FT-IR measurement as a simple tool for following formation of acidic functional groups in maleic anhydride containing polymers

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Titration is a measurement for maleic-anhydride containing polymers with significant chemicals consumption, time and human resource requirement meanwhile all the carbonyl groups have to be supposed to be in the cyclic form but it is not always the situation. Core of the FT-IR method has been determination of carbonyl groups in various chemical environments. The FT-IR method is developed to obtain more precise and prompt results about anhydride rings in the copolymer chain than with titration in the whole coupling number range with minimal chemicals consumption. Quantitatively apprising FT-IR results peaks of carbonyl groups have been considered since those yield well-isolated and high intensity peaks in the spectrum. Two distinct methods have been adopted for integration of areas under the selected stretching vibrations. Not all the anhydrides have been supposed to be in ring form in the copolymers but partially in acidic form that can be only taken into account by double counting during titration instead of the correctly single counting. FT-IR spectrum has been feasible for tracing that progress but titration isn't.

Moreover, if difference between acid number from titration and FT-IR methods based on the chemical structure is high compatibilizing additive synthesis requires excess of reagents.

- A method enabling the identification of carbonyl groups in maleic-anhydride containing polymers in various chemical environment without chemical consumption.
- The method is based on the calculation of functional group ratios applying the integrated area of selected absorption peaks.

Specifications table

Subject area:	Materials science
More specific subject area:	Chemistry
Name of your method:	FT-IR measurements for following formation of acidic functional groups in maleic anhydride containing polymers
Name and reference of original method:	N.A.
Resource availability:	N.A.

Method details

There are no doubts about advantages of FT-IR measurement as it is a prompt, low cost technique without damaging of the sample investigated [1–5]. Carbonyl Index (CI) is already used to determine extent of oxidation of polyolefins since 50 years because oxygen-containing functional groups such as carbonyl groups appearing in the polymer chains provide stretching vibrations in the

FT-IR spectrum in a well-isolated range between 1900 cm^{-1} and 1650 cm^{-1} [6–8]. There are countless but barely comparable calculation methods for CI. The only common feature of the CI methods is that the carbonyl stretching vibrations between 1900 cm^{-1} and 1650 cm^{-1} are compared to an other characteristic functional group. There are methods that calculate ratios from intensities of vibrations of selected functional groups. It also occurs that stretching vibrations of carbonyl functional groups are set against deformation vibrations of other functional groups. Based on the aforementioned the idea was born to evaluate the structure of experimental olefin-maleic-anhydride copolymers from FT-IR spectra with the similar approach, moreover, to promote industrial production of the copolymer with an easy, fast and low cost measurement requiring minimal sample preparation. Stretching vibration of carbonyl groups was not used to follow oxidation reactions in the present research but to determine the relationship on the one hand between the coupling ratio of the olefin and maleic-anhydride calculated from molar ratios applied for the synthesis and the ratio of the integrated area of cyclic carbonyl groups in the FT-IR spectrum, and on the other hand to describe the relation of the coupling ratio and the acid number based on classic titration. A better method than titration was required. Not only because it is a measurement with significant chemicals consumption, time and human resource requirement but also because during titration all the carbonyl groups have to be supposed to be in the cyclic form but it is not always the situation however determination of other forms of carbonyl groups is not possible. Core of the FT-IR method used in the present research has been determination of carbonyl groups in various chemical environments then calculation of ratio of the functional groups based on the integrated area of selected absorption peaks. Ratio of the various functional groups is often calculated from the ratio of absorbance values in the simplest way nowadays also for Carbonyl Index even if the same thickness of the samples is not guaranteed which provide misleading results. Fig. 1 showed possible structure of the experimental olefin-maleic anhydride copolymer synthesized from olefin and maleic anhydride during radical polymerization.

Various copolymers are provided by the synthesis in which polarity of the product can be changed by molar ratio of the olefin and the maleic-anhydride. Theoretical ratio of the olefin and the maleic-anhydride in the copolymer is described by the coupling ratio (CR) calculated from the formula below (1):

$$CR = \frac{E \cdot M_{olefin}}{112 \times 10^3 - E \cdot 98.6} \tag{1}$$

where: CR = coupling ratio, equal to average number of maleic anhydride groups connected to one olefin molecule, E = acid number, mg KOH/g sample, M_{olefin} = number average molecular weight of the olefin.

Theoretically all the maleic anhydride molecules are assumed to be in the cyclic form in the copolymer chain and that do not change until humidity is ruled out. Mainly classic analytical measurements have been available for following the ratio of maleic anhydride introduced into the copolymer chain during synthesis so far. Both acid number and maleic-anhydride content (MA-content) were determined by titration. Acid number covers information about all the anhydride rings (both in the copolymer chain and in free form), while MA-content determines the free maleic anhydride molecules that were not built into the copolymer chain. Difference of the two values is the ratio of rings in the copolymer. MA-content of copolymers synthesized in laboratory scale were measured in the range of 0.2 −0.7 mg KOH/g sample which did not considerably influenced ratios of the rings in the copolymers.

Acid number is determined by the consequent reaction Fig. 2) taking place during titration from the following formula ((2):

$$\text{acid number (mg KOH/ g sample)} = \frac{2 \times \text{factor} \times \text{loss (ml)} \times M_{KOH} \times \text{concentration (N)}}{\text{cross} - \text{check (g)}} \tag{2}$$

The formula (2) obviously demonstrated by the double multiplier that all the carbonyl groups are assumed to be in the ring form during titration since the reaction is conducted only until neutralizing the first group derived from the opening ring. Simplifying the process, the titration result is then doubled because the second titration reaction requires other pH, therefore, other indicator that all would significantly increase measurement time. Determination of the acid number by titration was quite well-applicable for olefin-maleic anhydride copolymers until coupling ratio of one because it showed good correspondence with theoretical acid number values (Fig. 3) However acid number from titration revealed even higher distinction from theoretical values for coupling ratios over 1. Those disparities were much higher than deviation of the method, therefore it was worth revealing the reasons. Not all the anhydrides were first supposed to be in the ring form in the copolymers but partially in acidic form that can be only taken into account by doubling during titration instead of the correctly single counting.
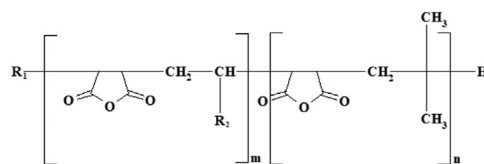

Fig. 1. Structure of the derivatives of the experimental olefin-maleic-anhydride copolymer (R$_1$: alkyl group with length of the olefinic monomer (C$_{10}$–C$_{26}$); R$_2$: alkyl group with R$_1$−2 carbon number).
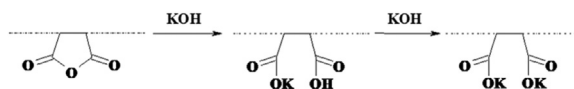

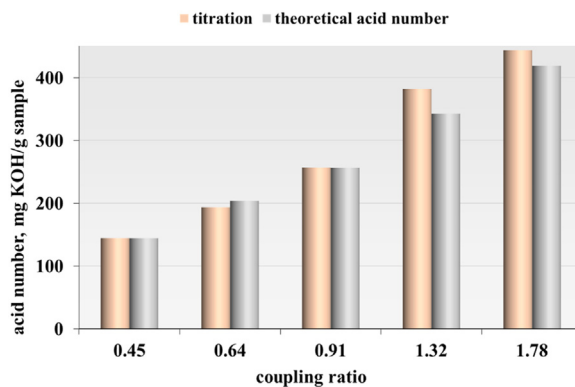**Fig. 2.** Reactions taking place during determination of acid number.

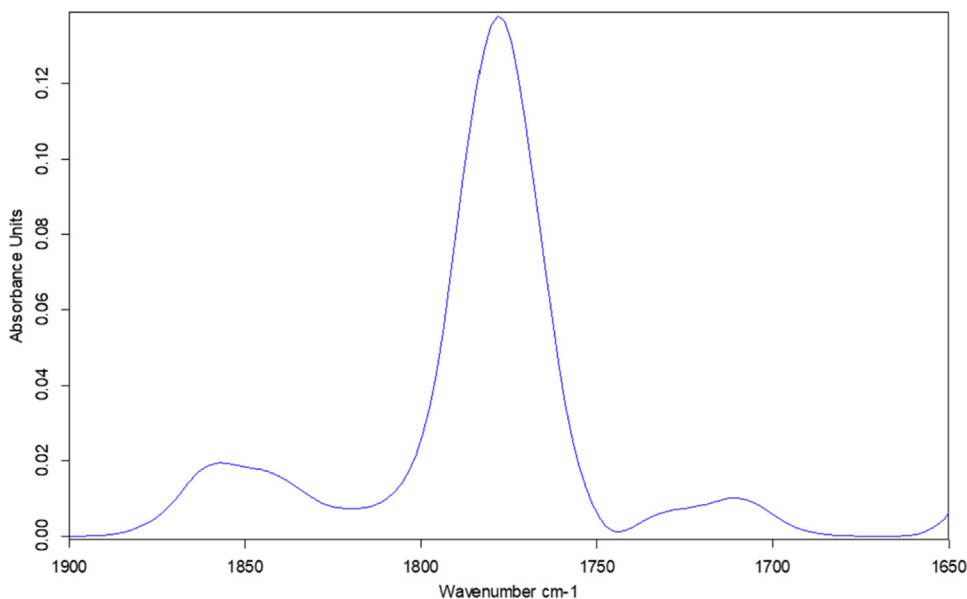**Fig. 3.** Acid number of the experimental olefin-maleic anhydride copolymer in function of the coupling ratio.

Fig. 4. A typically spectra for experimental olefin-maleic anhydride copolymer.
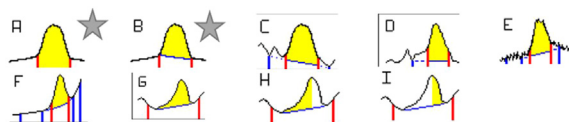

Fig. 5. A range of opportunities for FT-IR integration methods in the software OPUS 5.5.

Exactly therefore, the core of the developed FT-IR method is to obtain more precise and prompt results about anhydride rings in the copolymer chain than with titration in the whole coupling ratio range with minimal chemicals consumption. Quantitatively apprising FT-IR results absorption peaks of carbonyl groups were considered since those yield well-isolated and high intensity peaks in the spectrum (Fig. 4).

For testing the idea and calculating the area beneath the peaks, methods of Fig. 5 signed by stars were selected from the plenty of opportunities of the OPUS 5.5. software.

Table 1 summarized the integration results of olefin-maleic-anhydride copolymers having various coupling ratios. In the wavenumber range of carbonyl stretching vibrations three types of them in different chemical environments were identified. Stretching vibrations of the two carbonyl groups of anhydride rings appeared at 1855 cm^{-1} and 1778 cm^{-1}. Symmetric type of stretching vibration was identified at the higher wavenumber, the asymmetric one appeared at the lower wavenumber and corresponding to the literature data [6,8] the peak was wider and more intensive. The third carbonyl stretching vibration at 1707 cm^{-1} was identified as the carbonyl group of acidic form.

Table 1

FT-IR integration results of carbonyl stretching vibrations of olefin-maleic-anhydride copolymers having different coupling ratios.

Coupling ratio	Absorbance				Method and range of integration					
					„A"			„B"		
	1855 cm^{-1}	1778 cm^{-1}	1707 cm^{-1}	1778 cm^{-1}/ 1707 cm^{-1}	1st	2nd	3rd	1st	2nd	3rd
0.45	0.0008	0.0132	0.0259	0.5097	0.1791	0.9329	0.0861	0.0776	0.8301	0.0613
0.64	0.0004	0.0068	0.0215	0.3163	1.1958	6.1733	0.4448	0.7519	5.4642	0.1652
0.91	0.0004	0.0055	0.0205	0.2683	1.2634	6.6206	1.3708	0.8157	5.5567	0.6542
1.32	0.0003	0.0059	0.0194	0.3041	1.5215	7.3336	1.0333	0.9556	5.6862	0.0239
1.78	0.0009	0.0048	0.0203	0.2365	0.5659	7.6797	5.1929	0.5588	2.9054	4.6594

Integration range 1st: 1870 cm^{-1} −1825 cm^{-1}; 2nd 1815 cm^{-1} −1745 cm^{-1}; 3rd: 1745 cm^{-1} −1690 cm^{-1}.
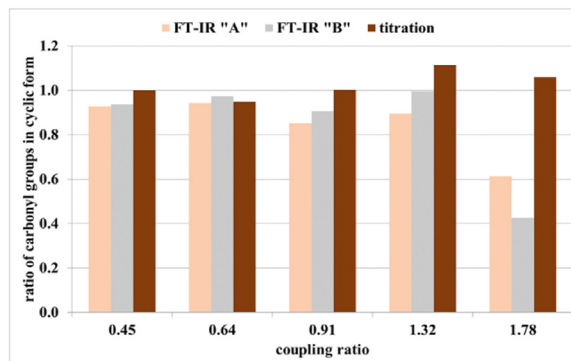

Fig. 6. Ratio of carbonyl groups in cyclic form with increasing coupling ratio of the copolymer.

The latter is formed during opening the anhydride rings of the olefin-maleic-anhydride copolymers that can happen in the presence of e.g. humidity [8,9]. Intensity ratio of the asymmetric cyclic carbonyl stretching vibration (1778 cm^{-1}) and the carbonyl stretching vibration of the acid form (1707 cm^{-1}) was derived as 0.5 for the copolymer with the lowest coupling ratio. Since absorbance of the same groups in the copolymers with other coupling ratios did not considerably differ from each other, no additional information was revealed about transformation of the carbonyl groups as the absorbance ratios were similar.

Two distinct methods ("A" and "B") were adopted for integration of areas under the selected stretching vibrations. In order to make a correct comparison the same wavenumber range was the basis for the integration. The wavenumber range was determined from Fig. 4, meanwhile Table 1 comprised the exact values. Integrated areas were applied to estimate the carbonyl groups in cyclic form. As the first step of the calculation areas corresponding to the carbonyl groups in cyclic form (1855 cm^{-1} and 1778 cm^{-1}) were summarized, then areas for all types of carbonyl vibrations. Ratio of carbonyl groups in cyclic form was obtained by the division of the aforementioned areas. Results were represented in Fig. 6 comprising results calculated from titration either. In that case the values for ratio of carbonyl groups in cyclic form were calculated from the acid number of titration divided by the theoretical acid number. Based on the results the followings were stated. Until the coupling ratio of 1 the results calculated from titration indicated that almost all the carbonyl groups are in cyclic form in the copolymer. Above coupling ratio of 1 the ratio of carbonyl groups in cyclic form was even higher than it theoretically could be. That could be obviously because the reagent consumption of titration was considered by the double multiplier even in the case of groups that were not in cyclic form in the copolymer chain as the two groups cannot be distinguished by the classic analytical method.

Results from classic titration and FT-IR methods did not pretend significant difference for copolymers having much lower coupling ratio than 1. The distinction between methods was arisen for the copolymer with coupling ratio of 0.91 and ever more significant divergence was calculated with increasing coupling ratio. The trend can be attributed to increasing sensitivity of the copolymer against moisture as increasing coupling ratio mean higher ratio of anhydride rings in the copolymer chain, therefore, ring opening and turning into acidic form take more place. FT-IR spectrum was feasible for tracing that progress but titration was not. Ratio of carbonyl groups in cyclic form revealed no disparities with the FT-IR "A" and "B" integration methods just for the highest coupling ratio.

Method validation

As a control for the FT-IR method a copolymer with the coupling ratio of 0.91 was chosen and synthesized in industrial scale. Acid number of the copolymer was determined by titration immediately after synthesis with the value of 347.6 mg KOH/g sample. After one year storage at room temperature and at ambient humidity FT-IR measurements were repeated just from 25 sampling points according to Fig. 7.
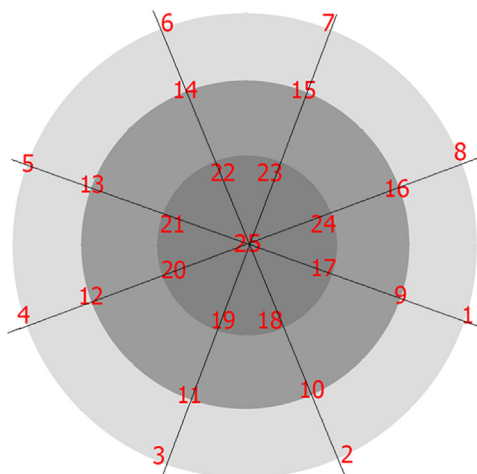
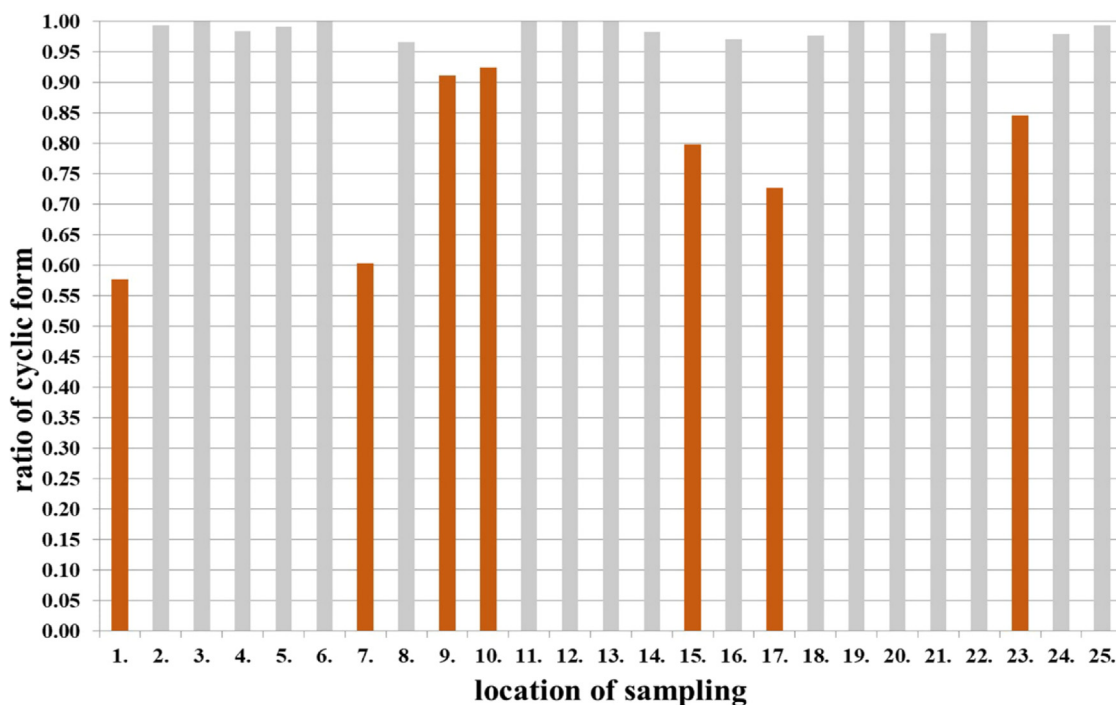Fig. 7. Location of sampling points.

Fig. 8. Results of FT-IR method "A".

FT-IR spectra of all the 25 samples were evaluated by both FT-IR "A" (Fig. 8) and FT-IR "B" (Fig. 9) in the region of carbonyl groups relevant for acid number titration. Values for classic titration were acceptable with ±10 % deviation, therefore, appropriate limits for FT-IR methods for determining carbonyl groups in cyclic form were set to 0.95 because a more precise calculation method was required. Difference for the acceptability limit of 0.95 were calculated for the same sampling points (1, 7, 9, 10, 15, 17 and 23) with both FT-IR methods. For samples signed with red in Figs. 8 and 9 acid numbers were determined by both titration and FT-IR "A" and "B" methods either. Acid number (347.6 mg KOH/g sample) determined immediately after synthesis was set as a reference in Fig. 10.

Fig. 11 is a representation for the importance of the accuracy of acid number values determined by classis titration and evaluated from FT-IR spectra. The copolymer being so far in the focus of the qualification is a raw material for a next synthesis such as esterification in order to get the proper additive structure for compatibilizing various plastic and rubber composites. The basis for calculation of the reagent molar ratios for the functionalization previously was acid number determined by titration. But if difference between acid number from titration and from FT-IR methods based on the chemical structure is high, compatibilizing additive
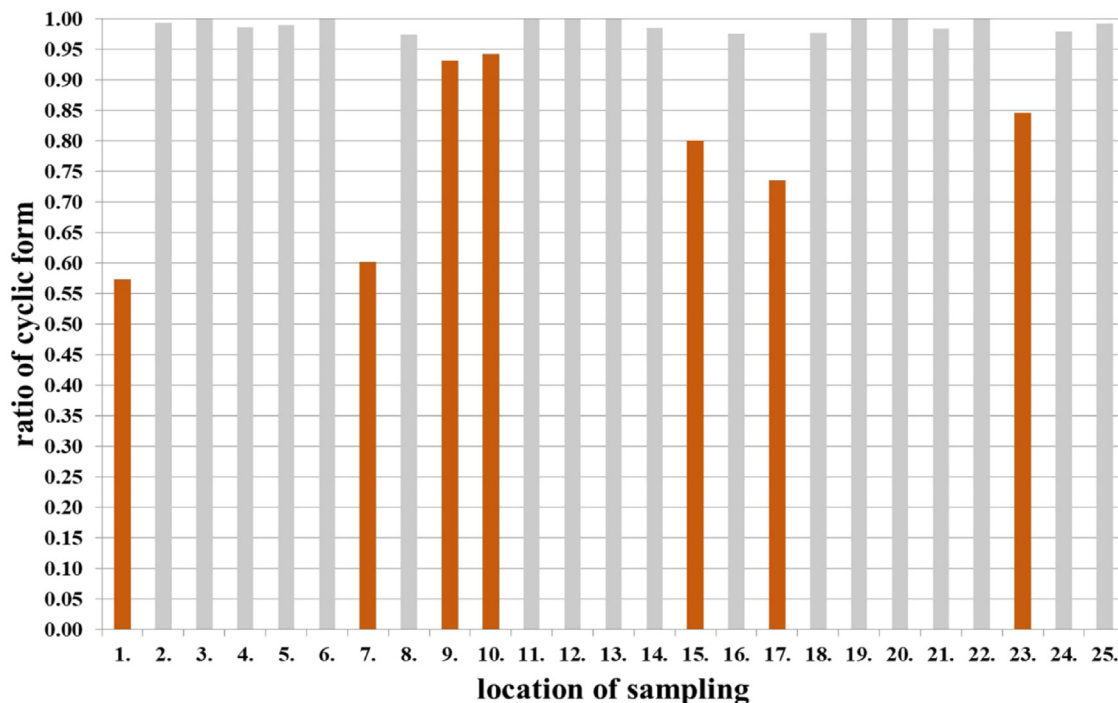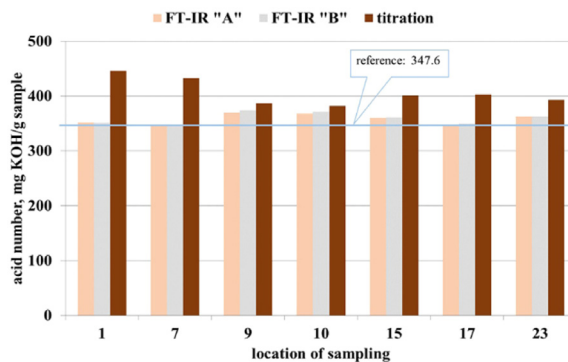
Fig. 9. Results of FT-IR method "B".

Fig. 10. Acid number of olefin-maleic-anhydride copolymers at different locations of sampling determined by titration and the two FT-IR methods.
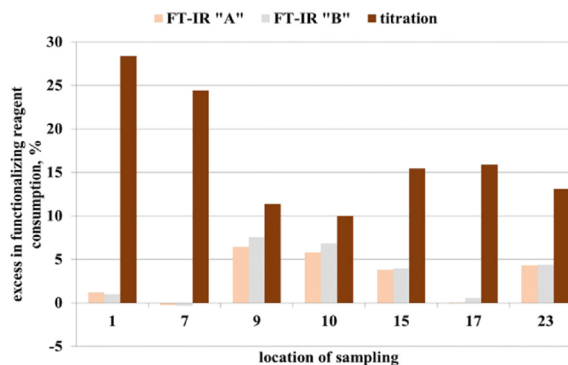

Fig. 11. Influence of the determination method of acid number and its accuracy on the excess in reagent consumption during functionalization of the selected olefin maleic-anhydride copolymer.

synthesis requires excess of reagents. Moreover, the synthesized additive may be improper as a compatibilizer in the selected composite system because other additive structure is created if reagent molar ratios are calculated on the basis of acid number from titration. For the represented samples the excess of reagent requirement was at least 10 % but could even reach up to 25 %.

Ethics statements

No ethical considerations were required.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Csilla Varga: Conceptualization, Methodology, Software, Validation, Investigation, Writing – original draft, Writing – review & editing, Visualization.

Data availability

Data will be made available on request.

Acknowledgments

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