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Natural antioxidants: a new way to stabilize polyethylene

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Résumé of the PhD Thesis

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1 Introduction

335 million tons of plastics were produced in 2016 worldwide, and the amount is increasing dynamically. This data clearly represents the decisive role of polymers in our daily life. Nearly one third of this huge amount comes from the production of polyethylene (PE), which proves the importance of this polymer group. Development and increasing production rate is required to satisfy this large demand, which leads to increased load on the material. Elevated temperature, shear forces and the small concentration of available oxygen initiate radical chain reactions, leading to difficulties during production or even to product failures.

The routes of degradation and the ways of stabilization have been studied for a long time¹. The main degradation processes are well known and effective stabilizer packages were developed, usually consisting of a primary and a secondary stabilizer. Primary stabilizers are typically radical scavenging hindered phenols, which scavenge radicals by hydrogen atom transfer from their phenolic hydroxyl groups. Secondary stabilizers decompose peroxides and they often contain phosphorous functional groups. The Laboratory of Plastics and Rubber Technology and the Polymer Physics Research Group have been working on this field since decades. Their cooperation with important industrial partners, like Tiszai Vegyi Kombinát, Clariant, and later Sabic, led to the development of efficient stabilizer packages applied by the industry even today.

Numerous questions have been answered during the years, and although the topic is not in the center of scientific interest at the moment, public demand towards health protection and changing regulations can heavily affect the currently applied synthetic, classic, hindered phenolic stabilizers and the polyolefin

¹Zweifel, H. Stabilization of Polymeric Materials. Berlin: Springer, 1998.

producing industry in general. The results of Brocca and coworkers² initiated considerable interest after the millennia. They proved that small molecular weight phenols are able to migrate out from the polyethylene matrix and their questions regarding this risk have not been answered properly since then. Stabilizers have to pass serious risk assessments before their application in products, especially in those products which are in contact with the human body or with beverages, however the effect of the reaction products of synthetic phenols on the human health are still unknown.

On the other hand, numerous natural substances have beneficial effects on human health, their antioxidant and antiviral activities are proved and well known. Natural antioxidants are applied by medicine since ancient times, but they are used recently as additives in beverages and some of them showed stabilizing effect in polymers too. The application of natural antioxidants as processing stabilizers for polyolefins was a novel approach which led to the writing of the PhD thesis of Dóra Tátraaljai.

This approach and the related papers form the groundwork of my thesis. The aim of our research was the throughout characterization of natural antioxidants as primary stabilizers in polyethylene, and the understanding of relationships among the physical properties, chemical structure, interactions and stabilizing efficiency of natural antioxidants.

2 Experimental part

An additive-free ethylene-1-hexene type copolymer powder (*MOL Petrochemicals*) was used in these studies, which was polymerized by a Phillips type catalyzer. The stabilizing efficiency of the following natural antioxidants: curcumin (*Sigma Aldrich*), quercetin (*Sigma Aldrich*), silymarin (*University of*

²Brocca D, Arvin E, Mosbæk H. Identification of organic compounds migrating from polyethylene pipelines into drinking water. *Water Res* 2002;36:3675-80.

*Debrece*n), rutin (*University of Debrece*n), dihydromyricetin (*Y&L Biotech*) and silybin (*Sigma Aldrich*) were studied under processing conditions of polyethylene, while the synthetic, hindered phenolic stabilizer Irganox 1010 (*Ciba*) was used as an industrial reference. The phosphonite mixture of Sandostab PEPQ (*Clariant*) was applied as secondary stabilizer in all the studied samples. Additive packages were created which contained a chosen primary and the secondary stabilizer in various amounts and they were added to the polymer powder. The mixtures were extruded six times consecutively with the following zone temperatures: 180 °C, 210 °C, 260 °C, 260 °C. Granulate samples were taken after each extrusion steps. These granules were used for characterization, except in the case of FTIR analysis: for which ~100 µm thin films were compression molded at 190 °C, 2 minutes preheating and 3 minutes molding times by a laboratory machine. The concentration of functional groups in polyethylene (vinyl and carbonyl) and the remaining amount of PEPQ were determined by FTIR spectroscopy, the spectra were recorded between 4000-400 cm⁻¹, with 2 cm⁻¹ resolution and 16 scans. Changes in the viscosity of the polymer were followed by the measurement of its melt flow rate (MFR) at 190 °C and 2.16 kg load. The residual thermo-oxidative stability of the samples was characterized by their oxidation induction time (OIT) at 200 °C in oxygen atmosphere. The color of the samples was characterized by the measurement of their yellowness index (YI) and optical L* parameter after each extrusion step. Molecular dynamic calculations were used for the characterization of interactions between the primary and secondary stabilizers were implemented, but FTIR, DSC and TGA measurements were also carried out on stabilizer mixtures.

3 Results

Based on some preliminary results we could conclude, that the natural antioxidant curcumin is more efficient processing stabilizer than the industrial reference, and its efficiency is further improved by the addition of the PEPQ secondary stabilizer. The effects of the substance is considerable even at 5 ppm concentration: it hinders the reaction of vinyl groups, the oxidation of the polymer chain and the depletion of PEPQ during processing (see Figure 1). The natural antioxidant prevents the decrease of the MFR of the polymer, which might even increase slightly during processing, if applied at least at 250 ppm concentration.

We found that the reactions of vinyl groups do not lead to the formation

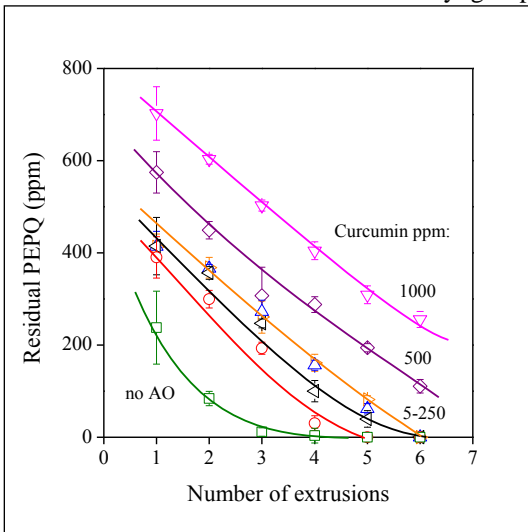


Figure 1: Effect of additive concentration and processing history on the residual amount of phosphonite antioxidant in polyethylene stabilized with 0 (□), 5 (○), 25 (◁), 50 (△), 100 (▷), 500 (◇), and 1000 (▽) ppm curcumin in combination with 1000 ppm PEPQ.

of long chain branches if a sufficiently large concentration of PEPQ is still present in the polymer. The larger residual PEPQ concentration beneficially influences also the residual thermo-oxidative stability of the samples. Because of these reasons the protection of PEPQ is of utmost importance during processing. The reason for the surprisingly large efficiency of curcumin lies in its chemical structure: not only its phenolic hydroxyl

groups, but the conjugated linear chain between its aromatic rings also participates in the stabilization reactions. Its double bonds react with the alkyl centered radicals formed during the processing. Curcumin outperformed the hindered phenolic reference stabilizer in the hindrance of the formation of long chain branches and in the protection of PEPQ.

The stabilizing efficiency of the flavonolignan mixture silymarin (Si) is compared to the flavonoid type natural antioxidant studied earlier, quercetin (Q). Figure 2 shows that silymarin is unable to prevent the formation of long chain

branches, resulting in the decrease of the MFR of the polymer. Flavonolignans in silymarin lack the catechol moiety, which carries the most active hydroxyl groups of the flavonoid backbone. The available hydroxyl groups in the silymarin mixture have larger O-H bond dissociation enthalpies (BDE) than the ones in quercetin, which leads to decreased efficiency. Moreover, the consumption of PEPQ accelerates

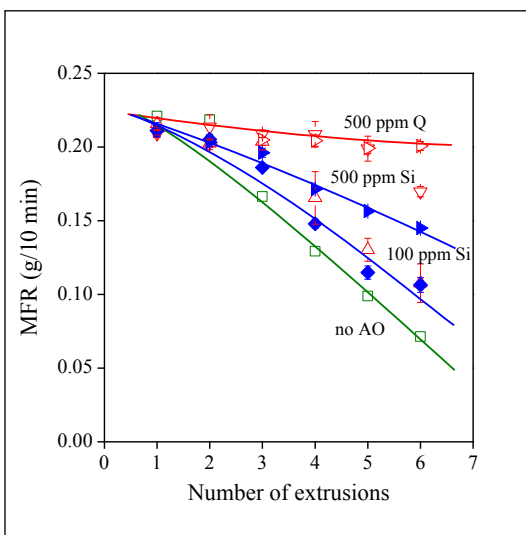


Figure 2: Comparison of the melt stabilization efficiency of the natural antioxidants studied. Symbols: (□) no antioxidant, (◆) 100 ppm Si, (▲) 500 ppm Si, (△) 25 ppm Q, (▽) 50 ppm Q, (▷) 500 ppm Q.

ates in the presence of silymarin, at least at small antioxidant concentrations, which can be explained with the chemical structure of the mixture, or with the formation of unfavorable interactions between silymarin and PEPQ, which is

confirmed by the changing of the thermal properties of silymarin and PEPQ in their blends.

Rutin (R) is a flavonoid glycoside, its chemical structure differs from quercetin only by the rutinose disaccharide group attached to ring C. The stabilizing efficiency of rutin is nearly equal to quercetin if applied at least at 100

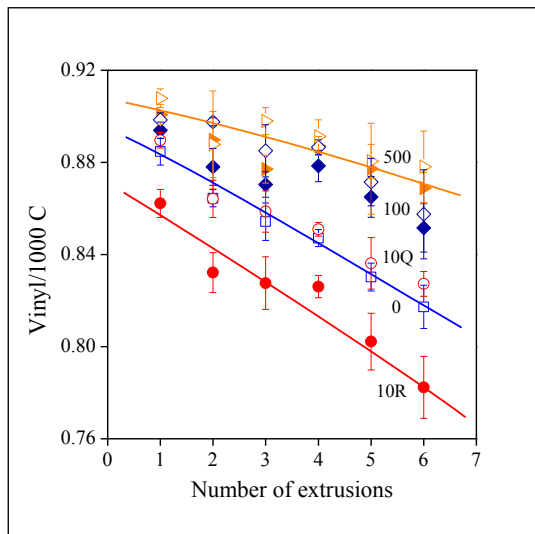


Figure 3: Effect of the number of extrusion steps and additive concentration on the vinyl group content of PE. Symbols: (□) neat, (○, ●) 10 ppm, (◇, ◆) 100 ppm, (▷, ►) 500 ppm additive; empty: quercetin, full: rutin.

ppm concentration. Below that amount however, quercetin outperforms rutin: the additive deteriorates the stability of the neat polymer if it is applied at 5-10 ppm concentration (see Figure 3), just as we saw in the case of silymarin. The number of available phenolic hydroxyl groups and their BDE values decrease somewhat due to the presence of the rutinose moiety, however, this phenomenon does not explain the different efficiency of rutin at small and large concentrations. FTIR and DSC measurements of mixtures containing the two natural antioxidants and PEPQ showed that dissimilar interactions formed between the primary and secondary stabilizers. The development of various interactions was proved also by molecular dynamic calculations. Based on these results we can conclude that hydrogen bonding and π - π interactions form between quercetin and PEPQ, while only the

ppm concentration. Below that amount however, quercetin outperforms rutin: the additive deteriorates the stability of the neat polymer if it is applied at 5-10 ppm concentration (see Figure 3), just as we saw in the case of silymarin. The number of available phenolic hydroxyl groups and their BDE values decrease somewhat due to the presence of the rutinose moiety, however, this phenomenon does not explain the different

latter was develops between rutin and PEPQ. However, the hydroxyl groups located in ring **B** of these flavonoids do not participate in any of these interactions, thus the poor efficiency of rutin cannot be explained by the effect of interactions. Decreased efficiency is caused by the poor thermal stability and thermo-oxidative decomposition of the rutinoside group under the processing conditions of polyethylene, which negatively affects the stabilization.

All of the studied natural antioxidants had coloring effects on the polymer even at small concentrations. The flavonoid type natural substance, dihydromyricetin (DHM), is a white material, because of the lack of double bond in its ring **C** ring, which could solve the undesired coloring effect. Dihydromyricetin hindered the formation of long chain branches and protected the secondary stabilizer from consumption more efficiently than quercetin, but the two flavonoid substances provided nearly the same residual thermo-oxidative stability for the polymer (see Figure 4). The reasons of these results originated partly from the smaller BDE values of the hydroxyl groups of dihydromyricetin compared to quercetin, but the different nature of interactions between the primary stabilizers and PEPQ also plays a role. The number of

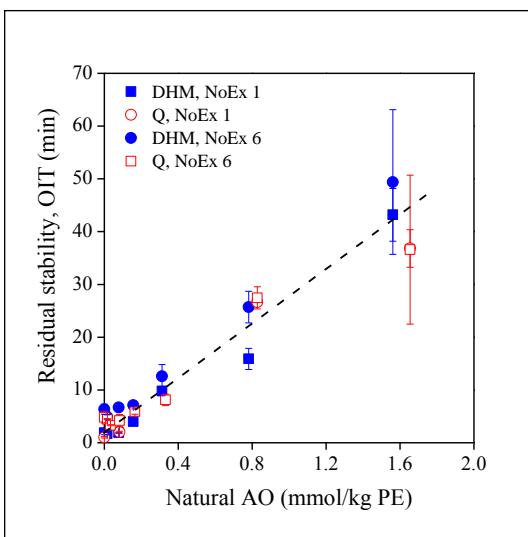


Figure 4: Unique correlation between the amount of the natural antioxidant used and the residual stability (OIT) of polyethylene. Symbols: (○) Q, 1st extrusion, (●) DHM, 1st extrusion, (□) Q, 6th extrusion, (■) 6th extrusion.

residual thermo-oxidative stability for the polymer (see Figure 4). The reasons of these results originated partly from the smaller BDE values of the hydroxyl groups of dihydromyricetin compared to quercetin, but the different nature of interactions between the primary stabilizers and PEPQ also plays a role. The number of

available hydroxyl groups, on the other hand, does not influence stabilizing efficiency. Contrary to expectations, dihydromyricetin colored the polymer with a characteristic brownish hue, which becomes intense with the increase of the amount of stabilizer or the number of extrusion steps. The coloring effect is caused by the quinoidal reaction product of dihydromyricetin, the concentration of which increases with processing time.

The stabilizing efficiency of the natural mixture silymarin, and its main component, silybin, were compared to each other. Silymarin outperformed silybin both in the hindrance of reactions of the vinyl groups and in the prevention

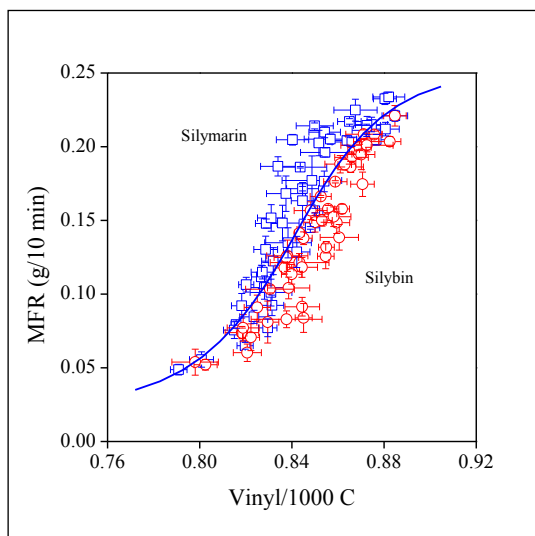


Figure 5: General correlation between the vinyl group content of polyethylene and its viscosity (MFR). Differences in the efficiency of the two products. Symbols: (○) silybin, (□) silymarin.

of long chain branching (see Figure 5), when it was applied at least at 100 ppm concentration. At small concentrations however, silymarin provided worse stability than the sample containing only PEPQ without any primary stabilizer, just as we saw in the case of rutin. The phenomenon can be explained by the composition of the silymarin mixture: accompanying components prevent the formation of crystallin-

ity the material, which increases the solubility of the additive in the matrix. However the mixture contains components (silydianin, silychristin) the BDE

values of which are smaller than that of silybin. The poor efficiency of the mixture is caused by the thermal instability of silymarin and its interaction with PEPQ.

4 Novel scientific results, thesis points

1. We proved that the secondary stabilizer plays an important role in the determination of high temperature oxidative stability of polyethylene if applied in combination with non-hindered phenolic antioxidants too [2].
2. We pointed out that curcumin is also an efficient stabilizer of PE and that not only its phenolic -OH groups, but the double bonds in the linear linkage between the two methoxyphenyl rings also take part in stabilization reactions. The double bonds react with alkyl radicals thus preventing the formation of long chain branches [2].
3. Through the analysis of the chemical structure of the natural antioxidants, we pointed out that the bond dissociation enthalpy of their phenolic hydroxyl groups play an important role in their efficiency as stabilizers under the processing conditions of polyolefins. However, other factors may also influence stabilization [5].
4. We established that rutin, another flavonoid type antioxidant, is also an efficient stabilizer, but its efficiency is decreased at small concentrations because of the partial decomposition of the saccharide moieties [7].
5. Using various measurements and model calculations, we proved that natural antioxidants and the secondary stabilizer used in the additive package can interact with each other. The interaction may leave the stabilizing efficiency of the natural antioxidant intact, but occasionally it can have a negative effect on efficiency [7].

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6. In another series of experiments carried out with dihydromyricetin as natural antioxidant, we pointed out that one result of additive interactions can be the efficient protection of the secondary antioxidant. Dihydromyricetin protects the secondary antioxidant better than other natural antioxidants examined by us and less phosphonite secondary stabilizer is consumed in its presence during processing than with the others [3].

 7. We proved the first time that the natural extract of flavonolignans could be a more efficient stabilizer than its main purified component. The better effect is the result of the multicomponent nature of the extract containing more efficient components and its improved solubility resulting from the presence of the accompanying natural compounds other than flavonolignans [8].

5 Possible applications of the results

The early stages of the research was carried out in collaboration with the polyolefin producer Tiszai Vegyi Kombinát (later MOL Petrochemicals). An additive package containing curcumin was developed and even the production of films stabilized with this package begun on a pilot line. However the project stopped at that point because of the severe UV sensitivity of curcumin. The understanding of the relationships among the chemical structure, interactions and stabilizing efficiency of flavonoid type antioxidants is very important for the future, in case the regulations prohibit the application of additives with any chance of risk to human health.

6 Publications

6.1 List of relevant publications

1. Tátraaljai D, Kirschweng B, Kovács J, Földes E, Pukánszky B.: *Processing Stabilization of PE with a Natural Antioxidant, Curcumin*, European Polymer Journal, **49**:1196-1203, 2013, IF: 3,477, I: 28.
2. Kirschweng B, Tátraaljai D, Földes E, Pukánszky B.: *Efficiency of curcumin, a natural antioxidant, in the processing stabilization of PE: Concentration effects*, Polymer Degradation and Stability, **118**:17-23, 2015, IF: 3,120, I: 11.
3. Kirschweng B, Bencze K, Sárközi M, Hégyely B, Samu Gy, Hári J, Tátraaljai D, Földes E, Kállay M, Pukánszky B.: *Melt stabilization of polyethylene with dihydromyricetin, a natural antioxidant*, Polymer Degradation and Stability, **133**:192-200, 2016, IF: 3,120, I: 40.
4. Kirschweng B, Bencze K, Sárközi M, Hári J, Tátraaljai D, Földes E, Pukánszky B.: *Phillips típusú polietilén feldolgozási stabilizálása a dihidromyricetin természetes antioxidáns felhasználásával*, Polimerek, **3(5)**:151-155, 2017, IF: 0.
5. Kirschweng B, Vörös B, Tátraaljai D, Földes E, Pukánszky B.: *Natural antioxidants as melt stabilizers for PE: comparison of silymarin and quercetin*, European Polymer Journal, **90**:456-466, 2017, IF: 3,477, I: 4.
6. Kirschweng B, Tátraaljai D, Földes E, Pukánszky B.: *Natural antioxidants as stabilizers for polymers*, Polymer Degradation and Stability, **145(11)**:25-40, 2017, IF: 3,386, I: 12.
7. Kirschweng B, Tilinger MD, Hégyely B, Samu Gy, Tátraaljai D, Földes E, Pukánszky B.: *Melt stabilization of PE with natural antioxidants: Comparison of rutin and quercetin*, European Polymer Journal, **103**:228-237, 2018, IF: 3,531, I: 2.
8. Kirschweng B, Vörös B, Arroussi M, Tátraaljai D, Pukánszky B.: *Melt stabilization of polyethylene with natural antioxidants: comparison of a natural extract and its main component*, **under review**.

6.2 Oral- and poster presentations

1. Tátraaljai D., Kirschweng B., Kovács J., Földes E., Pukánszky B.: A kurkumin hatása a polietilén feldolgozási stabilitására Kutatóközponti Tudományos Napok 2011, Budapest, MTA-KK, 2011. November 24. (*oral presentation*)
2. Tátraaljai, D., Kirschweng, B., Kovács, J., Földes, E., Pukánszky, B.: The Effect of Curcumin on the Processing Stability of Polyethylene, International Conference on Bio-Based Polymers and Composites 2012, Siófok, Hungary, May 27-31, 2012 (*poster*)
3. Tátraaljai, D., Kirschweng, B., Péntes, G., Szabó, P.T., Földes, E., Pukánszky, B.: Natural antioxidants – study of the processing stabilizing efficiency and mechanism of curcumin in polyethylene, Modification Degradation Stabilization Conference 2012, Praha, Czech Republic, September 2-6, 2012 (*oral presentation*)
4. Kirschweng, B., Tátraaljai, D., Földes, E., Pukánszky, B.: Processing stabilization of polyethylene with curcumin: effect and mechanism, International Conference on Bio-Friendly Polymers and Polymer Additives: From Scientific Aspects to Processing and Applications 2014, Budapest, Hungary, May 19-21, 2014 (*poster*)
5. Kirschweng, B., Tátraaljai, D., Földes, E., Pukánszky, B.: Processing stabilization of polyethylene with curcumin: effect and mechanism, 2nd International Conference on Bio-Based Polymers and Composites 2014, Visegrád, Hungary, August 24-28, 2014 (*poster*)
6. Kirschweng, B., Tátraaljai, D., Földes, E., Pukánszky, B.: Stabilization of Polyethylene with Natural Antioxidants, CEITEC - Polymer service-life: Estimation, durability and controlled performance, Brno, Czech Republic, October 22, 2014 (*oral presentation*)
7. Kirschweng, B., Tátraaljai, D., Földes, E., Pukánszky, B.: Processing stabilization of polyethylene with curcumin: effect and mechanism, XII. Oláh György Doktori Iskola Konferencia, Budapest, Hungary, February 5, 2015 (*poster*)

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8. Tátraaljai, D., Kirschweng, B., Havas, Zs., Földes, E., Pukánszky, B.: Stabilization of polyethylene with natural antioxidants: advantages and drawbacks, Biomaterials International, Kenting, Republic of China, June 1-5, 2015 (*oral presentation*)
 9. Kirschweng, B., Tátraaljai, D., Zsuga, M., Földes, E., Pukánszky, B.: Study of the stabilizing efficiency of rutin, a flavonoid type natural antioxidant in polyethylene under processing conditions, Polymer Degradation Discussion Group Conference, Stockholm, Sweden, August 30 - September 3, 2015 (*poster*)
 10. Kirschweng, B., Tátraaljai, D., Földes, E., Pukánszky, B.: Study of the stabilizing efficiency of dihydromyricetin, a flavonoid type natural antioxidant in polyethylene under processing conditions, Bratislava Young Polymer Scientist Workshop 2016, Zdiar, Slovakia, March 14-17, 2016 (*oral presentation*)
 11. Kirschweng, B., Hári, J., Tátraaljai, D., Földes, E., Pukánszky, B.: Efficiency of different flavonoid type natural antioxidants in the melt stabilization of polyethylene, 3rd International Conference on Bio-Based Polymers and Composites 2016, Szeged, Hungary, August 28 - September 1, 2016 (*poster*)
 12. Kirschweng, B., Tátraaljai, D., Földes, E., Pukánszky, B.: Stabilizing efficiency of quercetin and rutin under processing conditions - A comparative study, 9th International Conference on Modification, Degradation and Stabilization of Polymers, Cracow, Poland, September 4-8, 2016 (*oral presentation*)
 13. Kirschweng, B., Vörös, B., Tátraaljai, D., Földes, E., Pukánszky, B.: Processing stabilization of polyethylene with silymarin, a natural flavanolignan, 32nd Polymer Degradation and Discussion Group Conference, Taormina, Italy, September 3-7, 2017 (*oral presentation*)
 14. Kirschweng, B., Vörös, B., Arroussi, M., Tátraaljai, D., Földes, E., Pukánszky, B.: Processing stabilization of polyethylene with natural antioxidants: comparison of an isolated component and a natural extract, 4th International Conference on Bio-Based Polymers and Composites 2018, Balatonfüred, Hungary, September 2-6, 2016 (*poster*)

15. Kirschweng, B., Vörös, B., Arroussi, M., Tátraaljai, D., Földes, E., Pukánszky, B.: Processing stabilization of polyethylene with silymarin, a natural flavonolignan, International Conference on Automotive, Manufacturing, and Mechanical Engineering (IC-AMME) 2018, Bali, Indonesia, September 26-28, 2018 (*oral presentation*)