Testing of Polysulfone for Applications in Nuclear Facilities

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ABSTRACT: Polysulfone Tecason S samples, designed for use in nuclear facilities, were aged under different conditions to simulate their long-term use in nuclear power plants. The specimens, with thicknesses of 4 mm, were irradiated with ^{60}Co γ rays in oxygen and/or in air at different temperatures and thermally aged at 180°C. For all samples, the glass-transition temperature, the stepwise change in the heat capacity at the glass-transition temperature, and the oxidative induction temperature were measured with differential scanning calorimetry. Simultaneously, the mechanical properties were determined and correlated with the results obtained by differential scanning calorimetry. Although the material was aged under very harsh conditions (irradiation in oxygen with absorbed doses up to 500 kGy and thermal aging at 180°C up to 115 days), the detected changes were relatively small. Nevertheless, a tendency of the glass-transition temperature and oxidative induction temperature to decrease with advanced material degradation was evident. The color changes of the cross-sectional slices of some samples clearly indicated that the degradation was due to diffusion-limited oxidation not homogeneously distributed throughout the sample bulk. In addition, samples from the near surface layers and from the center of the sample were examined. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2395–2399, 2008

Key words: ageing; differential scanning calorimetry (DSC); glass transition; radiation

INTRODUCTION

All materials and equipment that have been designed for use in nuclear power plants have to be qualified before installation. The qualification aims to demonstrate that the material is capable to fulfill its functions until its planned life expiration. Qualification consists of the simulation of the main degradation factors that affect the material during the service lifetime. Temperature and ionizing radiation are the most important stressors. Nevertheless, mechanical shocks, vibrations, chemical contamination, accidents, and so on should also be taken into account.[1]

Polysulfone has been tested as a new and perspective insulation material for use in high-voltage penetrations in nuclear facilities. Its excellent physical and electrical properties are virtually unaffected by long-term thermal aging, and it is hydrolytically stable and has exceptional steam resistance.[2] Such properties predetermine its use in systems operating under very harsh conditions during the whole expected life of nuclear power plants. To assess the service lifetime, polysulfone samples were subjected to accelerated aging to simulate 10, 20, and/or 50 years of operation at elevated temperatures and high radiation doses.[1,3,4] At the end of testing, the glass-transition temperature (T_g), the stepwise change in the heat capacity (ΔC_p) at T_g, and the oxidative induction temperature (OITP) were determined with differential scanning calorimetry (DSC). The aged samples were also subjected to diagnostic mechanical and electrical measurements.

EXPERIMENTAL

Material

Transparent, amorphous polysulfone samples with thicknesses of 4 mm, manufactured by Ensinger Co. (Nufringen, Germany) as Tecason S were used for the tests.

Aging

Radiation aging was carried out in air and/or in oxygen at temperatures between 35 and 50°C with a ^{60}Co γ-ray source at a dose rate of about 0.2 kGy/h. Total absorbed doses up to 500 kGy, determined by alanine dosimetry, were applied. Thermal aging was performed in a Heraeus (Hanau, Germany) thermal chamber with forced-air circulation at 180°C. The aging lasted up to 115 days.

Instruments and methods

We measured OITP by heating the samples in pure oxygen at a heating rate of 10°C/min with a
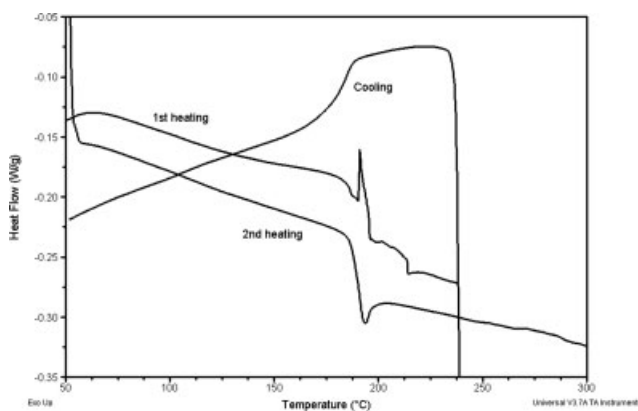
Figure 1 DSC thermogram of the unaged polysulfone sample.

PerkinElmer DSC 7 (Shelton, CT). OITP is the onset temperature of the exothermic oxidation of the material. The conditions for the determination of T_g and ΔC_p were as follows: nitrogen environment, heating/cooling rate of 15°C/min, first heating from 50 to 240°C, 5 min isothermal, cooling to 50°C, and reheating up to 350°C. A DSC Q-100 apparatus from TA Instruments (New Castle, DE) was used. The results of the second run were evaluated. At least three samples were used for each DSC measurement. The mechanical properties were evaluated with an Instron (High Wycombe, England) 4301 tensile testing machine at a testing speed of 10 mm/min. The electrical properties were measured at the High Voltage Testing Laboratory EGU Prague, Czech Republic.

RESULTS AND DISCUSSION

Glass transition

The T_g value was determined from the DSC second run because the first run was, in many cases, distorted by relaxation processes (cf. Fig. 1). However, this was generally not the case of the samples that were thermally aged at 180°C. This temperature was very close to the T_g value, and there was enough time to erase the thermal history (a similar process proceeded at the DSC first run). During the aging of polymers, the following processes, affecting the T_g value, may have happened:[5–9]

- Crosslinking (T_g increased).
- Degradation and chain scission (T_g decreased).
- Loss of additives, such as plasticizers (T_g usually decreased).
- Chemical changes and gas production (T_g either decreased or increased).

In the case of long-term aging in air, one can expect that the oxidation would lead to chain scission, that is, chain length changes. The scission prod-
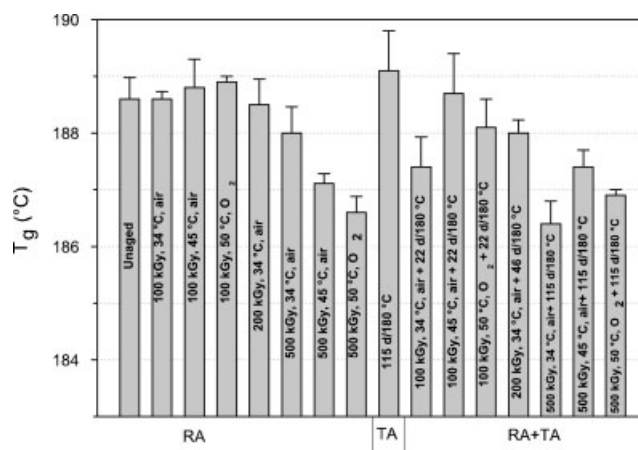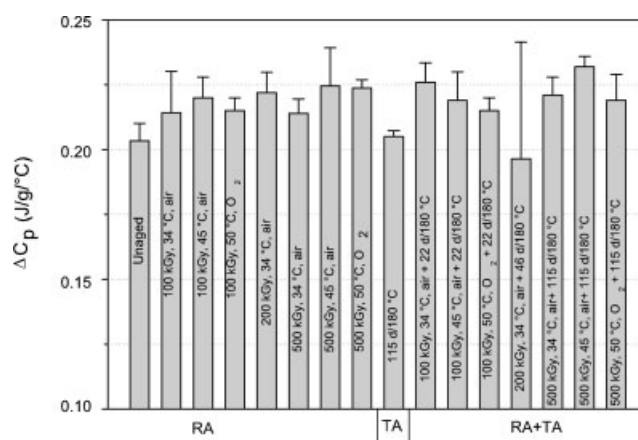

Figure 2 T_g values of unaged and aged polysulfone (RA = radiation aging; TA = thermal aging; RA+TA = radiation aging followed by thermal aging).

ucts have less restricted mobility and reduced chain stiffness, which may result in a T_g decrease.[6,10]

At the glass transition, ΔC_p is also observed because of a change in the degrees of freedom of the cooperative rearrangements. The stepwise changes take place only in the amorphous fraction.[5,11] Because of a higher disorder of scission products, a ΔC_p increase can be expected.

The changes in T_g and ΔC_p with aging are plotted in Figures 2 and 3. These results show that T_g slightly increased at the beginning of radiation aging, and with the prolonged aging, time it tended to decrease below the initial value. The T_g value decreased from 188.7 to 186.6°C for the sample irradiated with a dose of 500 kGy in an oxygen atmosphere. The temperature difference of 2.1°C was small and indicated that the physical and chemical changes were not very significant. The thermal aging at 180°C seemed to have no effect on T_g. Similar results were also reported by Murakami and Kudo.[12]

Figure 3 ΔC_p values of unaged and aged polysulfone (RA = radiation aging; TA = thermal aging; RA+TA = radiation aging followed by thermal aging).
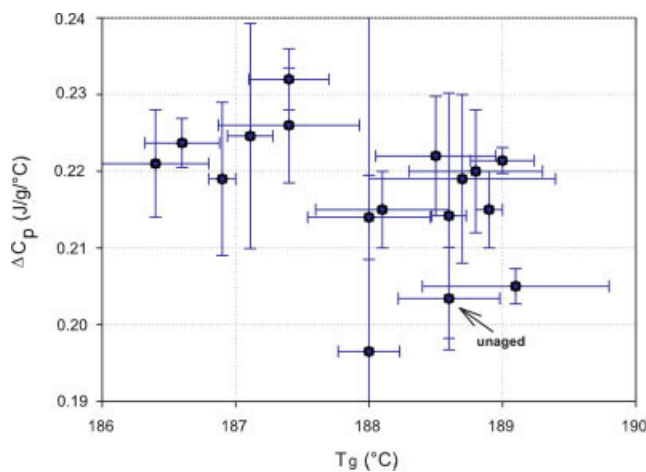
Figure 4 ΔC_p versus T_g for unaged and aged polysulfone. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 OITP as a function of the aging conditions (RA = radiation aging; TA = thermal aging; RA+TA = radiation aging followed by thermal aging).

If the polysulfone samples were irradiated and then subjected to thermal aging, the initial increase of T_g was not observed and the mean T_g values were usually slightly lower compared to samples that were only irradiated or only thermally aged. The hydroperoxide ROOH's, formed during the radiation oxidation, broke down at high temperatures, which initiated different chain branching reactions and led to polymer degradation.
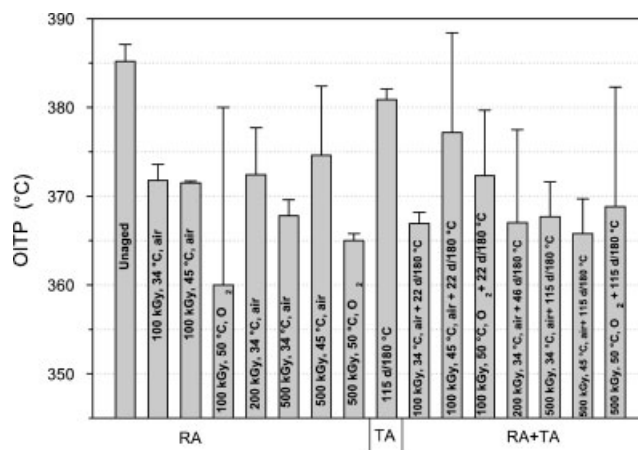
The ΔC_p changes, especially when the standard deviations were taken into account, were not very convincing. The values of ΔC_p increased from 0.20 to 0.23 J/g/°C for the most degraded sample. When ΔC_p was plotted against T_g, a tendency of ΔC_p to increase with decreasing T_g was observed (cf. Fig. 4).

OITP

Polymers age predominantly by means of a chemical reaction with oxygen. Antioxidants are chemicals added to polymers to inhibit oxidative reactions. As long as antioxidants remain in the polymer, the material does not degrade significantly. Because OITP is related to the content of antioxidants, it is a good parameter for monitoring polymer degradation.[12–14] The OITP results are summarized in Figure 5. From this diagram, the decrease of OITP with advanced degradation, caused by the combination of irradiation and temperature, is well observable. Thermal aging alone had a very small effect on OITP changes.

Mechanical properties

Because embrittlement is one of the major consequences of polymer degradation due to aging, the strain at break is considered a suitable degradation-sensitive property, which is generally accepted as a property reflecting the material functionality.[9,15] The results of the strain at break together with the standard deviations are summarized in Table I. The very high scatter of the results may have been a consequence both the material inhomogeneity (which is typical for commercial samples) and the inhomogeneous deformation process accompanied by necking formation. Two shoulders of the neck propagated along the sample from the drawn to the undrawn part of the specimen. In the shoulder zone, the material structure changed from the undrawn to the drawn one. This melting process was sensitive to structural inhomogeneities (e.g., microcracks, additives) and may have been stopped by them. This resulted in the crack initiation in the shoulder neck region and in the sample break during testing. This mechanism of cold drawing was the cause of the relatively large scatter of strain-at-break values.

At the beginning, the strain at break increased with aging from 51 to 80%. With continued aging, the strain at break decreased to 40%. Such behavior could be explained by crosslinking during the first stage of aging. As aging continued, the scission processes dominated, which led to a reduction in the mechanical properties. The T_g value exhibited the same

TABLE I
Strain at Break of Unaged and Irradiated Polysulfone

History	Strain at break (%)
Unaged	51 ± 22
100 kGy at 34°C in air	60 ± 13
100 kGy at 45°C in air	56 ± 32
100 kGy at 50°C in oxygen	80 ± 14
200 kGy at 34°C in air	70 ± 26
500 kGy at 34°C in air	49 ± 17
500 kGy at 45°C in air	40 ± 24
500 kGy at 50°C in oxygen	50 ± 22
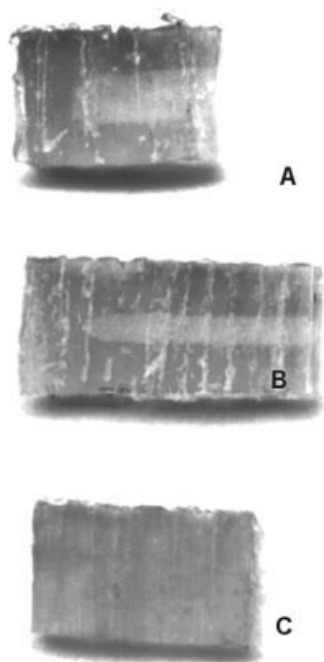
Figure 6 Degradation profile within the sample bulk. Samples were irradiated to a total absorbed dose of 500 kGy (A) in air at 34°C, (B) in air at 45°C, and (C) in oxygen at 50°C.

tendency (Fig. 2). When the strain at break values were compared with the T_g values, the tendency of T_g to decrease with advanced degradation was observable, although the changes were relatively small.

Electrical properties

Polysulfone samples $100 \times 100 \times 1$ mm were irradiated at 50°C in oxygen by doses of up to 500 kGy and then thermally aged at 180°C to simulate 50 years of service aging. In compliance with nuclear power plant requirements, the electrical strength and volume resistivity of the aged sample were measured and compared with the value for an unaged sample. Almost no change was detected between the unaged and aged samples, which suggested a relatively low extent of degradation. The electrical strength increased from 30.4 to 32.3 kV/mm. Such a difference was statistically insignificant. Also, the increase in volume resistivity from the original 2.2×10^{14} to 3.4×10^{14} Ω m after aging may have been due to measurement errors. All values were well above the acceptance criteria given in the technical specifications and nuclear power plant requirements.

Homogeneity of degradation

The conditions for accelerated tests to simulate long-term service aging should be chosen very carefully. Too-high accelerating factors generally cannot yield

predictive information on the degradation behavior in long-term applications. The heterogeneous oxidation in the bulk of the sample is one of the reasons. In principle, such an effect occurs in materials where oxidative degradation dominates and the rate of oxygen diffusion is insufficient to support the oxidation reactions that would occur within the material bulk in the case of a sufficient amount of oxygen. Such a diffusion-limited oxidation effect can result in a strong degradation profile within the sample.[10,16]

Slices with thicknesses of about 0.2 mm were cut out from the original 4-mm polysulfone samples perpendicularly to the surface. They are shown in Figure 6. From the figure, it is obvious that only under some aging conditions was homogeneous oxidation within the sample bulk was achieved. The darker parts around the surface indicate that the degradation took part mainly in the near-surface layer. Only for the sample irradiated at 50°C in oxygen was no degradation profile detected [Fig. 6(C)]. The samples that were only thermally aged showed no degradation profile.

The T_g values of the sample taken both from the surface layer and from the center of the polysulfone sample are plotted in Figure 7. The graph shows that the T_g value depended on the tested layer and on the aging conditions. For the samples irradiated at 34 and/or 45°C in air, a degradation profile was quite evident. This was not the case of the sample irradiated at 50°C in oxygen, in which no degradation profile was detected. T_g had the same value in the near-surface layer as in the center of the sample. This indicated that only in this case was homogeneous oxidation throughout the sample achieved.

CONCLUSIONS

Polysulfone samples were aged to simulate their long-term service in nuclear facilities. They were
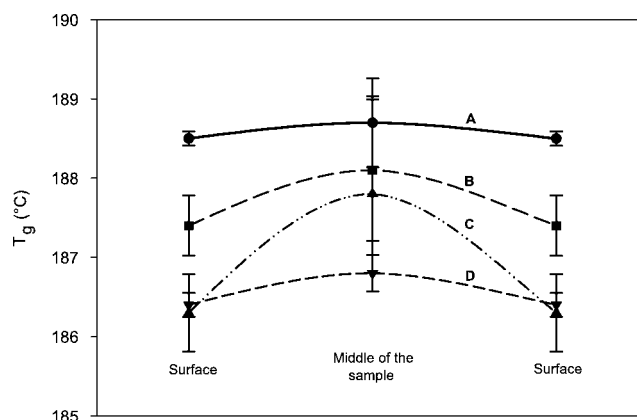
Figure 7 T_g profile within the sample bulk: (A) unaged, (B) 500 kGy and 34°C in air, (C) 500 kGy and 45°C in air, and (D) 500 kGy and 50°C in oxygen. The mean values with the standard deviations are plotted.

irradiated with doses up to 500 kGy either in air or in oxygen and then thermally aged at 180°C up to 115 days. Such aging should have simulated 50 years of service. The mechanical properties, T_g, enthalpy changes at T_g, and OITP were measured.

At the first stage of aging, the strain at break increased from an initial 50% to about 70% for the samples irradiated at a dose of 200 kGy. With prolonged aging, it began to decrease to 40% for samples irradiated in pure oxygen. Nevertheless, this value was still quite satisfactory for the intended use. An initial improvement of the mechanical properties with absorbed dose could be caused by the crosslinking of the polysulfone during the first stage of radiation aging. With continued aging, the degradation became more significant, and the mechanical properties deteriorated.

The T_g value decreased from an initial 188.7 to 186.6°C for the most aged sample. Thermal aging had no effect on the T_g value, even if the polysulfone was aged for 115 days at 180°C. Similar to the strain at break, the T_g value slightly increased at the beginning of radiation aging and decreased after very high doses when the degradation process prevailed.

The stepwise enthalpy changes around the T_g value tended to increase with aging. They increased from 0.20 to 0.23 J/g/°C for the most degraded sample.

OITP decreased for all of the aged samples. OITP decreased from 385 to 365°C for the most aged sample. Because OITP was related mainly to the amount of antioxidants in the sample, the initial crosslinking at the beginning of aging did not affect OITP. Hence, only an OITP reduction with aging was observed.

Thermal aging alone had almost no effect on any of the tested properties even when polysulfone was aged under very harsh conditions up to 115 days at 180°C. This corroborated the very high thermal endurance of polysulfone mentioned in the published literature.[2]

The cross section of the aged sample showed that homogeneous oxidation throughout the sample was achieved only for samples that were irradiated at a temperature 50°C in pure oxygen. This effect was confirmed by T_g determination when the near-surface layer and the layer from the center of the 4 mm thick sample were measured. The T_g values for the samples that were cut out from the surface were lower than that from the sample center, which was evidence for inhomogeneous degradation within the sample bulk.

From these results, we concluded that the reliable simulation of the long-term use of polysulfone in nuclear facilities was achieved only when the samples were irradiated at higher temperatures and in oxygen.

Both the electrical strength and the volume resistivity, measured with 1 mm thick plates, showed practically no change.

All of the measurements with unaged and aged samples confirmed the possibility of the use of the tested polysulfone in nuclear power plants.

Several approximations and limitations associated with the accelerated aging test mean that the predicted service lifetime need not be fully justified. Therefore, additional subsequent ongoing monitoring of the material degradation is recommended.[1,17,18] Ongoing monitoring is performed on real samples in nuclear power plants. Because no cutting out of any samples is allowed, a nondestructive method should be used. Because DSC measurements require only a small amount of sample, it can be considered essentially a nondestructive test.[13] This was, in fact, the second main task of this study, that is, to determine whether the T_g or OITP measurements with DSC could be used for future in-service monitoring of polysulfone material aging.

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