Multifunctional Bio-based Hybrid Thermosets: Synthesis, Characterization and Potential Use in Composites

Final report

This collaboration project between the Department of Polymer Engineering of the Budapest University of Technology and Economics, Budapest, Hungary and the Faculty of Chemistry and Chemical Engineering of the University of Ljubljana, Ljubljana, Slovenia is aimed originally at exploring the Diels-Alder (DA) chemistry for benzoxazine (BOX)/epoxy (EP) resin combinations to create multifunctional polymers and related composite systems. A further emphasis of the project was put on using chemicals from renewable resources when synthesizing BOX-derivatives, EP resins and hardeners of the latter. During the common work, however, the DA reaction possibility was explored in other polymers than BOX/EP systems, namely in polyurethane (PU) resins. This was reasoned by two facts: i) some of the initially proposed synthesis routes did not work at the Slovenian group, and ii) the very versatile chemistry makes PUs them ideal candidates to explore the potential of DA coupling. Beside of the DA modification, however, other chemical and physico-chemical aspects have also been taken into account to produce multifunctional EP-based systems. The latter was related to blending of EP with thermoplastics. The results achieved on these three groups of the investigated materials, viz. BOX/EP, PU and EP/polycaprolactone (PCL), are listed along with the related publications below. It is worth of noting that the results have also been presented in several international conferences [1-6]. The potential of the reversible DA reaction in different polymeric systems, covering also EP and EP/BOX hybrids, was outlined in two papers [7-8].

1) BOX/EP systems

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) – cf. Figure 1 - were cured at 70 ^{o}C.

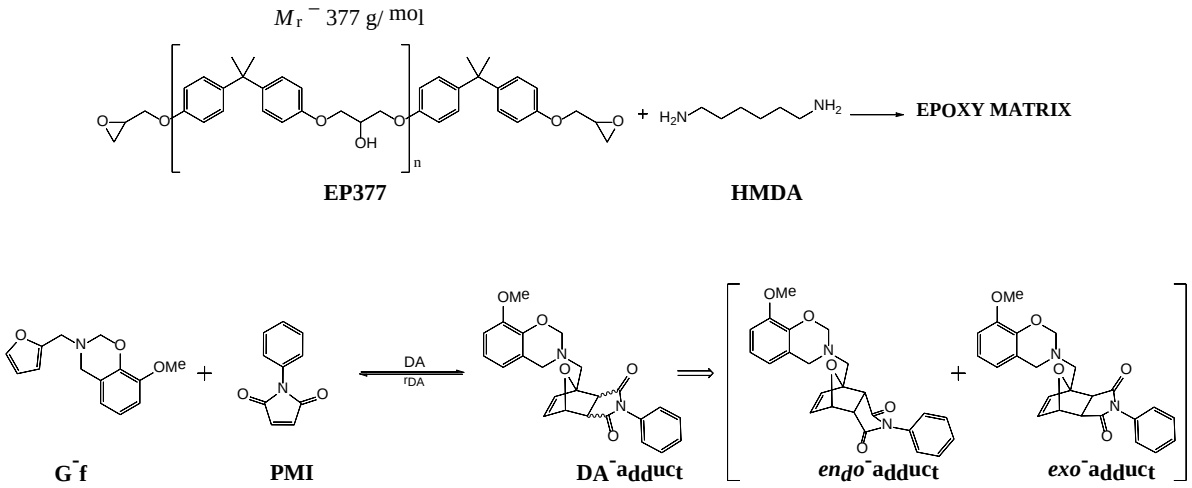

Figure 1. Chemical representation of the polymer matrix and DA system

Note that the renewable chemistry is given by the G-f compound. To check the chemical pathway epoxies containing G-f (EMGf) and PMI (EMM) only were also produced and tested. Mechanical and thermal properties of the EP 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 (cf. Figure 2).

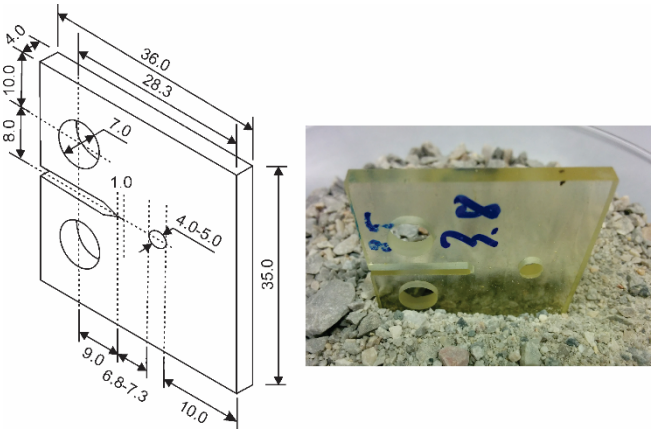

Figure 2. Compact tension (CT) specimen geometry (left) and processed (healed) specimen (right) used in the fracture toughness measurements

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 EPs. However, due to the incomplete curing of the epoxy formulations, self-healing was observed also in absence of the DA adduct in the reference EPs (víz. 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 EPs, 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 for the retro DA reaction required temperature step. Accordingly, in this T_g-assisted healing of EMDA the DA reactions might also be involved. The above results are summarized in a recently submitted paper [9]. Unfortunately, no healing could be observed with the above EP-based systems when adapting the microdroplet test for single fiber composite specimens. Therefore, no further composite specimens were produced.

To support our work and acquire the state-of-art knowledge the strategies to generate multifunctional properties, especially shape memory (SM) and self-healing, in EP resins were surveyed and shared with the peers [10].

2) PU systems

A basic learning from the literature survey was that the DA chemistry may be well adapted for polyurethanes (PUs). Therefore the project was extended to check this possibility. First linear polyurethanes (diisocyanate type and molecular weight of the polycaprolactone diol varied) have been produced with DA adducts in their main chains. These PUs were multifunctional polymers exhibiting promising shape memory behavior [11]. As follow-up of the former study with linear PUs [11], crosslinked PUs containing irreversible (allophanate) and reversible Diels-Alder chemical bonds were synthesized using various diisocyanates (methylene diphenyl diisocyanate MDI, 1,6-hexamethylenediisocyanate HDI) and poly(ε-caprolactone) (PCL) with different molecular weights as diol component. The melting/crystallization of PCL and the reversible DA bonds acted as temperature-activated switches for shape memory performances, while allophanate network provided the permanent crosslinks for these PUs. The reversible DA bonds were obtained by the reaction of diisocyanate-ended prepolymers with furfurylamine (FA) followed by the addition of bismaleimide (BMI). The permanent crosslinks between the linear chains containing DA bonds were achieved using additional amounts of diisocyanates (MDI or HDI). The above reaction path was supported by infrared spectroscopic results and swelling experiments. Tensile mechanical and shape memory (SM) properties in tension of the PUs were determined and discussed as a function of composition and crosslink densities deduced from swelling and dynamic mechanical analysis [12]. Noticing that the relative amount of the DA coupling sites in the above linear and crosslinked PUs was rather low, we made a further attempt to increase the occurrence of the DA sites. The related strategy was a straightforward combination of the PU and EP chemistry as highlighted in Figure 3.

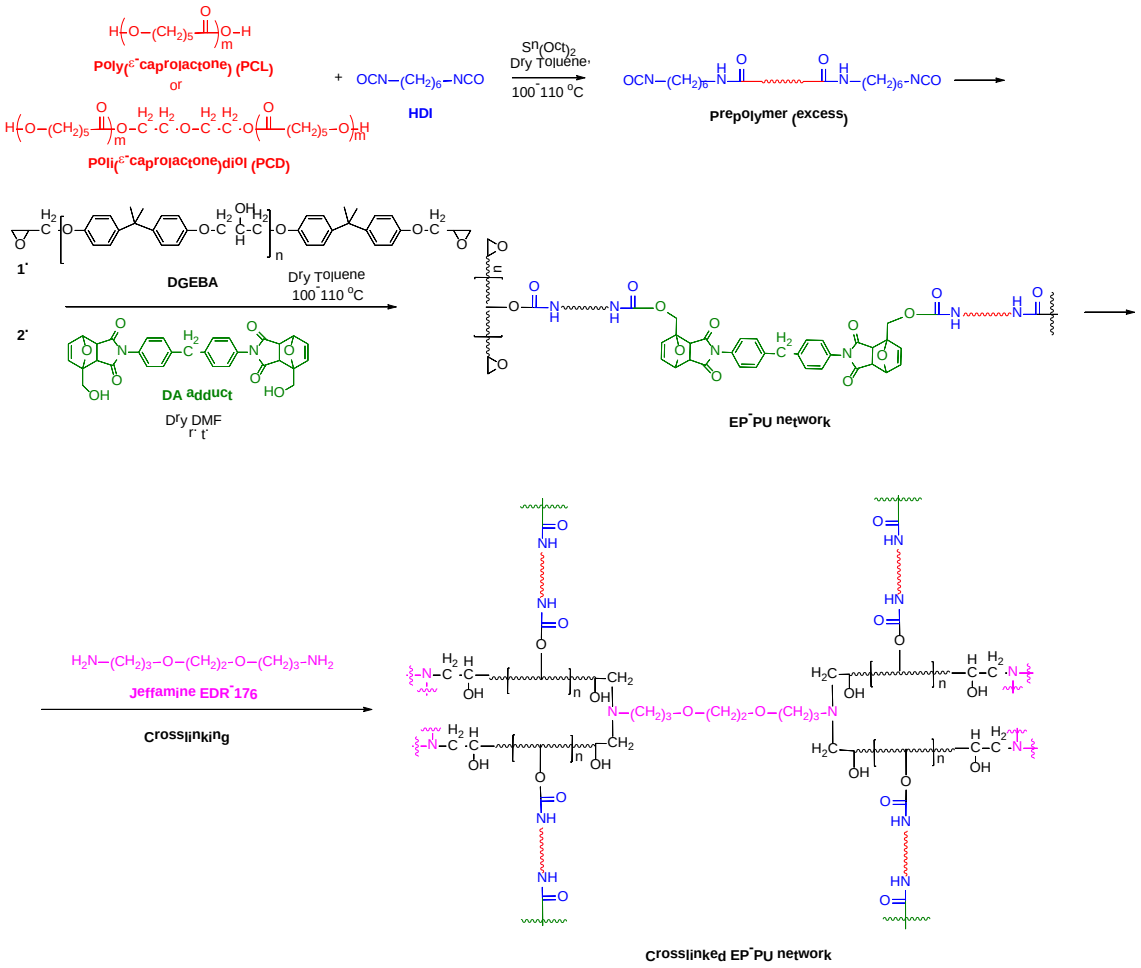

Figure 3. Synthetic pathway for the preparation of EP-PU conetworks containing DA-adducts.

The newly synthesized conetwork showed interesting SM behavior and the related work is now in submission stage [13]. Recall that in this part of the project the renewable aspect was considered by using PCL. This note holds also for the next part below.

3) EP/PCL blends

One of the basic learning from the works [11-12] was that the SM properties were controlled by the PCL and the role of the DA sites was marginal. This forced us to check the effect of PCL as possible healing and SM "switching" phase in EP [14]. It was found that the transition of PCL from disperse to continuous phase depends not only on the PCL amount, but also on the EP type and its curing. EP/PCL systems with semi-interpenetrating (semi-IPN, bi-continuous) network structure exhibited markedly higher healing efficiencies compared to those in which PCL was present as disperse phase. The healing efficiency depended also on the temperature difference between the healing temperature and the glass transition (T_g) of the EP with respect to that of the melting of PCL [14].

Possibilities to create a „smart interphase" in polymer composites have been summarized and updated forms of a review paper [15] and a book chapter [16]. Compiling the latter works and having in mind

the self-healing results achieved on EP/PCL blends, we have introduced a new concept, coined as "3D printing-assisted interphase engineering" [17]. Though the concept is general, thereby covering all possible interphase/matrix combinations, we checked it by patterning carbon fiber fabric with thermoplastic PCL prior to infiltrating it with an amine-curable EP resin. This interphase modification resulted in a pronounced improvement in ductility under static flexure, suggesting that some "intermittent bonding" of the reinforcement develops. Intermittent bonding means that the reinforcement „sees" EP and PCL phases alternatingly. Provided that the CF sizing was developed for EP then a good/weak bonding appear intermittently thereby considering the critical fiber length of the actual reinforcement during patterning with PCL. The latter occurred in fused deposition-type additive manufacturing process. The PCL-rich interphase healed well, and thus a remarkable restoration of the properties was observed in static flexure after heat treatment in the previously fractured specimen [17]. The patterned PCL-phase should work also for SM that was however not checked.

Additional remarks: in the framework of this project we were able to purchase a thermogravimetric analyzer (though in a 2nd trial) that we strongly needed to accomplish this project. Further, due to bad experience with the Hungarian public tendering (alias "közbeszerzés") some of the travels of JKK were financed by other sources including his own pocket. Last but not least, special attention was paid to publish the results in "open access" journals in order to meet the actual NKFIH requirements.

References:

1. J. Karger-Kocsis: (Multi)functional polymers and composites: Exploitation of the Diels-Alder reaction (invited lecture), PolymerTec-16, Merseburg (Germany), 15-17.06.2016
2. J. Karger-Kocsis: Chemical aspects in recent R&D works on polymers and composites (plenary lecture), Slovenian Chemical Days, Portoroz (Slovenia) 28-30.09.2016
3. J. Karger-Kocsis: Multifunctional polymers/composites via Diels-Alder reactions, (invited lecture, „Neujahrsvortrag"), Institut für Biomaterialforschung, Helmholtz-Zentrum Geesthacht GmbH, Berlin-Teltow (Germany), 13.01.2017
4. J. Karger-Kocsis: Some chemical aspects in recent R&D works on polymers and composites (plenary lecture), PACCON-2017- Green Convergence on Chemical Frontiers, Bangkok (Thailand), 2-3.02.2017
5. J. Karger-Kocsis: 3D Printing-assisted interphase engineering in polymer composites (invited lecture), Danube Vltava Sava Polymer Meeting, Wien (Austria), 5-8 September 2017
6. J. Karger-Kocsis: Recent trends in interphase/interlaminar engineering in composites (plenary lecture), Milan Polymer Days, Milano (Italy), 14-16.02. 2018

7. J. Karger-Kocsis: (Multi)functional polymers and composites via Diels-Alder reactions.- eXPRESS POLYM. LETT., 10 (2016), 525. DOI: 10.3144/expresspolymlett.2016.49

8. J. Karger-Kocsis: Multifunkciós polimerek és kompozitjaik: A Diels-Alder reakció szerepe. – Magyar Kémikusok Lapja 71 (2), 2016, 49-50

9. Ž. Štirn, A. Ručigaj, J. Karger-Kocsis and M. Krajnc: Effects of Diels-Alder adduct and glass transition on the repeated self-healing of aliphatic amine-cured epoxy resin (submitted)

10. J. Karger-Kocsis and S. Kéki: Review of progress in shape memory epoxies and their composites.- POLYMERS 10 (2018), 34

11. Cs. Lakatos, K. Czifrák, R. Papp, J. Karger-Kocsis, M. Zsuga and S. Kéki: Segmented linear shape memory polyurethanes with thermoreversible Diels-Alder coupling: Effects of polycaprolactone molecular weight and diisocyanate type. - eXPRESS POLYM. LETT., 10 (2016), 324-336.

12. Cs. Lakatos, K. Czifrák, J. Karger-Kocsis, L. Daróczi, M. Zsuga and S. Kéki: Shape memory crosslinked polyurethanes containing thermoreversible Diels-Alder couplings.- J. APPL. POLYM. SCI., 133 (2016), 44145

13. K. Czifrák, Cs. Lakatos, J. Karger-Kocsis, L. Daróczi, M. Zsuga and S. Kéki: One-pot synthesis and characterization of novel shape-memory poly(ε-caprolactone) based polyurethane-epoxy conetworks with Diels-Alder couplings (submitted)

14. J. Karger-Kocsis: Self-healing properties of epoxy resins with poly(ε-caprolactone) healing agent. - POLYM. BULL. 73 (2016), 3081-3093

15. J.Karger-Kocsis, H. Mahmood and A. Pegoretti: Recent advances in fiber/matrix interphase engineering for polymer composites. PROGR. MATER. SCI., 73 (2015), 1-43; DOI: 10.1016/j.pmatsci.2015.02.003

16. J. Karger-Kocsis, S. Kéki, H. Mahmood and A. Pegoretti: Interphase engineering with nanofillers in fiber-reinforced polymer composites in “INTERFACE/INTERPHASE IN POLYMER NANOCOMPOSITES”, Eds.: A. N. Netravali and K. L. Mittal, Scrivener Publishing, Beverly, MA, USA, 2017, Chapter 2, pp. 71-101

17. G. Szebényi, T. Czigány, B. Magyar and J. Karger-Kocsis: 3D printing-assisted interphase engineering of polymer composites: Concept and feasibility. - eXPRESS POLYM. LETT., 11 (2017), 525-530