HNBR elastomer composite with zero thermal contraction over a range of temperatures

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Abstract

Elastomers such as hydrogenated nitrile butadiene rubber (HNBR) are known to have inferior dimensional stability upon temperature changes compared to metallic materials. This can result in thermal contraction mismatches between metal and elastomer sealing components during cooling, possibly leading to seal leakage. It has also been reported that MnCoGe alloys have been developed that undergo a phase change which results in a volumetric expansion during cooling through the phase change temperature region. This article reports the effect of adding MnCoGe-alloy particles into a HNBR elastomer with the purpose using the thermal expansion of the alloy particles to counteract the thermal contraction of this elastomer during cooling. The composite material is produced using a combination of solvent casting and traditional shear mixing in a two-roll mill followed by compression moulding. With the MnCoGe volume fraction of $\approx 17\,\%$, a considerable suppression of the thermal expansion coefficient of the base elastomer was achieved, going from $185 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$ to nearly zero in the range of temperatures from -5 °C to +15 °C. The positive effect of the filler on the thermal expansivity was apparent in wider temperature range of -20 to +40 °C.

Keywords: Elastomer, composite, negative thermal expansion, HNBR, MnCoGe

1. Introduction

Most engineering elastomers exhibit large coefficients of thermal expansion (CTE) with values that are typically at least an order of magnitude higher than that of steel [1, 2, 3]. This property is of great importance for fluid retaining seals made of such elastomers that are utilised in engineering equipment exposed to considerable temperature fluctuations such as in aerospace or oil and

Table 1: Composition of the HNBR material used in this study

Component	Content, phr
HNBR	100
Antioxidant	3
Stearic acid	0.5
Zinc oxide	5
Magnesium oxide	10
Plasticizer	20
Peroxide	10

gas applications. Performance of elastomer seals in cold environment received scientific attention over the last 30 years which resulted in several publications dealing with static [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14] and dynamic [15, 16] applications. Recent experiments with leakage of static seals at low temperatures demonstrated that the cold seal failures are generally caused by the gaps which open due to the thermal contraction mismatch between the elastomer and metal components during cooling [13, 14]. In addition, the inhibited shape recovery of the elastomer seal at low temperatures ("frozen-in" deformation state) prevents the elastomer rearranging to compensate for the increased gap as would be expected at higher temperatures.

Elastomer composites with reduced CTE can be produced by incorporating particles of negative thermal expansion (NTE) materials into the elastomer composition. In previous work [17], the effect of zirconium tungstate ZrW_2O_8 particles on the CTE of hydrogenated nitrile butadiene rubber (HNBR) was reported. ZrW_2O_8 is a ceramic material with a constant CTE of $\alpha \approx -9 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$ in the temperature range of interest here, i.e. a negative thermal expansion [18]. With zirconium tungstate as a filler, the magnitude of CTE reduction of the composite is substantial only if a large filler volume fraction is introduced which would have negative implications for the elasticity and compression set in the composite material [17]. In this article, the effect of a different NTE particulate filler on the thermal dilation of composites of the same basic HNBR elastomer is reported. The NTE filler used in this work is based on a non-stoichiometric MnCoGe alloy, which undergoes a $\approx 4\,\%$ increase in volume induced by a phase transformation during cooling [19, 20].

2. Materials and methods

The elastomer composition used in the work is based on HNBR with 96 % saturated butadiene units with 36 % acrylonitrile content. The base elastomer composition is presented in Table 1.

In addition to the constituents listed in Table 1, MnCoGe particles are integrated into the HNBR formulation. The HNBR compound without filler loading is further referred to as "unfilled HNBR" whereas the HNBR compound with MnCoGe particle filler is referred to as "filled HNBR". The unfilled HNBR com-

pound has a T_g of $-23\,^{\circ}\mathrm{C}$ as determined by differential scanning calorimetry (DSC) carried out at a heating rate of $20\,^{\circ}\mathrm{C/min}$ [17].

The MnCoGe alloy used in this study was made in an induction furnace in argon atmosphere. The purity of the constituting components was no less than 99.98 %. The ingot was annealed within one week at $850\,^{\circ}\mathrm{C}$ in argon atmosphere and turned into powder after the heat treatment. On cooling, the material exhibits the first-order martensitic-type phase transition from the hexagonal phase with low magnetisation to the orthorhombic phase with high magnetisation and the inverse transition on heating. As can be seen from Figure 1 where the temperature dependence of magnetisation on heating and cooling is presented, a major portion of the phase transition in the material takes place in the interval -30 to $10\,^{\circ}\mathrm{C}$. The magnetic properties of the samples were investigated using a vibrating sample magnetometer (VSM, Lake Shore 7407).

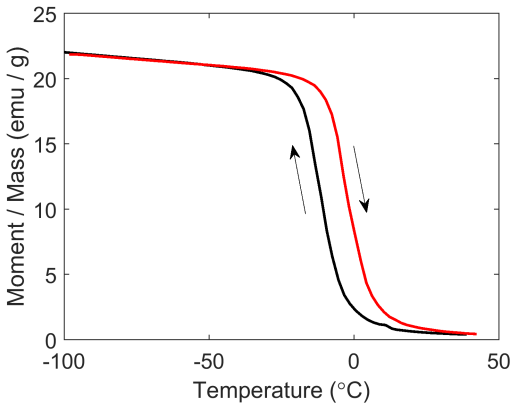

Figure 1: Temperature dependence of magnetisation of the MnCoGe powder measured in 1000 Oe applied field.

The process used to manufacture the MnCoGe filled HNBR samples was as follows. An HNBR compound comprising an HNBR polymer and the mix of additives listed in Table 1 was combined in an internal mixer to yield a single HNBR masterbatch, as described in a previous study [17]. This masterbatch was used for subsequent production of MnCoGe-particle filled and unfilled HNBR compounds materials. In order to integrate the MnCoGe powder into HNBR, a solution casting method was used. In the procedure schematically illustrated in Figure 2, a predefined mass of uncured HNBR compound was dissolved in chloroform, after that the solution was stirred while adding the MnCoGe particle filler and left to dry to form a filler-rich batch of HNBR. This mixture was then combined with a larger volume of HNBR and peroxide using a Schwabenthan Polymix 110P open two roll mill. The formulation was subjected to continuous mixing on the mill for 10 minutes to ensure proper distribution of the filler in the material.

After compounding, the materials were compression moulded into 10x10x6 mm

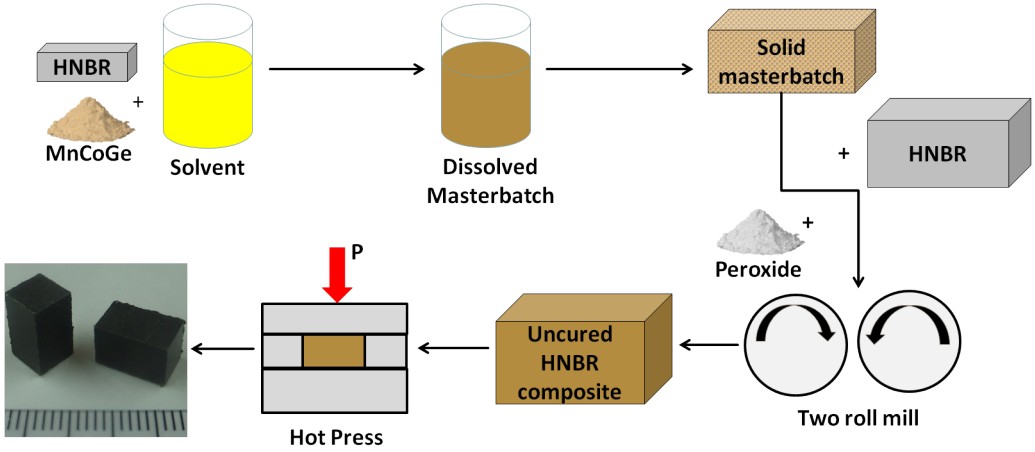

Figure 2: Schematic of the HNBR-MnCoGe composite specimen production process. The scale bar on the photograph is in mm

specimens using a hot press. The materials were cured at 170 °C (443 K) for 20 min in the press, followed by post-curing at 150 °C (423 K) for 4 h in an oven. The obtained volume fraction of MnCoGe in filled HNBR was ≈ 17 % which was comparable with one of the volume fractions of zirconium tungstate employed as an NTE filler in the previous work [17].

The thermal expansion of the produced materials was measured using a Netzsch DIL402C dilatometer during heating from -80 to 130 °C (193 to 473 K) at a heating rate of 2 °C per minute. Two specimens of the composite material were studied in the dilatometer.

Additionally, Shore A hardness was measured by a Bareiss automated durometer according to ISO 7619-1 using the dilatometer specimens with a test time of 3 s. The unfilled HNBR demonstrated Shore A hardness of 71 and the filled HNBR yielded Shore A hardness of 77. It should be noted that the dilatometer specimens are smaller than the minimum surface dimensions specified by ISO 7619-1 for shore hardness testing, and therefore edge effects may give slight underestimates of the true hardness of the materials. Since both sets of samples had the same dimensions, these hardness values may be considered relative but might not be absolute.

3. Results

The incorporation of the MnCoGe filler has a profound effect on the thermal expansivity of the elastomer as demonstrated in Figure 3. The unfilled HNBR compound continuously expands with heating as is normal for most materials, although the rate of thermal dilatation increases by a factor of 2.5 when the material passes through the glass transition temperature of the HNBR compound. The filled HNBR compound also expands with heating, however it has

a peculiar plateau region with no changes in length. This is attributed to the volume decrease caused by the phase transition in the MnCoGe filler counteracting the thermal dilatation of the HNBR during heating. When cooling down the filled elastomer, the same thermal expansion characteristics will happen, i.e. the material will not contract in the temperature range.

The right graph in Figure 3 essentially shows how the one-dimensional CTE $\alpha = \mathrm{d}\varepsilon_T/\mathrm{d}T$ of HNBR changes with temperature in heating. It is clear the CTE of the filled compound is nearly zero (or even slightly negative) in the range from -5 °C to +15 °C where the major portion of the phase transition of the MnCoGe particulate filler takes place. It is also possible to assess the whole phase transition of the MnCoGe particles as being within a window of approximately -20 ÷ +40 °C.

The effect of any particulate filler on CTE will certainly be enhanced by a higher filler loading and potentially smaller particle size distribution, although these effects are not explored in this work.

In the dilatometry experiment, a heating rate of 2 °C/min was utilised and the effect of faster or slower rates of heating or cooling was not specifically investigated. However, experiments using MnCoGe powder (not presented here) at rates of heating and cooling within 2-5 °C/min did not reveal significant alteration in the temperature variation of MnCoGe-alloy magnetisation, which is in agreement with the martensitic nature of the phase transformation in the filler alloy. On the other hand, the behaviour of the composite material can be more complex. Thus, compressive stresses forming during contraction of the polymer matrix with cooling might affect the phase transition. In similar alloy systems of NiMnGe NiMnSi, bulk compression leads to a considerable decrease in the phase transition temperature [21]. In the present case, this effect does not take place as it can be apparent when comparing Figure 1 and Figure 3. Nevertheless, the influence of rates of changes in environmental parameters is quite important and deserves special attention in a separate study.

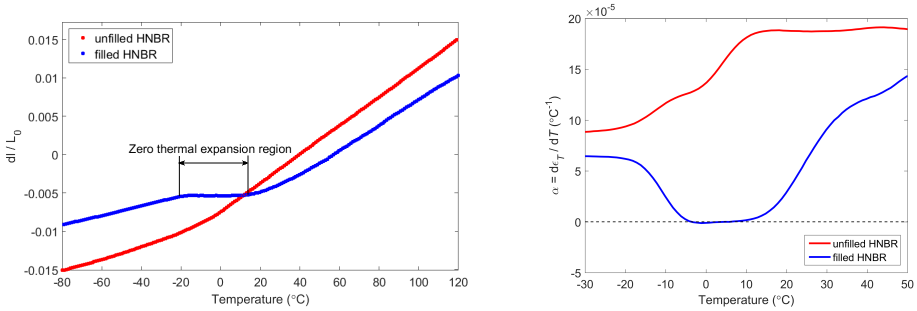

Figure 3: left - dilatometric curves measured using MnCoGe filled and unfilled HNBR; right - smoothed first derivative of dilatation strain as function of temperature for filled and unfilled HNBR.

The results demonstrate that the loading of MnCoGe-alloy into an HNBR elastomer drastically reduces the CTE of the material to nearly zero in the phase

transition temperature window. In a static immovable seal, such a reduction in CTE would be expected to result in reduced leakage. Since the seal failures are caused by the seal-counterface separation, the expansion of the MnCoGe filler during cooling may compensate for the shrinkage of the base elastomer. The contact pressure of a seal made from this compound would therefore be maintained much better at low temperatures than in seals made of unfilled elastomer materials under the same conditions. Based on the thermal expansion behaviour, the magnitude of decrease in the leakage temperature for the investigated composite material can be estimated to be as high as 10 °C.

In this work, the filler volume fraction is approximately 17 % . An even greater MnCoGe loading would be expected to lead to an NTE effect in the seal meaning that the seal would expand in cooling over a certain temperature interval due to phase transition of the MnCoGe particles. However, an optimal filler loading is yet to be found considering the other properties relevant for sealing applications, like compression set or tear strength for high-pressure gas vessels. For some applications, several particulate NTE fillers with various transition temperatures might be necessary to widen the transition interval. This effect should be feasible to attain by alternating the ratio between alloying elements. It is believed that the studied filler system can be integrated into an elastomer using established industrial mixing and compounding equipment and techniques, e.g. internal mixers or two-roll mills.

4. Conclusions

Composites of hydrogenated nitrile butadiene rubber (HNBR) and a MnCoGe-alloy (a material undergoing a phase transition with $\approx 4\,\%$ volume increase on cooling) were prepared with an objective to reduce the thermal contraction of an elastomeric material used in sealing applications. The filler loading of 17 vol.% yielded a decrease of the HNBR thermal expansion coefficient from 185×10^{-6} $°C^{-1}$ down to about 0×10^{-6} $°C^{-1}$ in the range of temperatures from -5 °C to +15 °C. It is predicted that this reduction in CTE would help to retain the contact pressure in elastomer seals exposed to low temperatures near or below the glass transition of the base elastomer and thereby maintain their tightness. Such elastomer composites might be useful in other applications requiring dimensional stability in cooling or heating.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability statement

The dilatometric datasets generated in the project are available in the OSF repository (https://osf.io/hsqrv/files/).