

THE ABSORPTION OF AUTOMOTIVE COOLANT FLUIDS IN GLASS FIBRE REINFORCED POLYAMIDE 6,6 AT ELEVATED TEMPERATURES

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Abstract

Polyamide 66 and two glass fibre composite (DS1110 and DS1143) samples were conditioned in common automotive fluids, water and ethylene glycol at a range of temperatures and their dimensional changes were monitored over a range of times up to 2500 hours. Percentage weight changes in the samples suggested absorption due to Fickian diffusion and that an increase in temperature increased this process.

1 Introduction

Glass fibre reinforced polyamides, such as polyamide 6 and 66, are excellent composite materials in terms of their high levels of mechanical performance and temperature resistance. However, the mechanical properties of polyamide based composites decrease markedly upon absorption of water and other polar fluids. It is also well known that polyamide materials absorb relatively high levels of moisture when exposed to hydrothermal conditioning in water and that this can cause significant dimensional changes [3]. Short fibre reinforced thermoplastics have been used in the automotive industry for many years and there has recently been a strong growth in the use of polyamide based materials in under-the-hood applications [5]. These applications place stringent requirements on such materials in terms of dimensional stability and mechanical, temperature and chemical resistance. There has been a rapid increase in the number of molded composites exposed to engine coolant at high temperatures [1, 3,6] and this has led to a need for an improvement in our understanding of the performance of glass-reinforced-polyamide under such conditions. Despite our knowledge of moisture absorption this, and the fact that such hydrothermal testing has become commonplace for under-the-hood applications, there has been little systematic investigation of dimensional change of glass-fibre reinforced polyamide composites during such conditioning in coolant fluid. In particular there has been little clarification of the action of the two individual coolant components during the conditioning process [7, 8]. Typical testing for these applications involves measurement of mechanical properties before and after conditioning of the test material in model coolant fluids for a fixed time, up to 1000 hours, at temperatures in the 100-150°C range [3]. It is not always easy to obtain a good understanding of the structure-performance relationships of a material from such snapshots of performance taken at a single condition. However, it has been known for some time that the chemical nature of the glass fibre sizing can have a strong influence on the retention of some mechanical properties of composites exposed to such hydrothermal conditioning [3].

In an attempt to gain further insight this report presents the results of a systematic study of the changes in the weight and dimensions of injection molded glass fibre polyamide 66 composites during hydrothermal conditioning in model coolant fluid and its two main components of water and ethylene glycol. The weight and dimensional changes and mechanical properties of injection molded glass fibre polyamide 66 composites based on two glass fibre products with different sizing formulations and unreinforced polyamide samples have been characterised during conditioning in water, ethylene glycol and a water-glycol mixture at 70°C and 90°C for a range of times up to 2500 hours. This report focuses on the absorption processes and mechanical property changes during the material conditioning.

2 Experimental

2.1 Materials

The injection molded polymer and composite bars for this study were supplied by the 3N Fibre Glass Company. The polyamide 66 used was DuPont Zytel 101. Composite samples with 30% weight fibre content were produced using this polyamide 66 and two chopped Advantex E-glass products. Advantex is a boron free E-glass formulation. These products were chopped to a length of 4mm and the individual fibres were had a nominal average diameter of 10µm. Both samples were coated with sizings which are designed for polyamide reinforcement. Three series of samples were molded. Series A using DS1143 glass, series B using DS1110 glass and series R containing only the polyamide 66 resin. The glass and polyamide were compounded on a twin screw extruder and injection molded to produce end-gated rectangular bars with nominal dimensions of 80x10x4 mm.

2.2 Procedure

In order to further understand, how materials known to absorb moisture behave when in contact with typical under the hood, fluids the following experiments were carried out. It was decided that based on past experiments it was expected that testing would show all three materials to absorb moisture following Fick's laws of diffusion(7,8), exhibit physical increases in dimensions due to absorption (4) and would allow conclusions to be drawn about how conditioning affected the material properties. The experiments that were carried out to test these expectations were: sample conditioning at range of temperatures and in various liquid mixtures, namely pure water, pure ethylene glycol (EG) and a 50:50 water, ethylene glycol mixture and then further testing at 70°C of each material samples in two different water limiting mixtures, a 10% water, 90% ethylene glycol mixture and a 25% water, 75% ethylene glycol mixture.

All materials were stored in the laboratory in sealed airtight containers with silica gel to keep absorption of moisture in the air to a minimum. Samples were found to have some irregularities in dimensions so small alterations were carried out using a diamond cutter to ensure each sample was dimensionally similar at the start of the experiment (75mm length, 10mm width and 4mm thickness). Due to the time taken to make these alterations it was deemed necessary to dry out the samples overnight in an oven in order to ensure each sample entered conditioning completely dry. Three samples of each material were immersed in each of the three conditions and an average value was generated.

Polypropylene air tight containers were used to isolate the three conditions and a metal matrix was constructed and inserted into the containers in order to stop the samples from grouping together. The metal matrix allowed the samples to stand up separately allowing maximum surface area exposure of samples to the solutions. The three containers were then placed in a preheated water bath at the set temperature. The first and second sets of experiments were placed in a water bath at 70°C, and 90°C for the third. A standard process was set up and maintained throughout testing for measuring the dimensional changes of the samples.

Containers were removed from the water bath individually, whereby each sample was removed one by one and firstly wiped to remove excess solution. The samples were then weighed using a Mettler Toledo XS205 balance with an accuracy of 0.01mg. A manual outside micrometer with an accuracy of 0.001mm was used to measure the thickness and width of the sample and then vernier calipers were used to measure the sample length. All results were recorded and then the samples were placed back in solution. This process was carried out over a range of times up to 2500 hours during the 70°C experiments and for 1000 hours during the 90°C experiments.

3 Results and Discussion

Graphs generated for testing at 70°C and 90°C are shown in figure one.

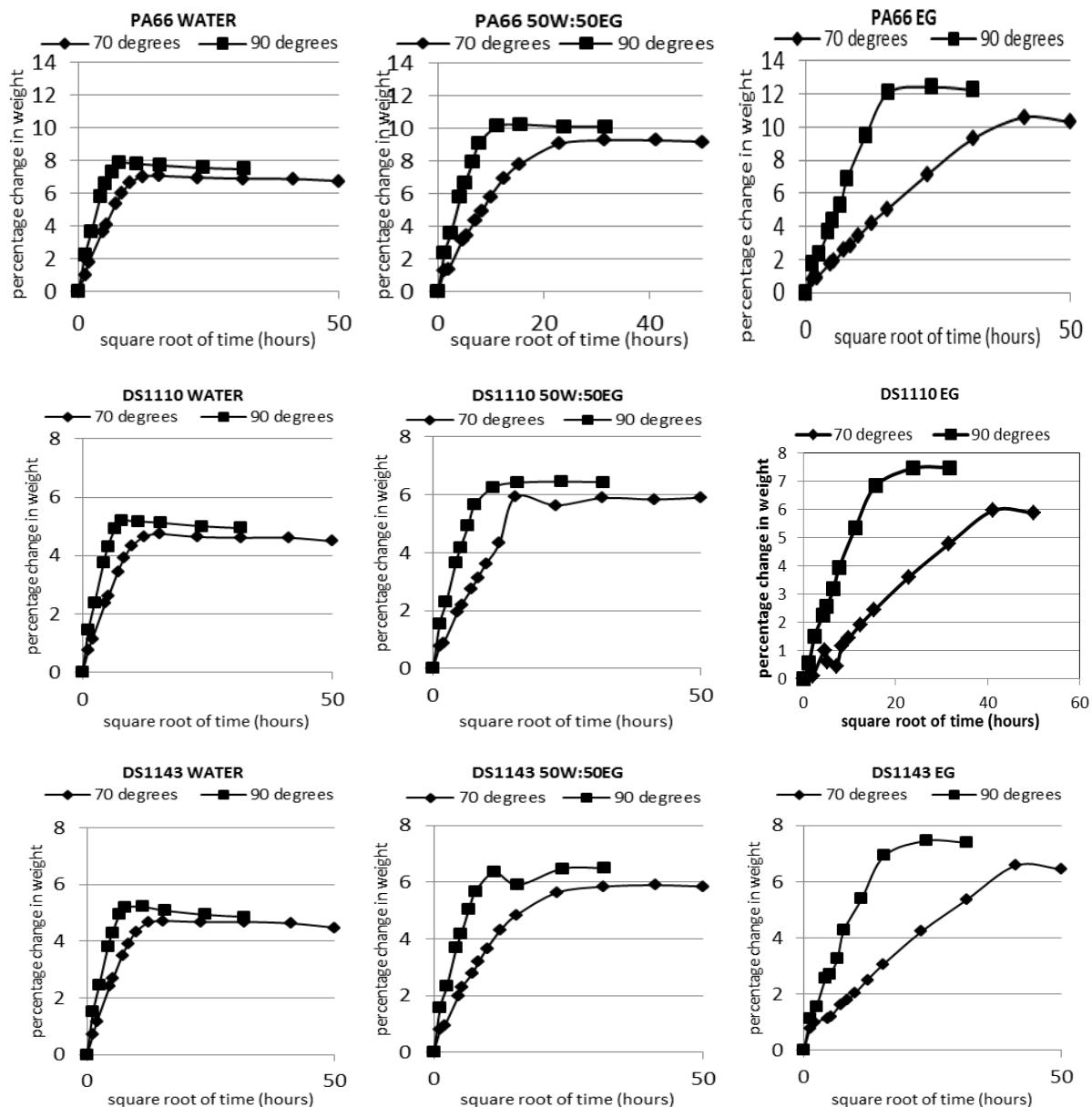


Figure 1. Percentage weight changes of PA66, DS1110 and DS1143 samples after conditioning at 70°C and 90°C in a pure water, pure ethylene glycol or a 50:50 mixture.

When comparing figure one, the results generated from 1000hours testing at 90°C and 2500 hours testing at 70°C, it was first noticed that each graph followed the same trend whereby there was a larger percentage increase gradient in the samples at 90°C than was exhibited over more hours testing at 70°C. The average difference in maximum percentage weight increase from 70°C to 90°C testing was 1%. When conditioned in water material samples tested at a temperature of 90°C reached its maximum weight increase and leveled off approximately 25 hours before those conditioned at 70°C did. When conditioned in the 50:50 mixture a time difference of approximately 400 hours existed between samples reaching maximum weight increase, in pure EG conditioning, 650 hours difference predicted the point at which a sample undergoing 70°C testing would reach a maximum value and level off after the same sample tested at 90°C would. These findings support the prediction that increasing temperature speeds up the process of diffusion, although this theory varies with the solution being tested.

Based on these initial findings further tests were carried out at 70°C by varying the concentration of EG in the solutions. The following graphs were set up comparing the varying degrees of EG in the solution and the resulting percentage weight changes for each sample.

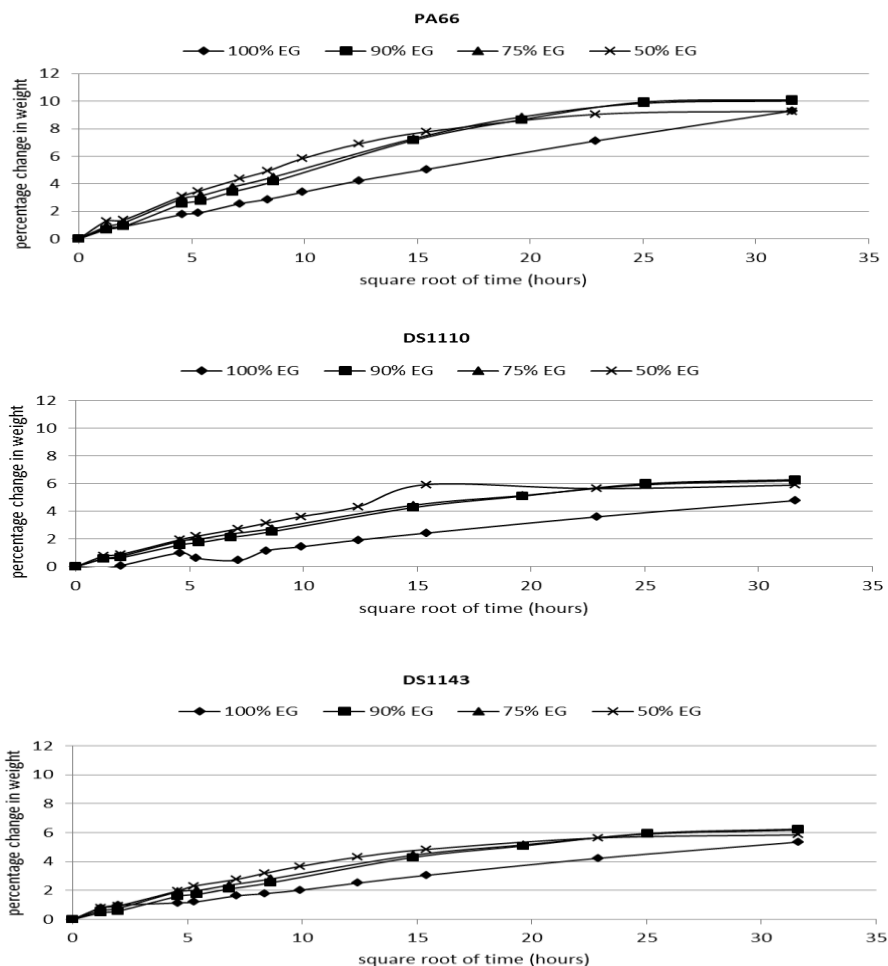


Figure 2. Percentage weight changes of PA66, DS1110 and DS1143 samples after conditioning at 70°C in different EG concentrated mixtures.

It was expected that the samples conditioned in pure EG was exhibit the largest percentage change in weight, however upon analysing the results, it soon became apparent that this conditioning did in fact yield the smallest percentage weight changes, with the samples

conditioned in a 50:50 mixture initially leading the weight change graph but leveling off soon after pure EG conditioning. The most interesting feature of these graphs is that the largest weight change in each sample occurs when conditioned in the 90EG:10W mixture. Once again the percentage weight changes were at a maximum in the polyamide 66 samples. Overall it was also noted that although each seemed on the brink of leveling off and this we know is true for the pure EG and 50:50 mixture further tested would be needed to ascertain if this was also the case for the other two mixtures namely: 10% water : 90% EG and 25% water : 75% EG.

4 Conclusions

It was effectively shown that conditioning on polyamide 66 and two glass fibre composites in a range of common automotive fluids at elevated temperatures over long periods of time resulted in significant changes in the weight and dimensions. All samples exhibited a weight increase as a direct result of hydrothermal conditioning and supported current findings that this weight increase was by Fickian diffusion. The conditioning of material samples in varying concentrations of EG contradicted expectations, in which it was predicted that solutions containing the highest concentration of EG would yield the largest weight percentage increase, but in fact the study showed effectively how even as small a presence as 10% water content in the solutions increased the overall percentage weight increase in the materials. Despite this it remained unclear the true content inside the samples of each fluid although these tests seemed to suggest an immediate water uptake within the samples with a slow and steady uptake of EG over time till the saturation point is reached.

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