

Proceedings

Bisphenol-Free Epoxy Resins Derived from Natural Resources Exhibiting High Thermal Conductivity †

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† Presented at the First International Conference on “Green” Polymer Materials 2020, 5–25 November 2020; Available online: <https://cgpm2020.sciforum.net/>.

Published: 3 November 2020

Abstract: Polymers commonly have low thermal conductivity in the range of 0.1–0.2 W·m⁻¹·K⁻¹, which is a limiting factor for their usage in the course of continuously increasing miniaturization and heat generation in electronic applications. Two strategies can be applied to increase the transport of phonons in polymers: (i) the embedment of thermally conductive inorganic materials and (ii) the involvement of aromatic units enabling microscopic anisotropy by π – π stacking. In this study, the thermal conductivity of resins based on Bisphenol A diglycidyl ether BADGE and 1,2,7,8-diepoxyoctane DEO was compared. DEO can be derived from pseudopelletierine, which is contained in the bark of the pomegranate tree. The epoxy compounds were cured with isophorone diamine IPDA and *o*-dianisidine DAN. Notably, isophorone diamine is derived from isophorone, which naturally occurs in cranberries. The formulations were produced without filler and with 5 wt.-% of SiO₂ nanoparticles. Significantly enhanced thermal conductivity in the range of 0.4 W·m⁻¹·K⁻¹ occurs only in DEO-based polymer networks that were cured with DAN (and do not contain SiO₂ fillers). This observation is argued to originate from π – π stacking of the aromatic units of DAN enabled by the higher flexibility of the aliphatic carbon chain of DEO compared to that of BADGE. This assumption is further supported by the facts that significantly improved thermal conductivity occurs only above the glass-transition temperature and that nanoparticles appear to disrupt the π – π stacking of the aromatic groups. In summary, it can be argued that the bisphenol-free epoxy/amine resin with an epoxy compound derivable from natural resources shows favorably higher thermal conductivity in comparison to the petrol-based bisphenol-based epoxy/amine resins.

Keywords: polymers from natural resources; bisphenol-free epoxy resins; crosslinked polymers; thermal conductivity; π – π stacking

1. Introduction

Polymers are indispensable components for electronic applications such as microelectronics or in high-voltage technology [1]. In addition to the electrical insulation properties, their potential lies in their diverse positive properties such as easy processability, durability, good availability, mechanical properties or thermal and chemical resistance [2–4]. For diverse applications of polymers in the electronic industry, such as parts in microchips, the challenge arises from removing the heat generated during operation. Moore’s law, which, according to current calculations, is coming to an end soon, shows that the number of transistors on a computer chip doubles every two years [5]. There is a direct connection of the number of transistors with the generation of thermal energy. With this miniaturization and, above all, the continuing complexity in electronic components, the challenge of

sufficient heat transport becomes apparent, as active cooling elements reach their technical limits due to the fact that components are often difficult to access. In this regard, there is a need to use the highest possible thermal conductivity of all materials used in the electronic component, such that the formation of thermal insulating barrier layers is minimized [6].

For the electronic industry, epoxides have become the electrical insulation materials of choice due to their availability, low cost production, and temperature resistance. Curable epoxy thermosets, which usually consist of bivalent monomers such as Bisphenol A diglycidyl ether BADGE, are commonly cured by amines or anhydrides. These curing reactions yield a high network density, mechanical robustness and temperature stability. Epoxy/amine thermosets show a variety in the choice of available monomers, which allows a wide range of polymer properties to be tailor-fabricated. Due to the high flexibility and easy handling, these thermosets can often be implemented for commercial applications [7,8].

Due to the amorphous structure of the polymeric chains, epoxides usually exhibit low thermal conductivity in the range of $0.1\text{--}0.2\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [9]. Nonetheless, thermal conduction and electrical insulation are basic requirements for polymer-based dielectrics in modern electronic applications. Various strategies to increase the thermal conductivity can be applied. The traditional approach is the preparation of epoxy-based composites [10–12]. It should be noted that the increase of the thermal conductivity should not coincide with the deterioration of electrical insulation properties, such as a change in permittivity through the use of unsuitable fillers [13]. It is effective to add ceramic fillers with high thermal conductivity such as nitrides [14,15], oxides [16,17] or carbides [18,19], since phonons can be transported across the crystal lattice of the particle regardless of the amorphous structure of the epoxide. Hexagonal boron nitride hBN or diamond show exceptionally high thermal conductivity [20,21]. It should be noted that factors such as particle distribution, particle content or particle shape have an enormous influence on the actual heat transfer of the system, as the proximity of the heat-conducting components is a basic requirement (percolation threshold) [22,23]. Also the microscopic arrangement of polymer chains at the interface of polymer and nanoparticles has been reported [24,25], which can lead to the formation of semi-crystalline regions with enhanced conduction of phonons.

Further measurements for enhancing the thermal conductivity can be taken with regard to the chain arrangement within the polymer matrix [26]; semi-crystalline areas potentially enhance the thermal conductivity due to optimized molecular arrangement. One prominent example are aromatic units, which are arranged according to $\pi\text{--}\pi$ stacking of the ring structures, yielding anisotropic units with increased thermal conductivity. Especially biphenyl units appear to have a great potential in the formation of microscopic anisotropic units that enhance the thermal conductivity [27–29].

The amount of data of a combined effect of inorganic fillers and the presence of inorganic units is still limited [30,31]. In this study, hence, the synergism/antagonism of this approach was investigated with special respect to the flexibility of the structural motifs of the polymer chain as well as their origin from renewable resources: In addition to (comparably less flexible) BADGE, 1,2,7,8-diepoxyoctane DEO, which can be derived from pseudopelletierine (contained in the bark of the pomegranate tree), was investigated as diepoxy compound. These epoxy compounds were cured with amines, namely isophorone diamine IPDA and *o*-dianisidine DAN. Isophorone diamine is derived from isophorone, which naturally occurs in cranberries. As inorganic filler, silica nanoparticles were used.

2. Experiments

Materials and Instrumentation. DEO (>97%) and DAN (>98%) were purchased from TCI (Eschborn, Deutschland). BADGE (97%), IPDA (>98%) and SiO₂ nanopowder (5–15 nm) were purchased from Sigma Aldrich (Vienna, Austria). All chemicals were used without further purification. Glass-transition measurements were performed utilizing a Perkin Elmer Simultaneous Thermal Analyzer (STA) 6000. A heating rate of $20\text{ K}\cdot\text{min}^{-1}$ was applied. The determination of the thermal conductivity was performed using a Guarded Heat Flow Meter DTC 300. The thermal

conductivity measurements have been carried out at a temperature range of 30 to 180 °C, namely at 30, 60, 90, 120, 150, and 180 °C.

Preparation of crosslinked epoxy resins and nanocomposites. For the preparation of the unfilled and filled test specimens, 1 equiv. of BADGE or DEO was mixed with 1 equiv. of IPDA and DAN in a glass vial, wherein the two hardeners were added in the following proportions:

- 0 wt.-% IPDA; 100 wt.-% DAN; 1 equiv. of hardener
- 33 wt.-% IPDA; 67 wt.-% DAN; 1 equiv. of hardener
- 67 wt.-% IPDA; 33 wt.-% DAN; 1 equiv. of hardener
- 100 wt.-% IPDA; 0 wt.-% DAN; 1 equiv. of hardener

Since *o*-dianisidine has a melting point of 137 °C, all chemicals and templates were previously heated to 150 °C. For the production of nanocomposites, 5 wt.-% of SiO₂-nanoparticles were dispersed in the epoxy compound by sonication for 5 min prior to heating at 150 °C. By transferring the reaction mixture into a circular-shaped steel templates and curing at 150 °C for 30 min, test specimens with a diameter of 50 mm and height of 2 to 3 mm were obtained.

3. Results

In this study, $2 \times 4 \times 2 = 16$ different epoxy/amine resins and composites were prepared: This material library was composed of the epoxy compounds BADGE and DEO (2 compounds), which were cured with 100% IPDA, 67% IPDA + 33% DAN, 33% IPDA + 67% DAN or 100% DAN (4 ratios) and filled with either 0 or 5 wt.-% of nanoscaled SiO₂ (2 filler contents). The epoxy/amine resins and composites (Figure 1) were cured at 150 °C. Notably, DEO and IPDA can be derived from renewable resources.

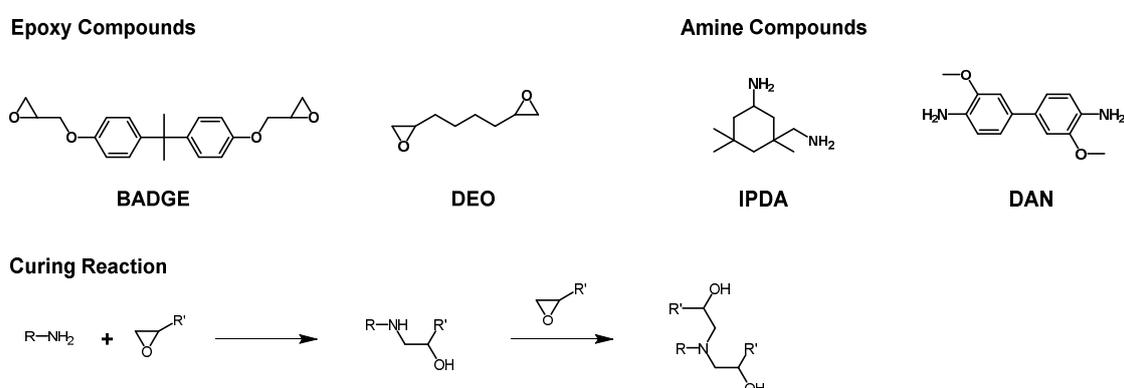


Figure 1. Top: Chemical structures of the epoxy compounds BADGE and DEO and the amine compounds IPDA and DAN. **Bottom:** Curing reaction of epoxy compounds with primary amines.

Preceded by differential scanning calorimetry measurements (for the determination of the glass-transition temperatures; not reported in here) and the calculation of the surface energy from contact-angle measurements (not reported in here), further physico-chemical characterization focused on the thermal conductivity of the resins and the composites, which was quantified by Guarded Heat Flow Meter measurements at 30, 60, 90, 120, 150, and 180 °C.

The BADGE-based resins and nanocomposites exhibit thermal conductivity in the range of 0.15 to 0.20 W·m⁻¹·K⁻¹ (Figure 2). For both types, the unfilled resins as well as the composites filled with silica nanoparticles, the increase of DAN (that contains biphenyl units) in the amine mixture, does not significantly enhance the thermal conductivity. Also the increase of temperature (above the glass-transition temperature) has no relevant effect on the thermal conductivity of the BADGE-based resins and composites.

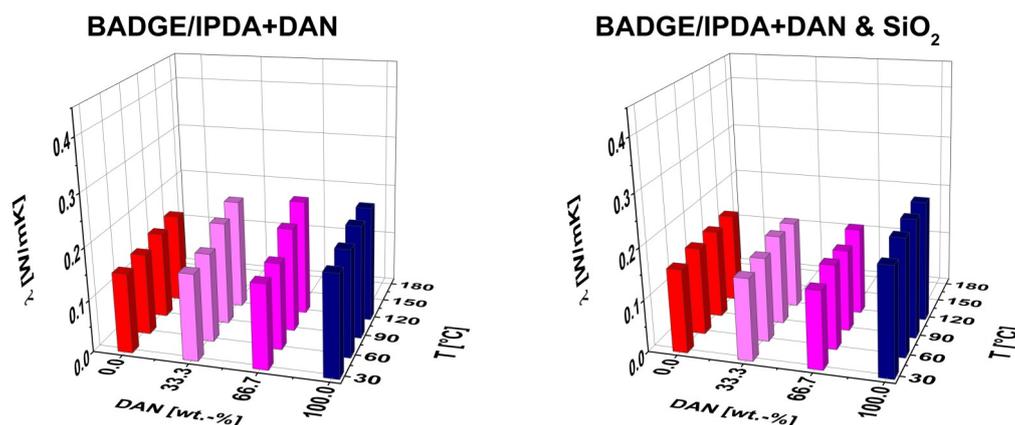


Figure 2. Thermal conductivity of unfilled BADGE-based epoxy/amine resins (**left**) and the corresponding nanocomposites with SiO₂ fillers (**right**). (For comparison, the Z-scales of Figures 2 and 3 have been drawn to the same height.).

The Guarded Heat Flow Meter measurements of the DEO-containing resins and nanocomposites, on the contrary, display trends with respect to the temperature and the filler content: At 30 °C, the thermal conductivity of both, the unfilled resins as well as the silica nanoparticle-filled composites, is in the range of 0.08 to 0.15 W·m⁻¹·K⁻¹. At temperatures of or above 90 °C, the unfilled resins and silica-containing nanocomposites that contain comparably low amounts of the amine DAN (0 and 33 wt.-%, respectively) show no significant increase of the thermal conductivity. On the other hand, the unfilled resins with comparably high amounts of DAN (67% and 100%, respectively) exhibit significantly increased thermal conductivity. Notably, the increase of the thermal conductivity is higher in the resins that were cured with DAN only and, correspondingly, contain no IPDA. Above 120 °C, hence, above the glass-transition temperature, no further increase of the thermal conductivity can be observed. In contrast, the silica nanoparticle-containing composites reproduce this trend to lesser extent.

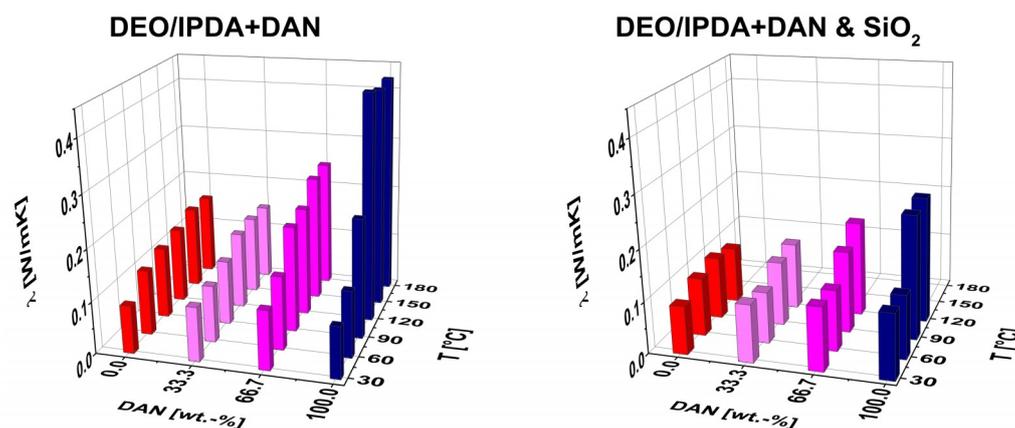


Figure 3. Thermal conductivity of unfilled DEO-based epoxy/amine resins (**left**) and the corresponding nanocomposites with SiO₂ fillers (**right**). (For comparison, the Z-scales of Figures 2 and 3 have been drawn to the same height.).

4. Discussion

The DEO-based resins and composites with 67% and 100% of DAN (as amine curing agent) exclusively exhibit increased thermal conductivity at elevated temperatures starting from 90 °C. This observation is likely to originate from π - π stacking for two main reasons: (i) The increase of the thermal conductivity occurs in particular above 90 °C, hence, above the glass-transition temperature, above which the segmental mobility increases. Correspondingly, above 120 °C, the thermal

conductivity does not increase further. (ii) In contrast to the unfilled resins, the silica nanoparticle-filled DEO-based composites show comparably lower thermal conductivity, which can be retraced to steric hindrance of π - π stacking due to the presence of the inorganic fillers (Figure 4).

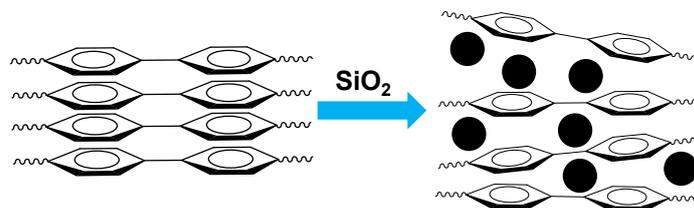


Figure 4. Disorder of the π - π stacking due to the addition of silica nanoparticles.

In contrast to the DEO-based resins and composites, the BADGE-analogues exhibit a comparably high rigidity. The epoxy monomer offers only little flexibility due to the aromatic groups in the main chain. As BADGE-containing resins and composites do not show any significant increase in the thermal conductivity, the formation of microscopic anisotropic units is assumed not to be achieved due to insufficient mobility of the polymer chain.

5. Conclusions

π - π Stacking preferably occurs in the DEO-based resins and composites. The aliphatic chains of DEO are more flexible (in comparison to BADGE) and, hence, facilitate the π - π stacking of the biphenyl units of the crosslinker DAN. Nanoparticles prevent the π - π stacking of the biphenyl groups. BADGE-based epoxy resins, on the other hand, do not show any significant increase in the thermal conductivity, since the aromatic main chain does not offer sufficient flexibility.

Notably, DEO can be derived from pseudopelletierine, which is contained in the bark of the pomegranate tree. By using DEO as epoxy compound, competitive resins and composites with enhanced thermal conductivity can be prepared.

Author Contributions: M.S.W. and E.D. prepared the test specimens; M.S.W. performed the physico-chemical analyses; M.S.W. and F.W. analyzed the data and wrote the paper. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: The research work was performed within the K-Project ‘PolyTherm’ at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology and the Federal Ministry for Digital and Economic Affairs with contributions by the Graz University of Technology. Funding is provided by the Austrian Government and the State Government of Styria.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

BADGE	Bisphenol A diglycidyl ether
DEO	1,2,7,8-diepoxy octane
DAN	<i>o</i> -dianisidine
IPDA	isophorone diamine

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