



Research article

FT-IR combined with oscillatory rheology: How to evaluate chemical structure of ester derivatives of MA-containing compatibilizers

Csilla Varga^{*}, Lilla Simon-Stóger*Sustainability Solutions Research Lab, University of Pannonia, 10. Egyetem Str., Veszprém, 8200, Hungary*

ARTICLE INFO

Keywords:

Olefin–maleic anhydride copolymer
Compatibilizing additive
FT-IR spectroscopy
Ester-index
Oscillatory rheology

ABSTRACT

Ester derivatives of experimental olefin–maleic anhydride copolymers synthesized at the University of Pannonia have been investigated by both classical and instrumental analytical methods that contribute to a deeper understanding of how that type of additives functions as compatibilizers for plastics and rubbers.

Titration-based acid and saponification numbers have provided limited information about the chemical structure of the experimental copolymer compounds. A prompt, precise and low-cost method or combination of methods has been required to access to the ratio of the various derivatives not only straight after esterification but also for quality control during long-term storage considering the even stricter sustainability aspects either. Reproduction and scaling-up syntheses can be also followed by the combined measuring techniques of Fourier-transform infrared spectroscopy (FT-IR) and oscillatory rheometry. Structural changes occurred in the additives could be followed through monitoring their Ester Indices (EI) during the measurement, which can be connected also to the long-term properties. Experimental additives (AD) like AD-1 and AD-2 types with lower EI values of 21.5 % and 32.1 %, respectively, resulted in higher upper limits of the linear viscoelastic (LVE) range (15 % and 10 %). Conversely, the higher EI values of AD-3 and AD-4 led to significantly lower or even immeasurable upper limits of the LVE range. Additives with solid behaviour showed slight dependence on frequency above the crossover point that indicated strong connections disappearing.

1. Introduction

Compatibilizing additives are highly needed in the vast majority of cases to enhance compatibility between the components in various plastic and rubber composites and blends [1–11]. More advantageous mechanical, thermal and rheological properties can be achieved through compatibilization in a composite due to the improved interactions and solubility during product development, whether it concerns original or waste raw materials [12–17]. Commercial compatibilizing additives and coupling agents can be categorized into two main groups based on their chemical structures: silane-type and maleic anhydride (MA) containing polymer-type [18–23].

Many examples can be found in the literature for the latter one, such as MA-grafted polymers or copolymers [24–26]. MA plays a

^{*} Corresponding author.

E-mail address: varga.csilla@mk.uni-pannon.hu (C. Varga).

significant role in terms of improving compatibility, as it can form covalent bonds through its reactivity [27–30]. The ratio of MA rings in these compatibilizers carries significant information, which is defined by the acid number or the MA content/ratio, depending on the consistency of the additive [31–34]. In the additives containing functionalized MA, the acid number and the MA content/ratio do not offer sufficient information to select the appropriate compatibilizing additive for a given composite material based on its chemical structure, which would be more advantageous in many cases. The experimental olefin-maleic anhydride copolymer based additive, synthesized at the University of Pannonia, in which the anhydride ring was functionalized with various compounds, proved to be more advantageous in numerous composite system compared to the commercial MA-grafted polymer types [35–40]. The synthesis of olefin-maleic anhydride copolymer-based additives allows to applying the additive with the proper chemical structure in the various composite systems, since the structure of the additive can be tailored to the structure and polarity of the polymer and/or rubber components.

Examination and an appropriate level of knowledge of the additive structure are crucial factors for designability. Widely used classical and instrumental analytical methods can be applied to the structural analysis of polymer-type additives. Measurement of the acid number and saponification number, which are used to determine functional groups like anhydrides, esters and carboxyls, can be conducted using classical titrimetric methods. For a more in-depth structural analysis, the measurement of MA content and iodine number can be employed from classical methods. For determining the additive structure and examining the mechanism FT-IR can be employed, while rheological properties and viscoelastic deformations can be studied using oscillatory rheometry. Molecular weight determination of the additives can be performed using e.g. gel permeation chromatography.

Nowadays FT-IR spectroscopy is frequently employed to examine the structure of different polymers and composite systems due to the simplicity and precision of the method. Since FT-IR spectroscopy is suitable for both qualitative and quantitative analysis, it provides an easy way to study the structure of the additive synthesized at University of Pannonia. This can provide insight into the ratios of functional groups present in the additive in various chemical environment. FT-IR method has been applied in numerous studies to determine the maleic anhydride and carbonyl groups [41–45], because stretching vibrations of carbonyl groups of maleic anhydride and its derivatives are easy to identify in the wavenumber range of 1900 cm^{-1} – 1600 cm^{-1} .

For MA-grafted polymer type compatibilizers one of the most important property is the grafting yield, which means the ratio of MA groups connected to the polymer chain. Machado et al. [46] determined grafting yield by FT-IR and the extent of cross-linking/degradation by dynamic rheological measurements. Determination of storage (G') and loss (G'') moduli constitute the most relevant and enriching rheological procedure in polymer science. Small Amplitude Oscillatory Shear (SAOS) tests are conducted in the linear region and low amplitudes, while Large Amplitude Oscillatory Shear (LAOS) tests are used in the non-linear regime. The analysis of the terminal zone is used for quality control, practically the G' and G'' versus frequency is obtained by SAOS measurements. Generally, study of nonlinear viscoelasticity by LAOS measurements focuses on studies of topology, morphology, concentration in a variety of polymeric systems [47].

Double aims were set for the experimental work. One was development of an easy and prompt evaluation method for the ratio of the carbonyl groups in different chemical environment in the ester derivatives of olefin-maleic anhydride copolymer based on the FT-IR spectrum. Further aspects for the new method were decreasing both the chemical reagent and energy consumption and human resource requirements of classical titration measurements. Also, an attempt was made to reveal whether oscillation rheology measurements offer more information about the relationship between the chemical structure and rheological parameters and behaviour of the additives.

2. Materials and methods

Additives were produced in a two-step synthesis. In the first step the copolymer chain was synthesized from the olefin (INEOS Group Ltd.) and maleic-anhydride monomers (MOL Plc.) then the anhydride rings were functionalized with alcohol reagent (Sigma-Aldrich, purity: 99.0 %) in xylene solution [48]. Esterification was conducted in $90\text{ }^{\circ}\text{C}$ – $200\text{ }^{\circ}\text{C}$ temperature range during 1–8 h. Xylene was removed from the end-product by vacuum distillation. In the present research the same copolymer was used for additive synthesis in order to eliminate the effects of difference in copolymer chains on the rheology since it is an influencing factor beside the grafted MA content on rheology of the MA-g-polyolefins [46]. Wide range of alcohol molar ratio was selected for the esterification in order to

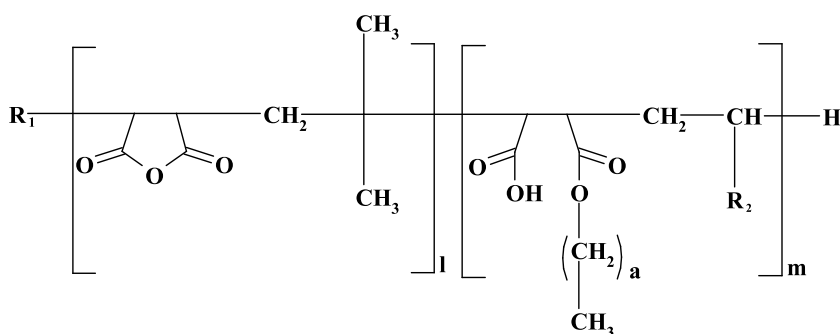


Fig. 1. The possible structure of the experimental olefin-maleic anhydride copolymer-based ester derivatives.

investigate synthesis products having various levels of ester functional groups (Fig. 1).

Titration-based classic analytical measurements were performed to characterize the compatibilizers, and the results were summarized in Table 1.

FT-IR measurements were carried out in order to study chemical structure of the functionalized olefin-maleic anhydride copolymers. FT-IR spectra were recorded by means of a Shimadzu IR Tracer 100 instrument in the region of 4000 cm^{-1} – 600 cm^{-1} . The samples were pressed into disks of appropriate thickness in order to make a comparison on the same basis. A total of 32 scans were accumulated with a resolution of 4 cm^{-1} .

Measurements of viscoelastic properties of the additives were carried out by an oscillatory rheometer (MCR 302, Anton Paar). Parallel plate (PP; plate radius = 25 mm) geometry was applied for samples with a constant gap of 1.0 mm. Firstly, an amplitude sweep test was run at a constant frequency of 1 Hz and at 25 °C for each material to obtain the linear viscoelastic range. The further measurements can be carried out safely within the LVE range avoiding irreversible structural damage of the molecular chains. Finally, frequency sweep tests ($\omega = 0.1 \dots 628\text{ rad/s}$) were carried out also at room temperature, applying a constant strain amplitude of 1 %.

3. Results and discussion

3.1. Chemical structure evaluation by FT-IR

The carbonyl stretching vibrations were employed to determine the relative ratios of the derivatives, as unreacted anhydride rings were expected to remain in the compound because of the reagent molar ratios used in the synthesis. Those vibrations appear in a well-isolated wavenumber range of the FT-IR spectrum of both the copolymers and the additives, and possess high intensities too (Fig. 2).

For calculating areas under the characteristic absorption peaks of carbonyl groups methods of Fig. 3 (method “A” and method “B”) were assumed from the possible integration methods of the OPUS 5.5. software since the peaks appear next to each other and may overlap in that wavenumber region. Calculating with FT-IR method “B” required a meticulous determination of the wavenumber range for integration, as the potential shifting of the peaks by a few cm^{-1} due to vibration overlap also needed to be considered.

Additives synthesized with various molar ratios of alcohols were assumed to be composed of unreacted anhydride and ester/half-ester functional groups based on the FT-IR spectra. Characteristic carbonyl vibrations were found at 1778 cm^{-1} , 1733 cm^{-1} and 1699 cm^{-1} in the spectra of the additives (Fig. 2).

The two characteristic carbonyl vibrations for the anhydride rings appeared at 1855 cm^{-1} and 1778 cm^{-1} [45,49] in the initial copolymer. The absorption peak at 1778 cm^{-1} belonged to one of the carbonyl groups in the anhydride rings in the additives and the decreasing intensity was thought to be caused by the esterification.

Ring opening during esterification of anhydride can be assumed from the vibrations of free carboxyl groups. When the anhydride ring opens, only one of the carbonyl groups reacts with the alcohol, resulting in the formation of a half-ester, while the other carbonyl group remains unreacted. Fig. 4 served as examples demonstrating the appearance of carbonyl vibrations in the additive spectra.

The vibration at 1707 cm^{-1} pertaining to carbonyl groups of free carboxyl groups originated from anhydride in the half-ester part of the additive shifted to 1699 cm^{-1} . The new peak appearing at 1733 cm^{-1} was suggested to belong to carbonyl stretching vibrations of ester groups derived from the opening anhydride rings. Ratio of the aforementioned vibrations varied in the additives with the molar ratio of the reagents.

Integrated areas determined by the different methods were compared in Fig. 5 represented for AD-4.

Ratio of the FT-IR integrated area of ester carbonyl groups related to areas for all types of carbonyl functional groups was the basis for calculating the ratio of the different derivatives in the additives (Table 2).

Only one of the carbonyl groups from the opening anhydride rings reacted with the alcohol reagent if its molar ratio was kept low, and the other carbonyl group remained free in carboxylic acid form. The free carboxylic acid groups are expected to react with increasing molar ratio of the alcohol, however esterification is an equilibrium reaction, so above a certain molar ratio the alcohol does not incorporate.

The Ester Index was set up from the FT-IR integration results serving for uniform characterization of chemical structure of ester derivatives of olefin-maleic anhydride copolymers. The Ester Index refers to the ratio of the integrated area under the stretching carbonyl vibration of the ester functional groups ($\nu = 1740\text{--}1730\text{ cm}^{-1}$) and the combined area of all the carbonyl (anhydride, ester, free carboxyl) stretching vibrations, expressed as a percentage (Table 2).

Table 1
Typical properties of the experimental additives.

Property	Acid number, mg KOH/g	Saponification number, mg KOH/g	Kinematic viscosity ^a , mm^2/s	Density ^a , g/cm^3
AD-1	110.2	100.6	0.7135	0.7040
AD-2	99.0	101.2	0.7720	0.7270
AD-3	91.6	115.1	0.9411	0.7331
AD-4	108.0	113.5	0.8930	0.7303

^a 10 wt % solution in heptane.

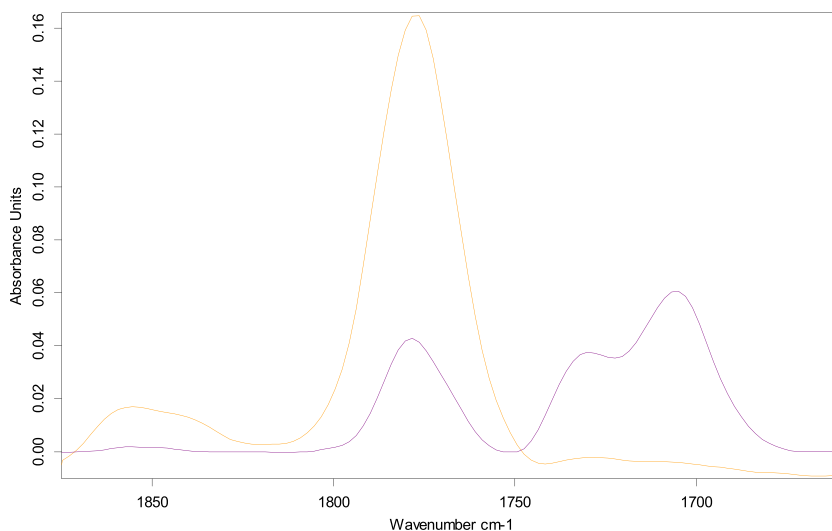


Fig. 2. FT-IR spectrum of AD-4 in the investigated wavenumber region (orange: olefin-maleic anhydride copolymer, purple: AD-4: product synthesized with alcohol reagent (molar ratio: 0.90)).

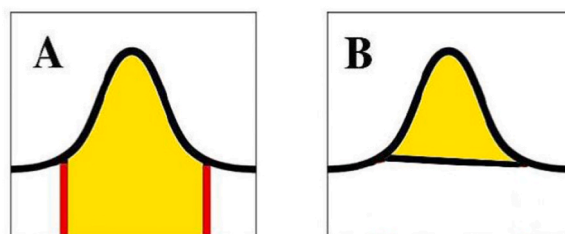


Fig. 3. Selected FT-IR integration methods (method “A” and method “B”).

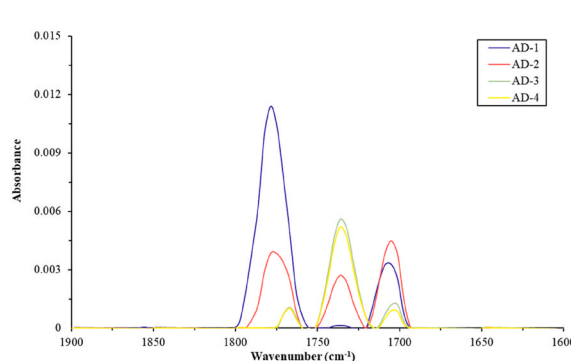


Fig. 4. Progress in esterification of the olefin-maleic anhydride copolymer with different molar ratios of alcohol in FT-IR spectra.

3.2. Rheology

The aim of the oscillatory rheological measurements has been to get information about the effect of structural changes in additives on their rheological behaviours and the main indicating properties since the ratio of ester groups of experimental additives varied based on FT-IR evaluation. The first rheological measurement of the olefin-maleic anhydride copolymer derivatives was amplitude sweep test, conducted to determine the linear viscoelastic range of the additives. Generally, if any of the moduli changes more than 5 % compared to the initial value, that is the indicator for leaving the LVE range. If the shear during the test exceeds the upper limit of the LVE range the structure of additive undergoes an irreversible change. As a result, the sample cannot express a long-term resistance against deformation, and the structure might be destroyed.

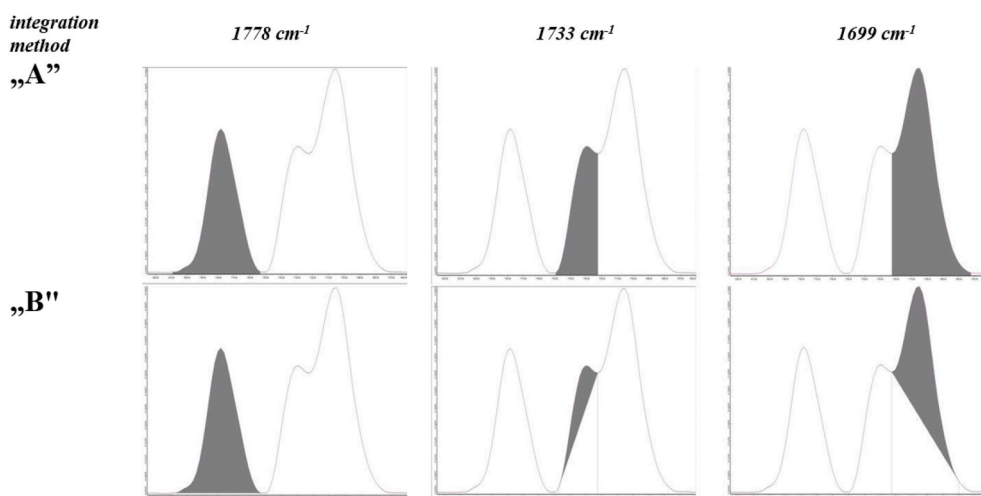


Fig. 5. Integrated areas beneath the various absorption peaks.

Table 2

Ratio of the derivatives calculated from the FT-IR integrated areas.

Additive	Alcohol reagent molar ratio	Total integrated area		Ratio of unreacted rings (1778 cm^{-1})		Ratio of ester groups (1733 cm^{-1})		Ester Index, %	
		A	B	A	B	A	B	A	B
AD-1	0.25	2.1353	1.4038	0.5008	0.4892	0.2150	0.2446	21.5	24.5
AD-2	0.50	3.3028	2.4767	0.5692	0.4721	0.3210	0.3279	32.1	32.8
AD-3	0.75	3.1082	1.7499	0.2933	0.2892	0.6870	0.6108	68.7	61.1
AD-4	0.90	4.0021	2.1627	0.2542	0.1439	0.7140	0.6561	71.4	65.6

3.2.1. Amplitude sweep test

The effects of different ester group ratios (Ester Indices) of the additives revealed during the amplitude sweep test too because of the physical appearance.

Fig. 6 was a good representation for the moduli curves after the amplitude sweep test of olefin-maleic anhydride copolymer ester derivatives synthesized with various molar ratios of alcohols.

AD-1 and AD-2 exhibited liquid-like behaviour that was indicated by the loss modulus curve being above the storage modulus curve within the LVE range based on the relative positions of the storage and loss moduli curves. In contrast to that AD-3 and AD-4 exhibited higher storage moduli than loss moduli in the investigated LVE range, so indicating solid behaviour. The relative position of the modulus curves offers even more information. The difference between the curves of storage and loss moduli for additives AD-1 and AD-2 increased even up to magnitude difference, indicating viscous character. The values of G' and G'' fell within the same magnitude for AD-3 and AD-4, indicating that the additives do not have a predominantly elastic or viscous behaviour [50,51]. Even the upper limit of the LVE range for the additives can be determined from the G' curve of the amplitude sweep test, as shown in Fig. 6 [50,51].

AD-1 and AD-2 had relatively wide LVE ranges, with the upper limit obtained at 15 % and 10 % shear amplitude, respectively. Contrary to those, AD-3 had very narrow LVE range as it exits LVE range above 0.02 % shear, practically not possessing an LVE range within those measurement conditions. AD-4 also does not have LVE range, as indicated by the slope of the curves. The explanation is that the sample initially existed in solid state and then transitioned to flow as the shear increased, thus resulting in values higher than G' above the crossover point.

A relationship was observed among the physical consistency, the ratio of ester functional groups and the upper limit of LVE for additives. An increase in the molar ratio of the alcohol reagent during the synthesis resulted in increasing ratio of ester groups, meanwhile decreasing the upper limit of LVE. The results were indicated in Fig. 6.

3.2.2. 2 Frequency sweep test

Shear amplitude for frequency sweep test is suggested to be selected within the LVE range [50,51]. For accurate comparison, the same (1 %) shear amplitude was applied for the frequency sweep test of the additives. Figs. 7 and 8 represented the results of the frequency sweep test of four ester derivatives synthesized with various Ester Indices.

The rheograms of the additive pairs significantly differed from each other at the selected shear amplitude ($\gamma = 1\%$). The relative positions of the storage and loss modulus curves of the samples AD-3 and AD-4 and the trend of the complex viscosity curves (Fig. 8) suggested a slightly crosslinked polymer structure [50,51]. The storage modulus showed a plateau in the low frequency range, and complex viscosities approach to infinity, which is characteristic for the rheograms of crosslinked polymers. However, all the signs

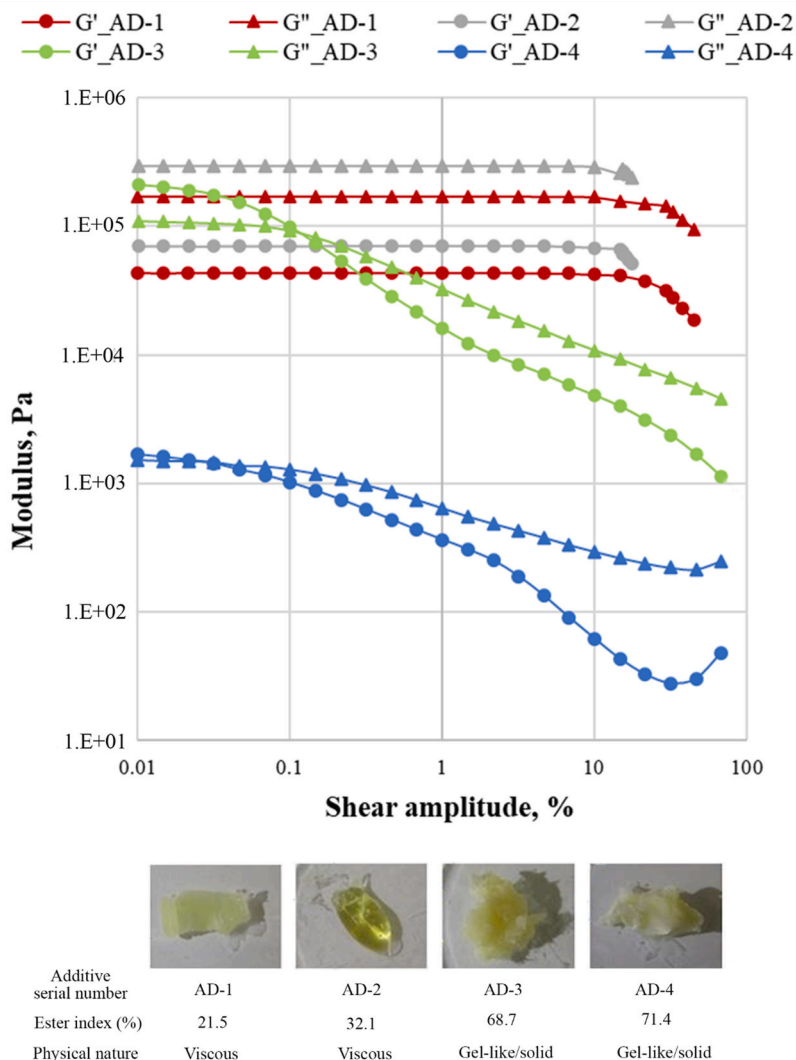


Fig. 6. Storage (G') and loss (G'') modulus of copolymer ester derivatives with various EI at room temperature in the function of the shear amplitude, $\omega = 10$ rad/s.

suggested that AD-3 and AD-4 contained crosslinks, but the chemical reactions during additive synthesis did not facilitate crosslinking reactions. Instead, the gel-like structure of the additive was observed. Below the critical shear, the storage modulus (G') often remains independent of frequency as it can be expected from a well-structured solid material where molecules are strongly interconnected. Plateau of the storage and loss moduli in low frequency range (0.010–0.734 rad/s) is well-described by the loss factor ($\tan \delta = G''/G'$) corresponding to the elastic character of the sample [50,51]. Based on data in Fig. 9, no significant difference was observed in loss factor with the molar ratio of alcohol reagent in the low frequency range.

Above the crossover point the structure of AD-3 and AD-4 was weakened, and loss moduli dominated over the storage ones. Above the crossover frequency, viscosity is generally expected to be independent of the frequency. However, for AD-3 and AD-4 additives the modulus values showed slight dependence on frequency, indicating that the strong connection between the molecules disappeared. Rheograms of AD-1 and AD-2 were corresponding to a material without crosslinking because loss modulus had higher values than the storage modulus.

4. Conclusion

The research was carried out on experimental olefin-maleic anhydride copolymer based ester derivatives by combining FT—IR and rheology measurements for a deeper knowledge about the structural properties of the compounds developed. The carbonyl stretching vibrations were employed to determine the relative ratios of the derivatives after esterification, as unreacted anhydride rings were also expected to remain in the compound. A concept of Ester Index was determined based on the integrated areas belonging to the carbonyl

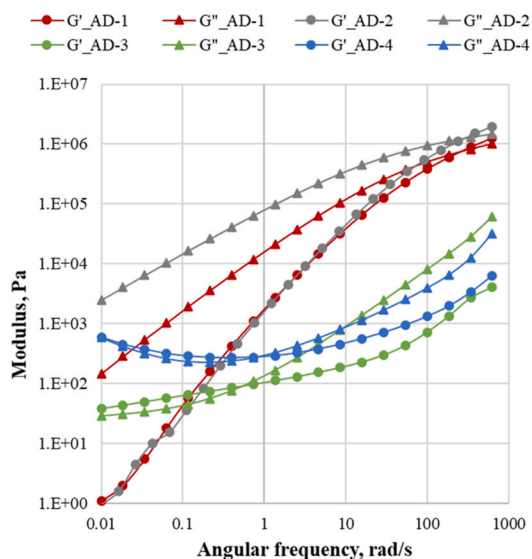


Fig. 7. Storage (G') and loss (G'') modulus of copolymer ester derivatives with various EI at room temperature and 1% shear amplitude.

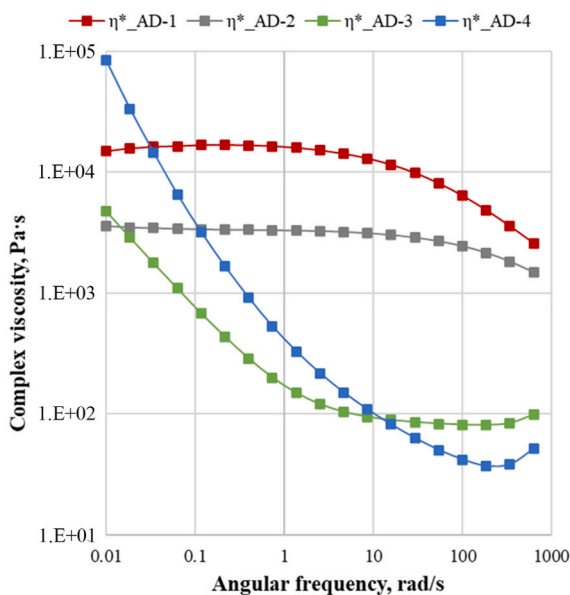


Fig. 8. Complex viscosity of copolymer ester derivatives with various EI at room temperature and 1% shear amplitude.

stretching vibrations, which gives the ratio of ester functional groups in the additive. The concept of EI is useful for characterization and following structural changes during rheological measurements or long-term storage either.

A relationship was observed among the physical consistency, the Ester Index and the upper limit of LVE of the additives. An increase in the molar ratio of the alcohol reagent during the esterification resulted in increasing Ester Index, meanwhile decreasing the upper limit of LVE. Reproduction and scaling-up syntheses can be also followed by the combined measuring techniques of FT-IR spectrometry and oscillatory rheometry. Elimination of classical titration qualification for olefin-maleic anhydride copolymer derivatives is a huge step toward a sustainable chemistry as high chemical- and time-consuming measurements can be exchanged with prompt, precise and low-cost measurements that are also useful for long-term control of structural quality. Statements stand at room temperature; therefore, more measurements are required whether those also stand at the temperature of polymer processing.

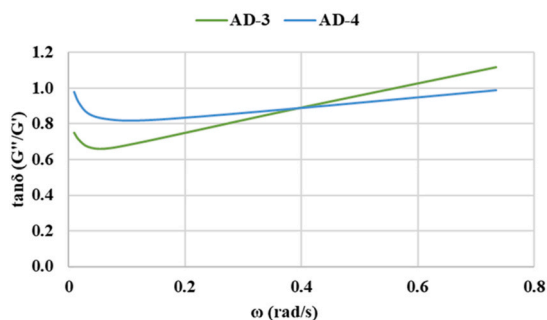


Fig. 9. Loss factor of AD-3 and AD-4 additives in the range of 0.01–0.734 rad/s.

Data availability

Data will be made available on request.

CRediT authorship contribution statement

Csilla Varga: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Conceptualization.
Lilla Simon-Stöger: Writing – original draft, Visualization, Methodology, Investigation.

Declaration of competing interest

Simon-Stoger Lilla reports financial support was provided by National Research Development and Innovation Office. Varga Csilla reports financial support was provided by National Research Development and Innovation Office. Varga Csilla reports a relationship with Janos Bolyai Research Scholarship of the Hungarian Academy of Sciences that includes: funding grants. Varga Csilla has patent issued to University of Pannonia.

Acknowledgement

This publication/research has been supported by the National Research, Development and Innovation Office through the project nr. 2022-1.1.1-KK-2022-00002, titled ‘Establishment of a waste management competence centre at the University of Pannonia’.

Csilla Varga’s contribution to this paper was supported by the Janos Bolyai Research Scholarship of the Hungarian Academy of Sciences.

We are indebted to Réka Martinecz for her participation in the experimental work.

References

- [1] R. Hsissou, O. Dagdag, M. Berradi, M.E. Bocuchiti, M. Assouag, A.E. Bachiri, A. Elharfi, Investigation of structure and rheological behavior of a new epoxy polymer pentaglycidyl ether pentabispheol A of phosphorus and of its composite with natural phosphate, *SN Appl. Sci.* 1 (2019) 869, <https://doi.org/10.1007/s42452-019-0911-8>.
- [2] N.E. Aouni, R. Hsissou, J.E. Azzaoui, M.E. Bouchti, A. Elharfi, Synthesis rheological and thermal studies of epoxy polymer and its composite, *Chem. Data Collect.* 30 (2020) 100584, <https://doi.org/10.1016/j.cdc.2020.100584>.
- [3] R. Hsissou, M.E. Bouchti, A.E. Harfi, Elaboration and viscosimetric, viscoelastic and rheological studies of a new hexafunctional polyepoxide polymer: hexaglycidyl ethylene of methylene dianiline, *J. Mater. Environ. Sci.* 8 (2017) 4349–4361.
- [4] R. Hsissou, A. Bekhta, A.E. Harfi, Viscosimetric and rheological studies of a new trifunctional epoxy pre-polymer with noyan ethylene:Triglycidyl Ether of Ethylene of Bisphenol A (TGEEBA), *J. Mater. Environ. Sci.* 8 (2017) 603–610.
- [5] K. Formela, Strategies for compatibilization of polymer/waste tire rubber systems prepared via melt-blending, *Adv. Ind. Eng. Polym. Res.* (2023), <https://doi.org/10.1016/j.aiepr.2023.08.001>.
- [6] G. Fredi, Compatibilization of biopolymer blends: a review, *Adv. Ind. Eng. Polym. Res.* (2023), <https://doi.org/10.1016/j.aiepr.2023.11.002>.
- [7] R. Taurino, F. Bondioli, M. Messori, Use of different kinds of waste in the construction of new polymer composites: review, *Mater. Today Sustain.* 21 (2023) 100298, <https://doi.org/10.1016/j.mtsust.2022.100298>.
- [8] P. Singh, P. Katiyar, H. Singh, Impact of compatibilization on polypropylene (PP) and acrylonitrile butadiene styrene (ABS) blend: a review, *Mater. Today: Proc.* 78 (2023) 189–197, <https://doi.org/10.1016/j.matpr.2023.01.350>.
- [9] S. Coba-Daza, E. Carmeli, I. Otaegi, N. Aranburu, G. Guerrica-Echevarria, S. Kahlen, D. Cavallo, D. Tranchida, A.J. Müller, Effect of compatibilizer addition on the surface nucleation of dispersed polyethylene droplets in a self-nucleated polypropylene matrix, *Polymer* 263 (2022) 125511, <https://doi.org/10.1016/j.polymer.2022.125511>.
- [10] A.F. Rigail-Cedeño, D. Cabrera-Alava, J. Vera-Sorroche, M. Lazo, E. Adrian, R. Perugachi, Effect of compatibilization agents and rice husk on the energy demand on the extrusion of recycled high-density polyethylene composites, *Energy Rep.* 8 (2022) 548–555, <https://doi.org/10.1016/j.egy.2022.07.101>.
- [11] S. Ramarad, M. Khalid, C.T. Ratnam, A.L. Chuah, W. Rashmi, Waste tire rubber in polymer blends: a review on the evolution, properties and future, *Prog. Mater. Sci.* 72 (2015) 100–140, <https://doi.org/10.1016/j.pmatsci.2015.02.004>.
- [12] Z. Mousavi, M.C. Heuzey, P.J. Carreau, Compatibilized polylactide/polyamide 11 blends containing multiwall carbon nanotubes: morphology, rheology, electrical and mechanical properties, *Polymer* 276 (2023) 125906, <https://doi.org/10.1016/j.polymer.2023.125906>.

- [13] P. Singh, P. Katiyar, H. Singh, Impact of compatibilization on polypropylene (PP) and acrylonitrile butadiene styrene (ABS) blend: a review, *Mater. Today: Proc.* 78 (2023) 189–197, <https://doi.org/10.1016/j.matpr.2023.01.350>.
- [14] Y. Wang, S. Zhang, H. Jiang, Y. Lin, H. Xing, T. Tang, Insight on compatibilization of LLDPE/PS blends from morphology, interfacial state, mechanical properties and melt properties: comb-like copolymer vs diblock copolymer, *Polymer* 218 (2021) 123540, <https://doi.org/10.1016/j.polymer.2021.123540>.
- [15] J. Pelto, C. Barreto, H. Anwar, L. Strobl, M. Schlummer, Compatibilized PC/ABS blends from solvent recycled PC and ABS polymers from electronic equipment waste, *Polym. Test.* 120, 107969. <https://doi.org/10.1016/j.polymertesting.2023.107969>.
- [16] S.H.K. Dewi, S. Hatna, The effect of styrene maleic anhydride compatibilizer on the performance of polycarbonate/acrylonitrile butadiene styrene blends, *Mater. Today: Proc.* 46 (2021) 2510–2514, <https://doi.org/10.1016/j.matpr.2021.01.531>.
- [17] J. Guan, W. Luo, S. Lu, Y. Yang, X. Shen, B. Tang, Y. Li, Synchronous toughening and strengthening of the immiscible poly(lactic acid)/thermoplastic polyurethane (PLLA/TPU) blends via the interfacial compatibilization with Janus nanosheets, *Compos. Sci. Technol.* 227 (2022) 109611, <https://doi.org/10.1016/j.compscitech.2022.109611>.
- [18] N. Yao, H. Wang, L. Zhang, D. Yue, M. Tian, One-pot solvothermal synthesis of silane-functionalized carbon nanodots as compatibilizers for the immiscible TPU/MVQ blends, *Appl. Surf. Sci.* 530 (2020) 147124, <https://doi.org/10.1016/j.apsusc.2020.147124>.
- [19] X. Ge, Z. Zhang, H. Yu, B. Zhang, U.R. Cho, Study on viscoelastic behaviors of bentonite/nitrile butadiene rubber nanocomposites compatibilized by different silane coupling agents, *Appl. Clay Sci.* 157 (2018) 274–282, <https://doi.org/10.1016/j.clay.2018.03.006>.
- [20] K. Chen, P. Li, X. Li, C. Liao, X. Li, Y. Zuo, Effect of silane coupling agent on compatibility interface and properties of wheat straw/poly(lactic acid) composites, *Int. J. Biol. Macromol.* 182 (2021) 2108–2116, <https://doi.org/10.1016/j.ijbiomac.2021.05.207>.
- [21] C.Q. Li, J.W. Zha, H.Q. Long, S.J. Wang, D.L. Zhang, Z.M. Dang, Mechanical and dielectric properties of graphene incorporated polypropylene nanocomposites using polypropylene-graft-maleic anhydride as a compatibilizer, *Compos. Sci. Technol.* 153 (2017) 11–118, <https://doi.org/10.1016/j.compscitech.2017.10.015>.
- [22] J.B. Olivato, M.V.E. Grossmann, F. Yamashita, D. Eiras, L.A. Pessan, Citric acid and maleic anhydride as compatibilizers in starch/poly(butylene adipate-co-terephthalate) blends by one-step reactive extrusion, *Carbohydr. Polym.* 87 (2012) 2614–2618, <https://doi.org/10.1016/j.carbpol.2011.11.035>.
- [23] L. Bazli, A. Khavandi, M.A. Boutorabi, M. Karrabi, Correlation between viscoelastic behavior and morphology of nanocomposites based on SR/EPDM blends compatibilized by maleic anhydride, *Polymer* 113 (2017) 156–166, <https://doi.org/10.1016/j.polymer.2017.02.057>.
- [24] G. Chen, Y. Zhang, X. Zhou, J. Xu, Synthesis of styrene-maleic anhydride copolymer esters and their surface enriched properties when blending with polyethylene, *Appl. Surf. Sci.* 253 (2006) 1107–1110, <https://doi.org/10.1016/j.apsusc.2006.01.068>.
- [25] S. Jinger, J. Chaudhary, A. Solanki, Maleimide copolymers of MMA/styrene: microwave -preparation and their properties, *Mater. Today: Proc.* 29 (2020) 316–320, <https://doi.org/10.1016/j.matpr.2020.07.282>.
- [26] W. Miao, W. Cheng, Z. Wang, R. Wang, J. Peng, Q. Zhu, Influence of n-butyl acrylate and maleic anhydride copolymer on the structure and properties of phenolic resin, *Mater. Today Commun.* 23 (2020) 100879, <https://doi.org/10.1016/j.mtcomm.2019.100879>.
- [27] R. John, K. Schreiter, K. Trommler, C. Siegel, A. Wagenführ, S. Spange, Maleic anhydride copolymers as adhesion-promoting reagent in wood veneer/biopolyethylene composite materials, *Polym. Compos.* 40 (2019) 1979–1988, <https://doi.org/10.1002/pc.24974>.
- [28] Y.F. Li, Y.X. Liu, X.M. Wang, Q.L. Wu, H.P. Yu, J. Li, Wood-polymer composites prepared by the in situ polymerization of monomers within wood, *J. Appl. Polym. Sci.* 119 (2011) 3207–3216, <https://doi.org/10.1002/app.32837>.
- [29] C. Müller, M. Ansoorge, M. Espig, S. Zschoche, J. Schiller, T. Pompe, Covalent binding of maleic anhydride copolymer monolayers to polyacrylamide hydrogels, *Macromol. Chem. Phys.* 219 (2018) 1800206, <https://doi.org/10.1002/macp.201800206>.
- [30] J. Bonilla-Cruz, B. Hernandez-Mireles, R. Mendoza-Carrizales, L.A. Ramirez-Leal, R. Torres-Lubian, L.F. Ramos de Valle, D.R. Paul, E. Saldivar-Guerra, Chemical modification of butyl rubber with maleic anhydride via nitroxide chemistry and its application in polymer blends, *Polymers* 9 (2017) 63, <https://doi.org/10.3390/polym9020063>.
- [31] F. Sarasini, J. Tirillo, L. Ferrante, C. Sergi, F. Sbardella, P. Russo, G. Simeoli, D. Mellier, A. Calzolari, Effect of temperature and fiber type on impact behavior of thermoplastic fiber metal laminates, *Compos. Struct.* 223 (2019) 110961, <https://doi.org/10.1016/j.compstruct.2019.110961>.
- [32] S. Fu, B. Yu, W. Tang, M. Fan, F. Chen, Q. Fu, Mechanical properties of polypropylene composites reinforced by hydrolyzed and microfibrillated Kevlar fibers, *Compos. Sci. Technol.* 163 (2018) 141–150, <https://doi.org/10.1016/j.compscitech.2018.03.020>.
- [33] H.S. Kim, B.H. Lee, S.W. Choi, S. Kim, H.J. Kim, The effect of types of maleic anhydride-grafted polypropylene (MAPP) on the interfacial adhesion properties of bio-flour-filled polypropylene composites, *Compos. Part A Appl. Sci. Manuf.* 38 (2007) 1473–1482, <https://doi.org/10.1016/j.compositesa.2007.01.004>.
- [34] A.K. Bledzki, O. Farouk, Creep and impact properties of wood fibre-polypropylene composites: influence of temperature and moisture content, *Compos. Sci. Technol.* 64 (2004) 693–700, [https://doi.org/10.1016/S0266-3538\(03\)00291-4](https://doi.org/10.1016/S0266-3538(03)00291-4).
- [35] B. Tóth, Cs Varga, L. Bartha, Olefin-maleic-anhydride copolymer based additives: a novel approach for compatibilizing blends of waste polyethylene and crumb rubber, *J. Waste Manag.* 38 (2015) 65–71, <https://doi.org/10.1016/j.wasman.2015.01.004>.
- [36] L. Simon-Stöger, Cs Varga, E. Greczula, B. Nagy, A journey into recycling of waste elastomers via a novel type of compatibilizing additives, *Express Polym. Lett.* 13 (2019) 443–455, <https://doi.org/10.3144/expresspolymlett.2019.37>.
- [37] N. Bianka, Cs Varga, K. Kontos, L. Simon-Stöger, Remarkable role of experimental olefin-maleic-anhydride copolymer based compatibilizing additives in blends of waste PET bottles and polyamide, *Waste Biomass Valoriz.* 12 (2021) 3035–3047, <https://doi.org/10.1007/s12649-020-01253-5>.
- [38] L. Simon-Stöger, Cs Varga, Valorization of waste polyethylene by blending with ethylene-vinylacetate and incorporating a new type of compatibilizer, *J. Vinyl Addit. Technol.* 27 (2021) 332–346, <https://doi.org/10.1002/vnl.21806>.
- [39] T. Kovács, L. Simon-Stöger, B. Heller, Cs Varga, Enhancing properties of PC/PA blends via compatibilization of olefin-maleic-anhydride copolymer based additives in masterbatch form, *J. Polym. Res.* 28 (2021) 294, <https://doi.org/10.1007/s10965-021-02656-1>.
- [40] Cs Varga, B. Heller, L. Simon-Stöger, É. Makó, A Practical Manner to gtr recycling in waste HDPE/ABS, *J. Polym. Res.* 29 (2022) 329, <https://doi.org/10.1007/s10965-022-03167-3>.
- [41] G. Busca, G. Ramis, V. Lorenzelli, On the mechanism of the selective oxidation of C4 linear hydrocarbons to maleic anhydride: an FT-IR study of the adsorption and oxidation of 1,3-butadiene on vanadia-titania, *J. Mol. Catal.* 55 (1989) 1–11, [https://doi.org/10.1016/0304-5102\(89\)80237-8](https://doi.org/10.1016/0304-5102(89)80237-8).
- [42] A.H. Kopf, M.C. Koorengvel, C.A. van Walree, T.R. Daffron, J.A. Killian, A simple and convenient method for the hydrolysis of styrene-maleicanhydride copolymers to styrene-maleic acid copolymers, *Chem. Phys. Lipids* 218 (2019) 85–90, <https://doi.org/10.1016/j.chemphyslip.2018.11.011>.
- [43] Y. Zhang, J. Chen, H. Li, Functionalization of polyolefins with maleic anhydride in melt state through ultrasonic initiation, *Polymer* 47 (2006) 4750–4759, <https://doi.org/10.1016/j.polymer.2006.04.040>.
- [44] H. Kaczmarek, A. Felczak, A. Szalla, Studies of photochemical transformations in polystyrene and styrene-maleic anhydride copolymer, *Polym. Degrad. Stabil.* 93 (2008) 1259–1266, <https://doi.org/10.1016/j.polymdegradstab.2008.04.011>.
- [45] S.R. Goswami, S. Wang, P. Gnanasekar, P. Chauhan, N. Yan, Catalyst-free esterification of high amylose starch with maleic anhydride in 1-butyl-3-methylimidazolium chloride: the effect of amylose content on the degree of MA substitution, *Carbohydr. Polym.* 234 (2020) 115892, <https://doi.org/10.1016/j.carbpol.2020.115892>.
- [46] A.V. Machado, J.A. Covas, M. van Dublin, Effect of polyolefin structure on maleic anhydride grafting, *Polymer* 42 (2001) 3649–3655, [https://doi.org/10.1016/S0032-3861\(00\)00692-3](https://doi.org/10.1016/S0032-3861(00)00692-3).
- [47] L. Sangroniz, M. Fernandez, A. Santamaria, Polymers and rheology: a tale of give and take, *Polymer* 271 (2023) 125811, <https://doi.org/10.1016/j.polymer.2023.125811>.
- [48] EP 200180839790, Polyfunctional Compatibilizing Additive Package of Plastic and Rubber Composites and Method of Making the Same..

- [49] C. Li, Y. Zhang, Y. Zhang, Melt grafting of maleic anhydride onto low-density polyethylene/polypropylene blends, *Polym. Test.* 22 (2003) 191–195, [https://doi.org/10.1016/S0142-9418\(02\)00079-X](https://doi.org/10.1016/S0142-9418(02)00079-X).
- [50] H.A. Barnes, J.F. Hutton, K. Walters, Linear viscoelasticity, in: H.A. Barnes, J.F. Hutton, K. Walters (Eds.), *An Introduction to Rheology*, Elsevier, Amsterdam, 1989, pp. 37–54.
- [51] T.G. Mezger, Oscillatory tests, in: T.G. Mezger (Ed.), *The Rheology Handbook: for Users of Rotational and Oscillatory Rheometers*, Vincentz Network, 2014, pp. 135–212.