of estimating the E_A usually used in cable industry consists in accelerated ageing of cables in a thermal chamber at various temperatures for different times and subsequent determination of their mechanical properties [4]. From the ageing curves (Fig. 1), that show the plot how the mechanical properties change with time and temperature of ageing, the E_A can be estimated. The standards [4, 5] permit to use, instead of mechanical properties, also many other properties, that change with ageing, like color, stiffness or break at bending, etc. From the practical point of view the end-point criterion used for estimation of the E_A should be based on such a property that is joined with the determination of material lifetime (serviceability). In the case of polymeric cable insulation materials the strain at break is often used as an end-point criterion. The activation energy is calculated from the points of 50 percent deterioration of prime strain at break (or an other property), according to the Arrhenius equation.

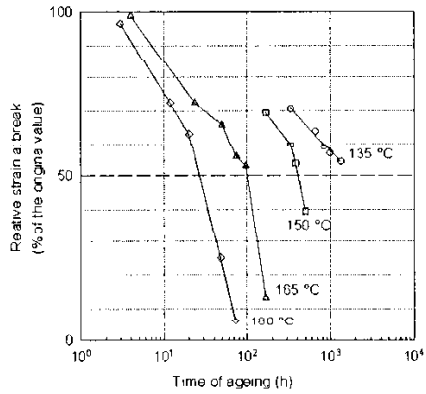

Fig. 1 Ageing curves for a PVC sheathing material. The E_A is calculated from the points of 50% deterioration of primary properties, according to the Arrhenius equation

But this procedure takes a long time: at least 5 000 h of ageing are necessary to evaluate the thermal endurance curves from the ageing curves. Also the material consumption cannot be neglected; according to the recommendation of IEC 216 [4] at least 240 tensile specimens (dumb-bells and/or tubes) should be used. Hence, this paper tries to describe how to replace this conventional procedure by a faster one, also saving the material consumption – by measuring the DSC characteristics.

DSC is widely used for kinetic analysis (estimation of E_A), because it is a quick testing procedure and employs a small amount of sample at once. A review on research of degradation kinetics of electrical insulating materials by thermal analysis gives Ozawa *et al.* [6]. Thermal analysis is also used for the lifetime prediction of polymers [e.g. 7–10]. But in these cases the lifetime assessment of plastics is joined with a high uncertainty. Therefore, the DSC kinetic results are used in this paper

only for calculating the appropriate parameters of accelerated thermal ageing and not for direct prediction of lifetime of NPP cables. This can be done only after the accelerated ageing by determining such properties, which directly reflect the functionality of cable insulations in their applications (strain at break, electric strength, insulation resistance, etc.) [5].

Experimental

The cables manufactured on the basis of crosslinked polyethylene (XPE), polyvinylchloride (PVC) and ethylene-propylene rubber/ethylene-vinylacetate copolymer (EPR/EVA) have been tested. Long-term ageing experiments have been carried out in thermal chambers Heraeus with forced air circulation (10 air changes per hour). The mechanical properties have been evaluated by using the tensile testing machine INSTRON 4301 at a test speed of 200 mm/min at the room temperature.

The DSC measurements have been performed with Perkin-Elmer DSC 7 and with DuPont 910/TA 2100 system (with autosampler). The experiments have been carried out in pure oxygen, both in the isothermal and in the dynamic mode. The sample weight was in the experiments 1.5 to 2.5 mg and the sample geometry (thin slices) was in all cases the same. The peak extreme of the degradation (in dependence on the instrument, it was minimum or maximum) has been previously chosen as the end-point criterion (this DSC characteristic is further called as the DSC response). In this work it has been assumed that the Arrhenius equation is applicable for all systems.

Three methods of estimation of E_A by using DSC have been tested:

1. According to ASTM E 698 [9]:

Unaged samples were heated in oxygen environment with up to 7 different heating rates from 1 to 20 K min^{-1}. The starting point was 50 K below the start of the exothermic reaction.

2. 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, in the dependence on the material. As the DSC response, the time to the peak extreme or oxidation induction time – OIT (laying between 5 and 400 min) have been chosen. The E_A has been calculated according to Arrhenius equation from the slope of the plot of the logarithm of DSC response as a function of reciprocal absolute temperature.

3. Modified conventional method:

At first, small samples had been aged in a thermal chamber at the temperatures of 120, 150 and 180°C for the time up to 76 days, at least for 5 different times at each ageing temperature. Then the mechanical properties measurements have been replaced by measuring the DSC response (time to the peak extreme or OIT) in isothermal mode. For each temperature the points corresponding to the time of 50% decrease of DSC response has been evaluated from the plot of DSC response as a function of ageing time in the thermal chamber (Fig. 2). These points have been used for the calculation of the E_A.

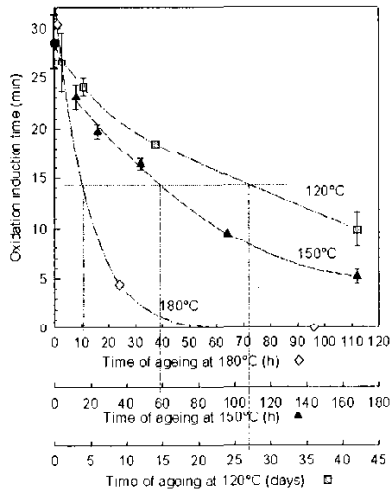

Fig. 2 The plot of DSC response as a function of ageing time (PVC sheath) at various temperatures. The doted line corresponds to the 50% declination of OIT in comparison with the OIT for a new sample

Results and discussion

Summarization of all values of activation energies are given in Table 1. These results show that different test methods give different values. Activation energies of thermooxidative degradation obtained according to the ASTM E 698 method (No. 1) and according to the isothermal method (No. 2) are in most cases higher in comparison with results obtained by conventional methods. The difference is usually about 15–50 kJ mol^{-1}, which corresponds to the difference up to 50%.

The reason for this phenomenon consists in the temperature range for the determination of E_A. In the case of methods Nos 1 and 2, the testing temperatures are about 50–80°C higher than the temperatures for determination of E_A by conventional methods. The modeling of short-term thermooxidative degradation by using the Arrhenius equation may not be generally valid for long term ageing, because the fundamental chemical and physical processes included at higher temperatures may be significantly different from those, which occur under more typical low-temperature thermal ageing. In other word, the temperatures usually used by DSC can be too high for reliable transmission of activation energy values for their application at lower temperatures.

Higher values of E_A (obtained by methods Nos 1 and 2) can also be the consequence of the selection of the end-point criterion, which practically corresponds to the total degradation of insulating materials. As end-point criteria at conventional methods the 50% change of chosen property is used.

Table 1 A comparison of activation energies of some cable insulations used in nuclear power plants

Cable material and cable component	E_A determined by using the new, unaged samples		E_A determined by using the in-thermal chamber aged samples and calculated from the points of 50% change of below mentioned properties				
	DSC* ASTM (meth. 1)	DSC** isotherm. (meth. 2)	DSC (meth. 3)	Strain at break (convent. meth.)	Tensile strength (convent. meth.)	Change of stiffness (convent. meth.)	Break at bending (convent. meth.)
PVC 1 sheath		128	111	114	107	103	
XPE 1 sheath	151	123	97	104		119	93
PVC 2 sheath	125		116	104		119	
PVC 3 sheath			121			116	93
XPE 2 sheath	154	151	108				
XPE 3 sheath	164		119			127	97
XPE 3 core	124		76			152	136
PVC 4 sheath		130	104			90	81
PVC 5 sheath			91			117	100
PVC 5 core			95			103	112
PVC 6 sheath			125			105	91
PVC 7 core		118		113	113		
EPR/EVA 1 core	196	196					
EPR/EVA 2 core		143		104	87		
sheath		153		113			

*according to the ASTM E 698 (different heating rates)

**measurement in isothermal mode at various temperatures

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% of measured values for all methods and for all samples. All results are given in kJ mol^{-1}.

Conclusions

The direct determination of E_A of a thermooxidative degradation by using of DSC is very quick and almost non-destructive method, which requires only a little amount of samples. But, if the E_A is estimated according to the ASTM E 698 or according to the isothermal method, too high values are very often obtained in comparison with the conventional methods. The difference between these values and the values obtained from conventional methods usually changes from material to material and there is no possibility to assess it before the testing. This fact may have disagreeable practical consequences: the higher E_A is determined, the shorter accelerated ageing time is then applied. It could result in unrealistic and optimistic data (too high lifetime prediction).

If the DSC is applied as a modified conventional method (this means that samples are evaluated by DSC after prior ageing), one can obtain acceptable results. For cables used in the hermetic zone of a nuclear power plant, where a sufficient length of sample for estimating E_A by classical elongation at break can not be often obtained, the application of DSC seems to be the solution, which is also in compliance with IEC 216 [4] and IEC 610 [5]. But this method can be recommended and used for nuclear power plant cables after measuring the large number of materials and after its verification. This program is now under progress.

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