

Publication III

M. Lahelin, I. Aaltio, O. Heczko, O. Söderberg, Y. Ge, B. Löfgren, S.-P. Hannula, and J. Seppälä. 2009. DMA testing of Ni–Mn–Ga/polymer composites. *Composites Part A: Applied Science and Manufacturing*, volume 40, number 2, pages 125-129.

© 2008 Elsevier

Reprinted with permission from Elsevier.



DMA testing of Ni–Mn–Ga/polymer composites

M. Lahelin^{a,*}, I. Aaltio^b, O. Heczko^b, O. Söderberg^b, Y. Ge^b, B. Löfgren^a, S.-P. Hannula^b, J. Seppälä^a

^a Department of Biotechnology and Chemical Technology, Helsinki University of Technology, Kemistintie 1, P.O. Box 6100, FI-02015 TKK, Espoo, Finland

^b Department of Materials Science and Engineering, Helsinki University of Technology, Vuorimiehentie 2A, P.O. Box 6200, FI-02015 TKK, Espoo, Finland

ARTICLE INFO

Article history:

Received 13 August 2008

Received in revised form 29 September 2008

Accepted 28 October 2008

Keywords:

A. Polymer matrix composites (PMCs)

B. Internal friction/damping

B. Adhesion

B. Mechanical properties

ABSTRACT

Ni–Mn–Ga/polymer composites are an interesting group of materials with new potential for applications such as vibration damping. Polymer selection is critical for Ni–Mn–Ga/polymer composites. The transition temperatures of both components should be selected carefully considering the future application, the contact between Ni–Mn–Ga and polymer is important and stiffness of the polymer matrix is one of the influencing factors. The adhesion between Ni–Mn–Ga and the polymer matrix was studied in shear stress tests. Ni–Mn–Ga adhered strongly to the tested epoxies but considerably less so to silicones. The damping properties of Ni–Mn–Ga/polymer composites were studied by dynamic mechanical analysis (DMA). Compared to the pure polymer sample, DMA measurements confirmed extra damping in the martensite–austenite transition temperature region of the Ni–Mn–Ga after a soft epoxy matrix had been applied.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Ni–Mn–Ga-based magnetic shape memory alloys (MSMAs) can be used to convert mechanical energy to magnetic energy and vice versa. Such materials are promising candidates for absorbing vibration energy (vibration damping). Several research groups have studied Ni–Mn–Ga bulk samples and found them to have good damping properties [1–5]. However, Ni–Mn–Ga martensites with modulated crystal structures are often brittle and, thus, difficult to shape and form. If MSMA particles are embedded in a polymer matrix, we could at least partially overcome this; Ni–Mn–Ga/polymer composites could then be more robust, easier to process, and less costly than Ni–Mn–Ga bulk material and yet retain sufficient damping capabilities in most applications. Polymers such as certain epoxies [6], polyurethanes [7,8], and silicones [9] have been studied by other research groups as matrix candidates, but so far no final breakthrough has been made. The contact structure between the Ni–Mn–Ga insert and the polymer matrix is even less studied, but for example, for silicones it has been confirmed that the Si of the polymer connects, at least to some degree, to the O of the oxides Ni–Mn–Ga surface [10].

Dynamic mechanical analysis (DMA), a standard method in polymer analysis, is very sensitive to any changes in material properties, and it is used to measure vibration damping capability, modulus, and transformation temperatures. The amount of dissipated energy (i.e., damping) can be estimated by either phase difference ($\tan \delta$) or loss modulus (E''). The phase difference ($\tan \delta$)

between the applied stress and resulting strain gives the vibration damping capability of the material. The storage modulus E' is the real part of the complex modulus and represents the material's elasticity, whereas the loss modulus E'' is the imaginary part and represents the material's ability to lose energy. DMA has been used in some transformation temperature studies of bulk MSMA materials [1,11], but only few studies are available on the use of DMA to evaluate the damping of Ni–Mn–Ga-based materials [4,5] and composites [12,13].

This study proposes three methods for producing composites consisting of Ni–Mn–Ga and polymer with either an epoxy or a silicon matrix. The composites we produced were (1) one with 15 vol % of Ni–Mn–Ga powder, (2) one in which ribbons are glued together, and (3) one in which thin bulk Ni–Mn–Ga sticks are glued together. We studied the damping of the composites by DMA and the adhesion between the Ni–Mn–Ga powder and the polymer matrix.

2. Experimental

The criteria for selecting the polymer matrix were based on the bulk studies in [5]. There it was determined that the matrix material and the selected Ni–Mn–Ga should be similar or slightly stiffer to produce sufficient stress in Ni–Mn–Ga and, thus, to cause deformation and possibly twin boundary motion. Conti et al. have come to this same conclusion via modeling [14]. Furthermore, in terms of manufacture, the curing time of the matrix must be long enough for the polymer and alloy to be properly mixed but shorter than required for the gravitational settling of the Ni–Mn–Ga powder. During curing, shrinkage should be minimal, and the thermal

* Corresponding author. Tel.: +358 9 4516176; fax: +358 9 4512622.
E-mail address: mika.lahelin@tkk.fi (M. Lahelin).

expansion of both polymer matrix and Ni–Mn–Ga should be comparable. Applying these criteria, we selected two commercial epoxies (Loctite Hysol 9455 and 9492), a soft epoxy (tensile strength ~ 1.5 MPa, elongation approximately 80%) and a medium hard epoxy (tensile strength ~ 30 MPa, elongation approximately 0.8%). Both of these two-component epoxies cure fully at room temperature, Hysol 9455 in about 6 h and Hysol 9492 in about three days. The third matrix material we applied was commercial, moisture-curing, one-component silicone (Loctite 5140) with a tensile strength of ~ 1.1 MPa and an elongation of about 150%; it takes up to three days to cure completely.

In the beginning of the present study, the adhesion between the different polymer matrixes and the bulk $\text{Ni}_{52.4}\text{Mn}_{27.3}\text{Ga}_{20.3}$ alloy was tested at room temperature with a specific laboratory test configuration (Fig. 1). The main reason for using such a test arrangement was the small size and the mechanical properties of the available Ni–Mn–Ga specimens. The Ni–Mn–Ga surfaces were finished with 800 grit sandpaper before joining to the specimen holders; the studied polymer was then applied between two holders. Five pairs of specimens were used in the tensile shear stress test to compare the adhesion of the polymers.

Table 1 lists the composite materials studied with the DMA. The chemical compositions of the inserted materials were examined by energy-dispersive X-ray microanalysis (LEO-1450 SEM/EDS). Their phase transformations were determined using a differential scanning calorimeter (Linkam DSC 600) with a 4 K/min heating/cooling rate, and their magnetic transition was established with an *ac* magnetic susceptibility method. The crystal structure of the Ni–Mn–Ga materials was confirmed by XRD measurements at room temperature. SEM images were taken with a Hitachi S-4700 FE-SEM using 1.0 kV acceleration voltage. Material preparation is described in detail below.

The Ni–Mn–Ga powder used was produced from melt-spun Ni–Mn–Ga ribbons in 4-min dry ball-milling at room temperature using steel balls. Particles over $150\ \mu\text{m}$ were sieved from the prepared powder; their morphology was not studied. The material

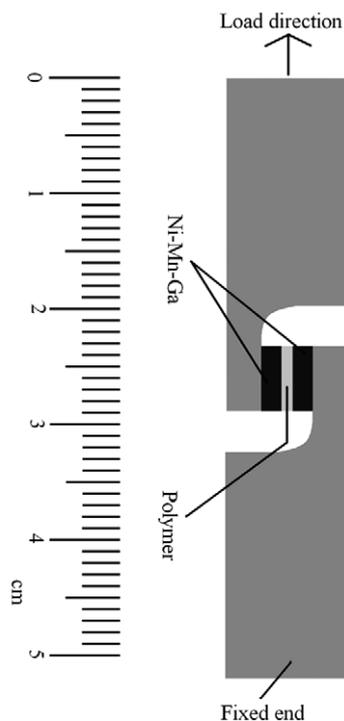


Fig. 1. Schematics of a pair of specimen holders for the adhesion test.

was annealed for 12 h at $800\ ^\circ\text{C}$. In addition to the Ni–Mn–Ga powder, also Ni (Osprey Metals Ltd., 99.5%), Cu (Merck, 99.7%), and Fe (BDH Chemicals, 99.5%) powders were used. Also, from them particles with diameter over $150\ \mu\text{m}$ were sieved away as above. The Ni particles were round, whereas the other powder particles were random in shape. For the powder–polymer matrix and for pure polymeric samples, weighted amounts of polymer component (85 or 100 vol %, respectively) and powder were mixed by hand and poured into a PTFE (polytetrafluoroethylene) mould at room temperature (RT). Silicone-based composites were placed in a temperature-controlled chamber (air humidity $\sim 50\%$ and temperature $\sim 25\ ^\circ\text{C}$) to speed up the sample curing. All work was done as carefully as possible to avoid air bubbles in the mixture, and no external magnetic field was used during the cure.

Two rapidly cooled ribbons, R1 and R2, with transformation regions close to room temperature and in a clearly higher range, respectively, were used in sandwich-type laminates with parallel plates. The ribbons were manufactured by melt-spinning from a polycrystal ingot and heat treated for 24 h at $800\ ^\circ\text{C}$ in vacuum quartz ampoules. The applied ribbons were unhomogeneous, having, for example, slightly different transformation temperatures in different places of the ribbon. Composites with a sandwich geometry consisted of about 20 layers of thin Ni–Mn–Ga ribbons embedded in very thin layers of epoxy. Such a laminate structure was necessary because individual ribbons are brittle.

For bulk composites, thin bulk Ni–Mn–Ga plates (about $35 \times 20 \times 0.7\ \text{mm}^3$) were cut by EDM from a single crystal piece. Cutting was not done along a specific crystallographic plane, because the size of the raw material limited sample preparation. The cut surfaces were wet-ground with SiC paper down to an 800 grit finish. The plates had a final thickness of 0.63 mm. The epoxy was poured between the plates and prevented from overflowing the sides while curing. In each epoxy layer, iron wire spacers were placed at the plate ends to secure an epoxy layer thickness of 0.83 mm, and the stack, when cured, was placed under a weight of about 100 g. The wire spacers were omitted in the measurement length in DMA tests. After curing, the stack surfaces were cleaned, and a sample was cut with a diamond saw and cutting fluid. The sample consisted of three plates, interspaced by two epoxy layers.

The damping properties of the Ni–Mn–Ga/polymer composites were studied mainly with a Perkin-Elmer Dynamic Mechanical Analyzer DMA-7. The parallel plate (PP) configuration was used for the softer polymer composites with Hysol 9455 epoxy and for the Loctite 5140 silicone, whereas for the hard Hysol 9492 based materials, a three-point bending (3 pb) configuration was used. The initial applied amplitude, left free during measurement, was 3–5 μm . The deformation caused by the applied initial amplitude varied depending of the matrix material and DMA geometry. For pure Hysol 9455 epoxy the initial deformation was $\sim 1.2\%$, and for the composite samples (Ni, Fe, Cu, Ni–Mn–Ga) with this matrix it was $\sim 1.0\%$ (PP geometry). For pure Hysol 9492 epoxy the initial deformation was $\sim 1.2\%$, and for the composite samples with this matrix it was $\sim 1.0\%$ (3 pb geometry). For the pure Loctite 5140 silicone the initial deformation was $\sim 2\%$, and for the composite samples with silicone matrix $\sim 1\%$ (DMA measurements carried out at temperatures over T_g , PP geometry). For ribbon composite samples (R1 and R2) the initial deformation was $\sim 0.8\%$ (3 pb geometry). The $\tan \delta$ value was measured as a ratio of the loss to storage modulus: $\tan \delta = \frac{E''}{E'}$. DMA measurements were performed at a fixed 1 Hz frequency in zero magnetic field (i.e., the earth's). The heating rate was 4 K/min, and the applied temperature range varied. Temperature was measured with a DMA thermocouple, which gives approximately $10\ ^\circ\text{C}$ higher transition temperature than DSC because the sample's inner temperature follows the thermocouple temperature with some delay due to the massive sample size

Table 1
Composite materials studied.

Inserted material	Matrix polymer	Composite type	Transformation temperatures of inserted material (°C)/crystal structure
Ni _{49.3} Mn ₂₇ Ga ₂₄ powder 15 vol %	Epoxy Hysol 9455 ^(a) Epoxy Hysol 9492 ^(b) Silicone Loctite 5140 ^(c)	Powder in polymer matrix	M _s 36, M _f 26, A _s 30, A _f 43, T _c 98/5M martensite
Reference samples with Ni, Fe, or Cu powder 15 vol %	Epoxy Hysol 9455 ^(a) Epoxy Hysol 9492 ^(b) Silicone Loctite 5140 ^(c) Epoxy Hysol 9455 ^(a) Epoxy Hysol 9492 ^(b) Silicone Loctite 5140 ^(c)	Powder in polymer matrix Polymer reference samples	
Ni _{49.3} Mn _{29.5} Ga _{20.8} R1 rapidly cooled ribbon	Epoxy Hysol 9455 ^(a)	Sandwich geometry	M _s 33, M _f 18, A _s 26, A _f 41, T _c 99/5M martensite
Ni _{51.6} Mn _{30.0} Ga _{18.4} R2 rapidly cooled ribbon	Epoxy Hysol 9455 ^(a)	Sandwich geometry	M _s 84, M _f 66, A _s 71, A _f 87, T _c 93/7M martensite
Ni _{52.3} Mn _{27.4} Ga _{20.3} bulk	Epoxy Hysol 9455 ^(a)	Bulk/epoxy composite	M _s 133, M _f 121, A _s 136, A _f 147, T _c 100/non-modulated tetragonal

Glass transition point (T_g) at approximately (a) 37, (b) 76, and (c) below -20 °C, measured by DMA. Full curing times, provided by the manufacturer, were (a) 6 h, (b) 3 days, and (c) 3 days.

and rather high heating rate [4]. The bulk thin-plate Ni–Mn–Ga/Hysol 9455 composite samples were measured with other DMA equipment, a Rheometric Scientific DMTA V, in single cantilever mode at room temperature. The frequency used for these samples was 20 Hz, at which it was first studied that harmonics did not appear.

3. Results and discussion

The good adhesion between polymer matrix and Ni–Mn–Ga insert is essential for the composite, especially at temperatures above the glass transition temperature of the polymer (T_g). The adhesion tests carried out at room temperature were made for all the studied matrix materials, epoxies Hysol 9455 and 9492 and the silicone Loctite 5140. The adhesions of the soft materials (Hysol 9455, Loctite 5140) to the Ni–Mn–Ga parts were readily measured while with the hard epoxy Hysol 9492 only one test could be finished reliably. The average maximum shear stress for the epoxy Hysol 9455/Ni–Mn–Ga-bonding was 3.43 ± 1.24 MPa and for the silicone Loctite 5140/Ni–Mn–Ga-bonding 0.68 ± 0.09 MPa. The only result for the epoxy Hysol 9492/Ni–Mn–Ga-bonding turned out to be 2.02 MPa. Thus, the adhesion with soft epoxy and Ni–Mn–Ga was very good, while with the silicone it was rather low.

In a SEM image Fig. 2 the morphology of the epoxy Hysol 9455/Ni–Mn–Ga composite sample is shown. The milled Ni–Mn–Ga par-

ticles are shown as light grey and the epoxy matrix as dark. The Ni–Mn–Ga particles are of variable size and shape but they seem to be attached well to the matrix.

Fig. 3a–c show the damping capabilities ($\tan \delta$) of the Ni–Mn–Ga/polymer powder composites compared to pure polymer as well as to the reference materials with Fe, Ni, or Cu powder.

According to Fig. 3a, all composite samples have higher damping capacity than the pure, soft epoxy Hysol 9455 polymer at above room temperature. The damping of the Ni–Mn–Ga powder/polymer composite improves at 38 °C, i.e., just above the T_g of the polymer, but at about 45 °C, damping drops again sharply. This temperature region corresponds well with the martensite \rightarrow austenite ($m \rightarrow a$) transition of the Ni–Mn–Ga alloy we used. In Fig. 3b, the harder epoxy Hysol 9492 polymer composites show no change in damping in the 30–50 °C range. Because the Ni–Mn–Ga particles are very tightly constrained in the epoxy and cannot deform, the composite does not show any additional damping in the $m \rightarrow a$ transition area. In this case, damping peaks are linked with the glass transition of the polymeric matrix. In the silicone-based composites with a heavily cross-linked matrix, no clear change occurs in the 30–50 °C range. However, a weak change can be observed in the Ni–Mn–Ga powder/polymer composite at about 38–44 °C. Apparently, the silicone material is too soft for the Ni–Mn–Ga powder to show additional damping in the $m \rightarrow a$ transition area. The polymer matrix yields around the Ni–Mn–Ga particles, and the energy is transferred poorly. The composites, especially with soft epoxy matrix (Hysol 9455) and 15 vol % of Ni–Mn–Ga powder, showed some increase in T_g . This may be explained partly by the good adhesion between the matrix and polymer that further restricts the movement of the polymer structure. Furthermore, the curing procedure of the epoxy – in particular cross-linking – is probably affected by the added powder which may have profound influence on T_g .

As the results with the soft epoxy Hysol 9455 turned out to be most successful in the powder tests, this matrix material was used also in other tests. The DMA measurements of the ribbon sandwich composites are shown in Fig. 4, where the storage modulus E' , loss modulus E'' , and damping ($\tan \delta$) are shown as a function of temperature. For both composites, with increasing temperature, $\tan \delta$ first increases slightly, and at about 10 °C above (DMA) the $m \rightarrow a$ transformation temperatures (from DSC), it decreases slightly again. This indicates some extra damping in the Ni–Mn–Ga/polymer ribbon composite at the phase transformation region.

In Fig. 5, the $\tan \delta$ of the bulk thin-plate Ni–Mn–Ga/Hysol 9455 composite samples is shown as a function of strain amplitude. $\tan \delta$ increases with the strain up to the maximum strain used (1%), where it is about 0.27. This indicates that a sufficient stress

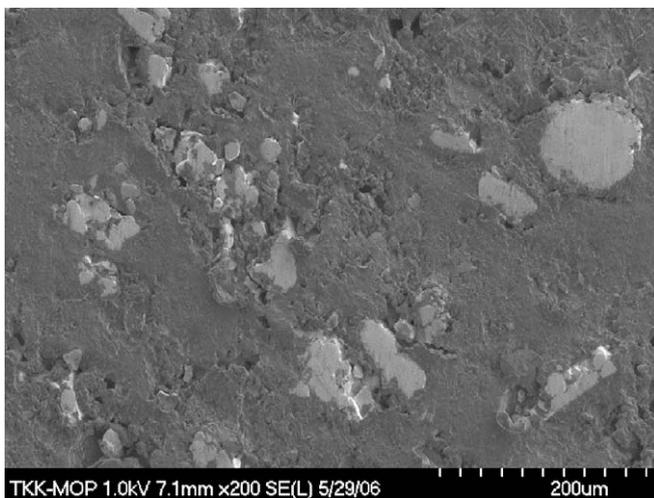


Fig. 2. Ni–Mn–Ga/Hysol epoxy 9455 composite cross-section by SEM image.

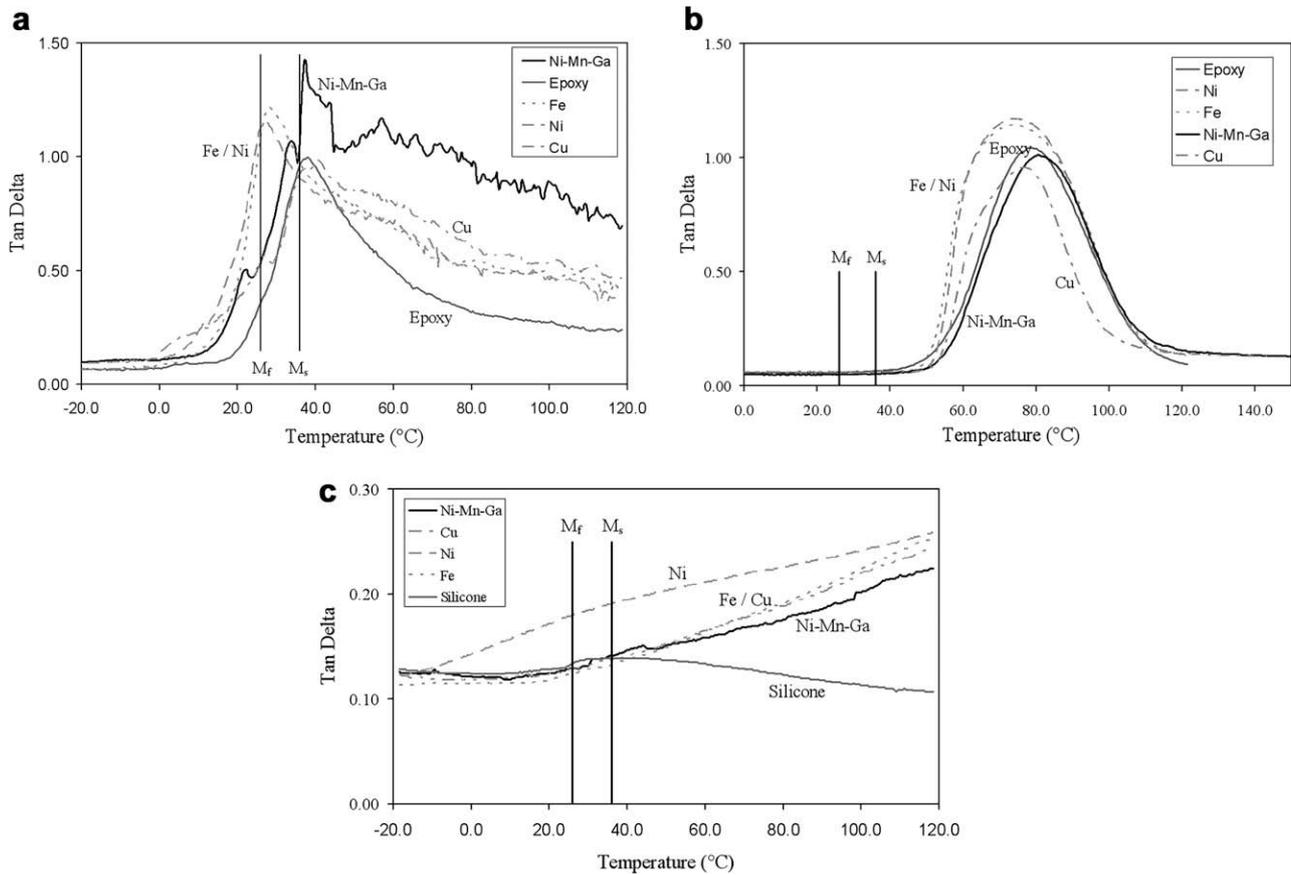


Fig. 3. Damping curves as a function of temperature for (a) epoxy Hysol 9455/powder composites, (b) epoxy Hysol 9492/powder composites, and (c) silicone Loctite 5140/powder composites.

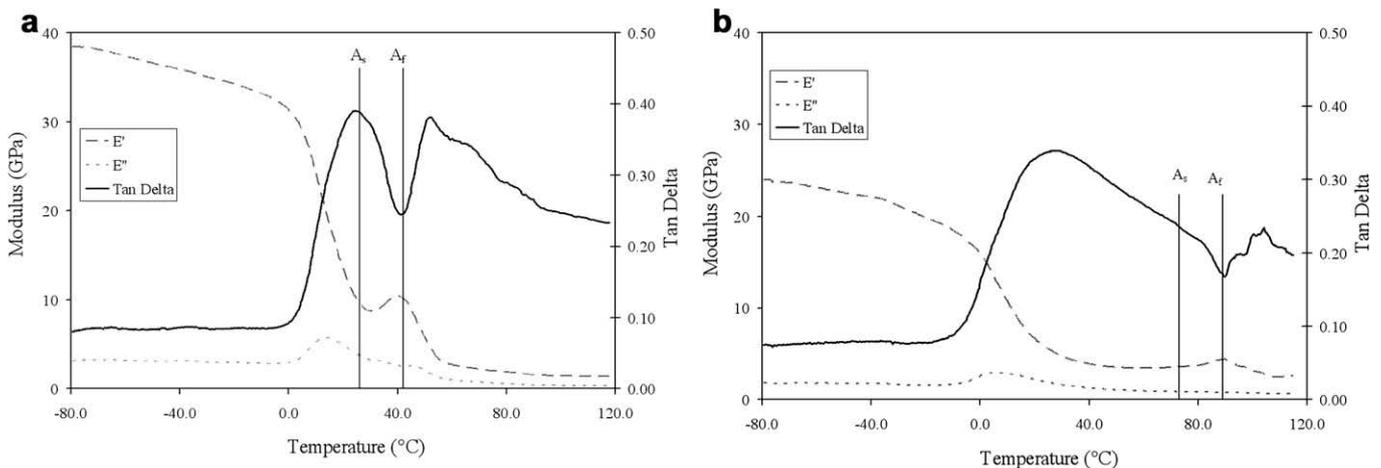


Fig. 4. DMA damping curves of (a) the ribbon (R1)/epoxy Hysol 9455 composite and (b) the ribbon (R2)/epoxy Hysol 9455 composite.

is required to achieve good damping in a Ni–Mn–Ga/polymer composite.

4. Conclusions

This study confirmed that the adhesion between matrix and Ni–Mn–Ga insert as well as damping properties while applying soft epoxy matrix having stiffness close with the Ni–Mn–Ga insert gave

the best results. In composites with this material selection, extra damping could be detected near the martensite–austenite temperature region. With too hard a matrix polymer, the Ni–Mn–Ga insert remains completely constrained without possibility for deformations needed for damping. If the matrix is too soft, it yields around the Ni–Mn–Ga particles, and the damping energy is transferred poorly. The epoxies adhered well to Ni–Mn–Ga, but the silicone only weakly.

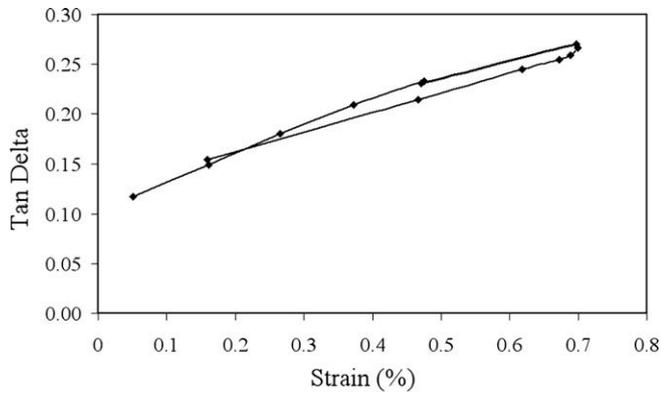


Fig. 5. DMA damping curve of bulk thin-plate Ni-Mn-Ga/Hysol 9455 composite.

Acknowledgements

We thank the Finnish Funding Agency for Technology and Innovation (Tekes) for the support.

References

- [1] Segui C, Cesari E, Pons J, Chernenko V. Internal friction behaviour of Ni-Mn-Ga. *Mater Sci Eng A* 2004;370(1–2):481–4.
- [2] Gavriljuk VG, Söderberg O, Bliznuk VV, Glavatska NI, Lindroos VK. Martensitic transformations and mobility of twin boundaries in Ni₂MnGa alloys studied by using internal friction. *Scripta Mater* 2003;49(8):803–9.
- [3] Feuchtwanger J, Michael S, Juang J, Bono D, ÓHandley RC, Allen SM, et al. Energy absorption in Ni-Mn-Ga-polymer composites. *J Appl Phys* 2003;93(10):8528–30.
- [4] Aaltio I, Lahelin M, Söderberg O, Heczko O, Löfgren B, Ge Y, et al. Temperature dependence of the damping properties of Ni-Mn-Ga alloys. *Mater Sci Eng A* 2008;481–482:314–7.
- [5] Aaltio I, Mohanchandra KP, Heczko O, Lahelin M, Ge Y, Carman GP, et al. Temperature dependence of mechanical damping in Ni-Mn-Ga austenite and non-modulated martensite. *Scripta Mater* 2008;59(5):550–3.
- [6] Hosada H, Takeuchi S, Inamura T, Wakashima K. Material design and shape memory properties of smart composites composed of polymer and ferromagnetic shape memory alloy particles. *Sci Technol Adv Mater* 2004;5(4):503–9.
- [7] Feuchtwanger J, Griffin K, Huang J, Bono D, ÓHandley RC, Allen SM. Mechanical energy absorption in Ni-Mn-Ga-polymer composites. *J Magn Magn Mater* 2004;272–276(4):2038–9.
- [8] Feuchtwanger J, Richard ML. Large energy absorption in Ni-Mn-Ga/polymer composites. *J Appl Phys* 2005;97(10):10M319.
- [9] Ham-Su R, Healey JP, Underhill RS, Farrell SP, Cheng LM, Hyatt CV, et al. Fabrication of magnetic shape memory alloy/polymer composites. In: Armstrong WD, editor. *Smart structures and materials 2005: active materials: behavior and mechanics: proceedings of SPIE*, vol. 5761. Bellingham: SPIE; 2005. p. 490–500.
- [10] Underhill RS, Stevens KA. Surfactant modified nickel-manganese-gallium powder and silicone composites. *Adv Sci Techn* 2008;59:35–40.
- [11] Segui C, Cesari E, Font J, Muntasell J, Chernenko VA. Martensite stabilization in a high temperature Ni-Mn-Ga alloy. *Scripta Mater* 2005;53(3):315–8.
- [12] Gans E, Henry C, Carman GP. High energy absorption in bulk ferromagnetic shape memory alloys (Ni₅₀Mn₂₉Ga₂₁). In: Lagoudas DC, editor. *Smart structures and materials 2004: active materials: behavior and mechanics: proceedings of SPIE*, vol. 5387. Bellingham: SPIE; 2004. p. 177–85.
- [13] Scheerbaum N, Hinz D, Gutfleisch O, Müller HK, Schultz L. Textured polymer bonded composites with Ni-Mn-Ga magnetic shape memory particles. *Acta Mater* 2007;55(8):2707–13.
- [14] Conti S, Lenz M, Rumpf M. Modeling and simulation of magnetic-shape-memory polymer composites. *J Mech Phys Sol* 2007;55(7):1462–86.