

Abstract

Polymers and polymer materials are smart invention and one of the technological driving force of twentieth century. Today, there is a strong desire for implementing self-healing properties into polymer materials, and not only that people desire products with unlimited usage-times, but also everlasting natural resources and costs in connection to the production of products, dictates production of polymer materials with self-healing properties. Therefore, presented work represents a pebble in construction of the mosaic called self-healing polymers.

In first phase of PhD thesis the Diels–Alder reaction between *N*-phenylmaleimide and benzoxazine bearing furan group was investigated for the purpose of successful appliance of self-healing in benzoxazine polymer networks. The reaction as a function of temperature/time was performed in molten state and in a solution, where also the kinetic study was performed. The Diels–Alder reaction leads to a mixture of two diastereomers: *endo* and *exo*. Therefore, the conversion rates and *exo/endo* ratio were studied in detail for both systems. For instance, in molten state the Diels–Alder reaction was triggered by the temperature of the melting point at 60 °C with *exo/endo* ratio preferable to the *endo* adduct. The study of the kinetics in a solution revealed that the Diels–Alder reaction followed typical bimolecular reversible second-order reaction. The activation energies were close to the previous literature data being: 48.4 and 51.9 kJ/mol for Diels–Alder reaction, and 91.0 and 102.3 kJ/mol for retro-Diels–Alder reaction, in acetonitrile and chloroform, respectively. The reaction equilibrium in a solution is much more affected by the retro Diels–Alder reaction than in a molten state. This study shows detailed investigation of DA reaction and provides fundamental understanding for further design of self-healing materials.

In second phase a new innovative synthetic approach for the preparation of maleimidobenzoxazines was developed. For the first time the phenolic diversity in maleimidobenzoxazine compounds was enabled, opening many possibilities for tailoring properties of maleimidobenzoxazines through phenolic diversity. The key in a successful implementation of a novel synthetic approach was utilization of aminomaleimide compound prepared by modified synthetic path, without the need for chromatographic purification. Yields of the reaction between aminomaleimide and phenols reached up to 95 %, which is a significant improvement prior to previous studies dealing with maleimidobenzoxazines. Aminomaleimide and all novel maleimidobenzoxazine substances were characterized by ¹H NMR, ¹³C NMR and IR spectroscopies. The curing behaviour of prepared maleimidobenzoxazines was investigated by DSC analysis and mechanical properties by DMA analysis. Novel maleimidobenzoxazines showed similar properties comparing to the already presented in the literature showing high glass transition temperature values over 240 °C. Thermogravimetric analysis proved improved thermal stability of maleimidobenzoxazines compared to anilinobenzoxazines. Finally, the use of prepared maleimidobenzoxazines was investigated by the means of Diels–Alder reaction as a possible benzoxazine bearing maleimide group precursor for self-healing purposes. In conclusion of second phase, successful qualitative demonstration

of self-healing potential base on Diels–Alder reaction was represented on benzoxazine material.

In third phase thermally reversible Diels-Alder (DA) adduct was incorporated via solution mixing in an aliphatic amine-curable bifunctional epoxy resin in order to trigger and support self-healing. The DA adduct was a reaction product of furan-functionalized benzoxazine (G-f) and *N*-phenylmaleimide (PMI). Epoxy formulations containing stoichiometric amount of hexamethylene diamine without (EM) and with additional DA (EMDA) were cured at 70 °C. To investigate the chemical pathway epoxies containing G-f (EMGf) and PMI (EMM) only were also produced and tested. Mechanical and thermal properties of the epoxy systems were studied by dynamical mechanical analysis and differential scanning calorimetry, respectively. For the repeated self-healing tests compact tension (CT) specimens with an arrest hole were used. Healing was achieved by a thermal cycle covering both the retro DA (140 °C) and DA formation temperature ranges (70–80 °C). Although the prepared materials were not completely cured considering their glass transition temperatures (T_g 's 60 °C), their stiffness values were similar to those of traditional epoxy systems. However, due to the incomplete curing of the epoxy formulations, self-healing was observed also in absence of the DA adduct in the reference epoxies (EM, EMM and EMGf). This T_g -assisted self-healing markedly dropped after the first healing (25 % at 1st healing cycle, 5 % at 2nd and 3rd healing cycle). Improved self-healing, compared to the reference epoxies, was detected when healing was supported by the reversible DA reaction superimposed to the T_g -assisted one (30 % at 1st healing cycle, 8 % at 2nd and 3rd healing cycle). Very high self-healing efficiency was found for the EMDA (70 % in all cycles) when the cracked CT specimens were healed at temperatures just above the T_g , i.e omitting the retro DA reaction required temperature step.

Keywords: self-healing Diels–Alder, furane, maleimide, benzoxazine.