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COMPETITIVE INTERACTIONS AND CONTROLLED RELEASE OF A NATURAL ANTIOXIDANT FROM HALLOYSITE NANOTUBES

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Abstract

Halloysite nanotubes used as potential carrier material for a controlled release stabilizer in polyethylene were thoroughly characterized with several techniques including the measurement of specific surface area, pore volume and surface energy. The high surface energy of the halloysite results in the strong bonding of the additive to the surface. Dissolution experiments carried out with eight different solvents for the determination of the effect of solvent characteristics on the amount of irreversibly bonded quercetin proved that adsorption and dissolution depend on competitive interactions prevailing in the system. Solvents with low polarity dissolve only surplus quercetin adsorbed in multilayers. Polyethylene is a very apolar polymer forming weak interactions with every substance; quercetin dissolves into it only above a critical concentration. Stabilization experiments confirmed that strong adhesion prevents dissolution and results in limited stabilization efficiency. At larger adsorbed amounts better stability and extended effect were measured indicating dissolution and controlled release.

Keywords: halloysite, nanotube, quercetin, natural antioxidant, interaction, controlled release

1. Introduction

The dispersion of an active component in a matrix or the controlled release of a substance into a medium are major issues in several areas and applications. Accordingly, many combinations of materials are explored both as supports or carriers as well as active components. A variety of materials and assemblies can be used as carriers like liposomes, polymer micelles and nanoparticles, nanogels, dendrites or silica nanoparticles. The complex structure and numerous hydrogen donor and acceptor groups of the cyclic

saccharides, cyclodextrins, makes them ideal for their use in delivery systems [1]. Metal, carbon and ceramic nanotubes also may be used as carrier materials. Halloysite is a naturally occurring mineral, which is available both in platelet like and tubular form. Numerous attempts have been made to use halloysite nanotubes as carriers for all kinds of bioactive molecules including drugs [2-14]. However, besides medical applications, halloysite nanotubes are used as supports in other areas as well. Shchukin et al. [15, 16] developed an anticorrosion agent in which halloysite nanotubes contain the inhibitor that is released in a controlled way during a certain period of time. Silver nanoparticles have been loaded onto the surface of halloysite [17], and magnetic nanotubes have been also prepared from this mineral [18] to achieve simple separation technique during the application of the tubes in adsorption procedures. Halloysite nanotubes are used as adsorbents to bind organic and inorganic molecules mostly in water treatment [19, 20].

Polyolefins usually contain a phenolic antioxidant as primary stabilizer. In the past decade, however, some concerns emerged on their possible negative effect on human health [21]. Natural antioxidants could be ideal candidates to replace synthetic phenolic stabilizers. Quercetin, a natural plant derived flavonoid with confirmed antiviral and anti-inflammatory effect, proved to be a very efficient melt stabilizer in polyethylene (PE) [22]. The compound protected PE from degradation during processing already at 50 ppm additive content and improved long term stability at 250 ppm compared to the 1000 ppm used routinely in industrial additive packages. However, quercetin has some drawbacks as well. Its melting temperature is 316 °C, thus it does not melt under the normal processing conditions of PE, it is very polar resulting in extremely limited solubility in PE, and it gives the polymer a very strong yellow color. The use of a support or a carrier material to disperse quercetin homogeneously in PE seemed to be an obvious solution to these problems and halloysite nanotube were selected for the purpose.

In order to check the possible use of halloysite nanotubes as support and controlled release device for the stabilization of PE, we characterized them as thoroughly as possible and studied the dissolution of the active molecule, quercetin, from their surface. The effect of the surrounding media on the characteristic concentrations related to the adsorption and desorption of quercetin were determined in eight solvents in order to predict the dissolution of the stabilizer in PE. Preliminary stabilization experiments were carried out and are reported here to check the stabilization efficiency of quercetin adsorbed on halloysite and its possible controlled release behavior.

2. Experimental

The quercetin used in the study was obtained from Sigma-Aldrich, USA and used as received. Its molecular weight is 302,24 g/mol, melting temperature 316 °C and purity >95 %. Stabilization experiments were carried out with the Tipelin FS 471 grade ethylene/1-hexene copolymer (melt flow index of the powder: 0.32 g/10 min, nominal density: 0.947 g/cm^3) polymerized by a Phillips catalyst. The additive-free polymer powder was provided by Tisza Chemical Ltd. (TVK), Hungary.

The halloysite nanotubes (Dragonite XR) were supplied by Applied Minerals, USA. The morphology of the mineral was characterized by scanning (SEM) and transmission (TEM) electron microscopy. SEM indicated the aggregation of the tubes to relatively large particles (**Fig. 1**). The average size of the particles was determined by a Horiba Partica LA950V2 particle size analyzer and proved to be 6.5 μm. The particles could be efficiently disintegrated by ultrasound. TEM micrographs verified tubular structure indeed (**Fig. 2**) and the average dimensions of the tubes could be determined from the images. The measurement of more than 70 particles yielded an average length of 203 ± 119 nm, outer tube diameter of 50 ± 23 nm and an inner diameter of 15 ± 6 nm. The specific surface area of the tubes, pore

size and volume were determined by nitrogen adsorption using a NOVA2000 (Quantachrome, USA) apparatus. The measurements were done at -195 °C after evacuating the sample at 120 °C for 24 hours down to 10^{-5} Hgmm. Nitrogen adsorption yielded a specific surface area of 57 m^2/g and total pore volume of 0.181 cm^3/g. Surface area was calculated also from the dimensions the tubes determined from TEM micrographs. A specific surface area of 49 m^2/g and a tube volume of 0.039 cm^3/g was obtained from the calculations. The agreement in specific surface areas is reasonable, but the large difference in pore and tube volumes indicates that nitrogen adsorption measures also pores around and inside the particles and not only the volume of the tubes. The dispersion component of surface tension was determined by inverse gas chromatography (IGC). The filler was agglomerated with water and the 250-400 μm fraction was used for the packing of the column. The dispersion component of surface tension was determined by the injection of n-alkanes at various temperatures between 160 and 300 °C, because of the high surface energy of the mineral. Surface tension extrapolated to 100 °C is 278 mJ/m^2.

The active component, quercetin, was loaded onto the surface of the tubes from ethanol solutions of increasing concentrations. The halloysite content of the suspension was kept at 10 g/dm^3 in all experiments. The suspension was treated with ultrasound for 60 min to separate the tubes and then evacuated to remove air from within the tubes. After evacuation the suspension was agitated with ultrasound for another 15 min and then ethanol was removed by evaporation. The samples were kept in a vacuum oven at room temperature overnight. The amount of adsorbed quercetin was determined by thermogravimetry (TGA). The correlation between the nominal and measured quercetin content of the tubes is presented in **Fig. 3**. The agreement between the two quantities is reasonable, especially if we consider the complicated procedure to cover halloysite with the target molecule.

Eight solvents with different characteristics were used to dissolve surplus quercetin

from the surface of the nanotubes. The solvents used, their source and the solubility of quercetin in them are listed in **Table 1**. Various quantities were used to characterize the polarity and possible interaction of the solvents with quercetin. The Hildebrand solubility parameter (δ), dielectric permittivity (ε), dipole moment (μ) characterize polarity, polarizability and interaction in general terms, while the donor (DN) and acceptor number (AN^*) of Fowkes indicates the tendency for specific interactions. The characteristics of the solvents are listed in **Table 2**. The coated filler was put into a vial containing the selected solvent, sealed and vigorously stirred for 24 hours. The suspension was centrifuged and then the concentration of quercetin in the solution was determined by UV-VIS spectroscopy, with the measurement of the intensity of the absorption peak appearing at 374 nm.

Preliminary stabilization experiments were carried out with PE samples homogenized in a Brabender W 50 ETH internal mixer. The PE powder and the additives were mixed first in a mechanical blender for 20 s and then the blend was introduced into the mixer. Processing was carried out at 250 °C and 50 rpm for 10 min. The obtained material was compression molded into 1 mm thick plates at 190 °C and 180 kN using a Fontijne SRA 100 equipment and the plates were placed into an oven at 100 °C and aged for 5 and 10 days. Stability was characterized by the oxygen induction time (OIT) measured at 180 °C in oxygen.

3. Results and discussion

The results are discussed in several sections. The dissolution of quercetin from the surface of halloysite is presented first together with the characteristic concentrations obtained. Competitive interactions are considered in the next section, followed by the discussion of correlations and consequences for practice.

3.1. Dissolution

The dissolution technique introduced by Papirer [2323] and adapted later by Fekete [24] is a very simple, but efficient approach to study the adsorption of various substances onto the most diverse surfaces. Up to now the method was mainly used for the study of the surface coating of mineral fillers with surfactants. The method consists of the coverage of the filler with increasing amounts of the surfactant or other active molecule followed by the dissolution of the surplus, not bonded material from the surface with an appropriate solvent. Strong interaction prevents the dissolution of the active molecules at small concentrations, below monolayer coverage, but more and more of the compound is dissolved as the amount used for treatment increases and multilayer coverage forms. In **Fig. 4** the concentration of quercetin dissolved in butanol is plotted against the amount used for treatment. The figure demonstrates well the procedure and the effect of surface coverage. Quercetin concentration is zero in the solution at small amounts used for treatment, all the molecules remain adsorbed on the surface. With increasing coverage quercetin appears in the solution first and then its concentration increases linearly, all additional amount added is dissolved in this range. **Fig. 4** shows two sets of data obtained after 24 and 85 hours of stirring. Dissolved amounts are practically the same proving that prolonged time does not lead to additional dissolution. All subsequent dissolution experiments were carried out for 24 h, as a consequence.

The results of dissolution experiments are plotted in a different way in **Fig. 5**. The amount of bonded quercetin is plotted against the quantity used for treatment. The two series shown were determined in two solvents, in butanol and ethyl-acetate. The obtained dissolution correlations indicate the physisorption of quercetin on the surface of the halloysite; both correlations tend towards a saturation value. Two characteristic quantities can be determined from such adsorption isotherms. c_{100} is the proportionally bonded additive when all the material used for treatment remains on the surface and nothing is

dissolved. The other characteristic concentration is c_{max}, the maximum amount of the compound used for treatment that remains on the surface without dissolution. The comparison of the two dissolution correlations presented in **Fig. 5** clearly indicates differences in the solvation power of the two solvents, butanol is more effective in dissolving the active substance from the surface. Both c_{100} and c_{max} are smaller in butanol than in the other solvent, ethyl-acetate.

Characteristic quantities determined with the eight solvents are compiled in **Table 2** together with characteristics which are related to their polarity and dissolution strength. c_{100} values change between 0.8 and 2.2 wt% related to the filler, with an average value of 1.5 wt%. The dependence of c_{100} on solvent characteristics differs from earlier experience [25]. During the treatment of $CaCO_3$ with stearic acid c_{100} was constant, practically independent of the solvent used. c_{max} values, on the other hand, changed in a relatively wide range in that case and we see much larger variation also for the halloysite/quercetin pair. c_{100} varies between 3.1 and 6.5 wt%, a twofold increase with changing solvent characteristics. The difference indicates the significance of competitive interactions and the influence of the surrounding medium, which is of importance also for the intended application.

3.2. Competitive interactions

As mentioned above the dissolution correlations clearly prove that quercetin is physisorbed on the surface of halloysite. This statement is further corroborated by the fact that characteristic concentrations depend on solvent characteristics, which is determined by competitive interactions acting during dissolution; chemisorption would result in a continuously increasing amount of bonded quercetin. Quercetin interacts with the surface of the halloysite, but also with the solvent, while this latter also adsorbs on the surface of the filler. Since the surface energy of halloysite is very large, quercetin is adsorbed very

strongly to it, the solvent can interact only with free surface or try to replace quercetin, which becomes easier with increasing solvent power. The fact that such an exchange may occur is shown by the effect of solvent characteristics on c_{100} and c_{max}.

In an attempt to express the effect of the solvent on the characteristics concentrations in quantitative terms, we plotted them against the properties listed in **Table 2**. In **Fig. 6** the characteristic concentrations are presented as a function of the solubility of quercetin in the solvents. The two correlations are very similar, quite interesting and difficult to explain. A minimum appears on the c_{max} vs. solubility correlation around 5 g/dm^3. Large amounts of quercetin remain on the surface of halloysite at small solubility, because the interaction between the solvent and the active molecule is not very strong, interaction with the filler is preferred. The slight increase observed at large solubility is more difficult to understand. Specific interactions and the actual concentration of quercetin on the surface and in the solution may play a role here. Preferential interactions must be influenced by the presence of all components as shown by Karasz [26] in copolymers and polymer blends.

Solubility parameter (δ), dielectric permittivity (ε) and dipole moment (μ) were used for the characterization of the solvents. Although the scatter of the points is rather large, a clear tendency could be observed for all three correlations; characteristic concentrations decrease with the increasing value of the variable in question. We calculated the solubility parameter of quercetin by using the group contribution of van Krevelen and Hoftyzer [27] and obtained the value of 26 MPa$^{1/2}$. The solubility parameter of the solvents ranges from 15 to 26 and characteristic concentrations decrease continuously as their solubility parameter increases. Since all the correlations are very similar, we present here only the one obtained between c_{100}, c_{max} and the dielectric constant of the solvents (**Fig.7**). Stronger effect and larger scatter is observed for c_{max}, but the same tendency prevails as for c_{100}. Obviously larger polarity and polarizability increases the solubility of quercetin in the solvents and

dissolves it from the surface of halloysite.

The characteristics of the solvents discussed above do not reflect specific interactions between the various compounds. These can be expressed much more adequately by the donor and acceptor numbers of Riddles and Fowkes [28 29]. Characteristic concentrations are plotted against the donor (DN) and corrected acceptor (AN^*) numbers in **Fig. 8**. The scatter of the points is significant, but some conclusions can be drawn from the figure, nevertheless. Characteristics values seem to be smaller at both ends of the range, at large DN and AN* values indicating that both acceptor and donor characteristics help dissolution. This conclusion is further confirmed by the fact that no points are situated in the middle of the range, since quercetin could not be dissolved in such solvents in sufficient amounts to carry out the experiments. These results also indicate that the dissolution of quercetin from the surface of halloysite must be very difficult in PE, a completely apolar polymer.

3.3. Discussion, consequences

The results above indicated that halloysite can be covered with a large amount of quercetin (see **Fig. 3**). Dissolution experiments, on the other hand, showed that a part of the active molecules is adsorbed very strongly onto the surface and cannot be dissolved from it (**Fig. 4**). Obviously the alignment of the molecules on the surface and surface coverage are of large importance, if we want to use the material combination as controlled release stabilizer in polyethylene. Since quercetin is a rather planar molecule one would assume that it is arranged parallel to the surface of the mineral and preliminary molecular modeling confirmed this assumption. Accepting this arrangement, the surface coverage of halloysite was calculated both from the c_{100} and the c_{max} values. A surface need of 0,81 nm^2 was assumed for the quercetin molecule and the surface area obtained by nitrogen adsorption

was used in the calculations. The results are summarized in **Table 3**. Surface coverages calculated from the c_{100} value, i.e. from the amount proportionally bonded to the surface are much smaller than 100 %, indicating an energetically heterogeneous surface and a loose arrangement of the molecules on it. Large free surfaces are available at this quercetin concentrations. Values derived from c_{max} are close to or slightly larger than 100 % surface coverage. Obviously partial multilayers remain on the surface of halloysite only if the solvation power of the solvent is small, its interaction with quercetin is weak.

Smaller than 100 % surface coverage raises also the question of the location of the active molecule on the surface. The chemical composition of halloysite is different inside the tubes and on the outer surface. In the inside the surface corresponds to kaolinite containing aluminum oxide hydroxide moieties, while the external surface of the tube consist of silicon dioxide units. Some sources claim that molecules can penetrate also into the interlamellar space [3030-33]. The majority of the groups using halloysite as carrier material for active molecules assume that these latter are located within the tubes and released from there to achieve prolonged effect [2-14]. Unfortunately, usually not much proof is supplied for this assumption and further study and model calculations must be carried out to define the location and distribution of quercetin molecules on the surface of the halloysite unambiguously.

Since the location of quercetin could not be defined without doubt, preliminary stabilization studies were carried out to check, if the desired controlled release effect can be achieved with the halloysite/quercetin combination. Quercetin was adsorbed onto the surface of the halloysite tubes in different amounts, homogenized with polyethylene at 0.33 wt% halloysite content and the residual stability of the polymer was determined after oven ageing. Oxygen induction time is plotted as a function of ageing time in **Fig. 9** at 50 and 250 ppm quercetin content corresponding to 1.5 and 7.5 wt% loading of the additive on the

halloysite. Considering the solubility parameter of PE (17 $MPa^{1/2}$)[34], and comparing both solubility parameters and characteristic concentrations, we come to the conclusion that the first concentration is around or below the expected c_{100} value, while the second is larger than c_{max}. Two sets of data are plotted in **Fig. 9** at 50 ppm quercetin content. The components, i.e. quercetin and halloysite, were added to polyethylene separately in one case, while quercetin was adsorbed onto the mineral, in the other. Time dependence of stability is completely different in the two cases. Relatively large stability is obtained initially in the first, indicating the stabilization efficiency of the additive, while practically none in the second showing that quercetin adsorbed below the c_{100} level is attached strongly to the surface of the halloysite and cannot stabilize the polymer. Stability remains very small throughout the time span of the experiment. At 250 ppm adsorbed quercetin, stability is considerably larger at the beginning of ageing and does not decrease much with ageing time. We must point it out here, though, that the absolute value of stability is very small, because of the high temperature and long processing time used in these preliminary experiments. The effect and behavior of the stabilizer must be confirmed with further experiments. Nevertheless, these results indicate that quercetin can be dissolved from the surface of halloysite only at concentrations larger than c_{100} in polyethylene and the time dependence presented in **Fig. 9** may indicate that a large amount of quercetin is located within the tubes and is released slowly with time.

4. Conclusions

Halloysite nanotubes used as potential carrier material for a controlled release stabilizer in polyethylene were thoroughly characterized with several techniques. Specific surface area, pore volume and surface energy determine the adsorption of the active molecule on the surface of the mineral. The high surface energy of the halloysite results in

strong bonding of the additive onto the surface. Dissolution experiments carried out for the determination of the effect of solvent characteristics on the amount of irreversibly bonded quercetin proved that adsorption and dissolution depend on competitive interactions prevailing in the system. Solvents with low polarity dissolve only surplus quercetin adsorbed in multilayers. Polyethylene does not contain functional groups, the polymer forming weak interactions with every substance; quercetin dissolves into it from the halloysite surface only above a critical concentration. Preliminary stabilization experiments confirmed that strong adhesion prevents dissolution and results in limited stabilization efficiency. At larger adsorbed amounts better stability and extended effect were measured indicating dissolution and controlled release. Further experiments are needed for the determination of the exact location of quercetin on the halloysite surface and the verification of controlled release action.

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6. References

1. L., Szente, J., Szejtli, Adv. Drug Delivery Rev. **1999**, *36*, 17–28
2. Y. M., Lvov, D. G., Shchukin, H., Möhwald, R. R., Price, ACS Nano **2008,** *2*, 814-820
3. E., Ruiz-Hitzky, K., Ariga, Y., Lvov, Bio-inorganic hybrid nanomaterials. strategies, syntheses, characterization and applications, **2008**, Wiley, Weinheim, Germany
4. N. G., Veerabadran, R. R., Price, Y. M., Lvov, Nano, **2000**, *2*, 115-120
5. R. S., Byrne, P. B., Deasy, J. Microencapsulation, **2005,** *22*, 423-437
6. R. R., Price, B. P. Gaber, Y., Lvov, J. Microencapsulation, **2001**, *18*, 713-722
7. K., Krejcova, M., Rabiskova, Chem. Listy, **2008**, *102*, 35-39
8. D., Fix, D. V., Andreeva, Y. M., Lvov, D. G., Shchukin, H., Moehwald, Adv. Funct. Mater., **2009,** *19*, 1720-1727
9. A. W., Smith, Adv. Drug Delivery Rev., **2005**, *57*, 1539-1550
10. S. R., Levis, P. D., Deasy, Int. J. Pharm., 2003, *253*, 145-157
11. H. M., Kelly, P. B., Deasy, E., Ziaka, N., Claffey, Int. J. Pharm., **2004**, *274*, 167-183
12. H., Cornejo-Garrido, A., Nieto-Camacho, V., Gómez-Vidales, M. T., Ramírez-Apan, P., del Angel, J. A., Montoya, M., Dominquez-López, D., Kibanova, J., Cervini-Silva, Appl. Clay Sci., **2012**, *57*, 10-16
13. A., Ghebaur, S. A., Garea, H., Ivou , Int. J. Pharm., **2012**, *436*, 568-573
14. R., Qi, R., Guo, M., Shen, X., Cao, L., Zhang, J., Xu, J., Yu, X., Shi, J. Mater. Chem., **2010**, *20*, 10622-10629
15. D. G., Shchukin, S. V., Lamaka, K. A., Yasakau, M. L., Zheludkevich, M. G. S., Ferreira, H., Möhwald, J. Phys. Chem. C, **2008**, *112*, 958-964
16. D. G., Shchukin, H., Moehwald, Adv. Funct. Mater., **2007**, *17*, 1451-1458
17. P., Liu, M., Zhao, Appl. Surf. Sci., **2009**, *255*, 3989-3993

18. Y., Xie, D., Qian, D., Wu, X., Ma, Chem. Eng. J., **2011**, *168*, 959-963
19. P., Luo, Y., Zhao, B., Zhang, J., Liu, Y., Yang, J., Liu, Water Res., **2010**, *44*, 1489-1497
20. W., Jinhua, Z., Xiang, Z., Bing, Z., Yafei, Z., Riu, L., Jindun, C., Rongfeng, Desalination, **2010**, *259*, 22-28
21. D., Brocca, E., Arvin, H, Mosbaek,Water Res., **2002**, *36*, 3675-3680
22. D., Tatraaljai, E., Földes, B., Pukanszky, Polym. Degrad. Stab., **2014**, *102*, 41-48
23. C. S., Fluor, E., Papirer, Ind. Eng. Chem. Prod. Res. Dev., **1982**, *21*, 337-341
24. E., Fekete, B., Pukanszky, A., Toth, I., Bertoti, J. Colloid Inerface Sci., **1990**, *135*, 200-208
25. E., Fekete, B., Pukanszky, J. Colloid Inerface Sci., **1997**, *194*, 269-275
26. F. E., Karasz, W. J., MacKnight, Multicomponent Polymer Materials, **1986**, *Ch. 4*, ACS
27. D. W., van Krevelen, K., te Nijenhuis, Properties of Polymers: Their Correlation with Chemical Structure; their Numerical Estimation and Prediction from Additive Group Contributions, **2009**, Elsevier, Amsterdam, Netherlands
28. F.L., Riddle, F. M., Fowkes, J. Am. Chem. Soc. **1990**, *9*, 3259-3264
29. U., Panzert, H. P., Schreiber, Macromolecules **1992**, *25*, 3633-3631
30. E., Joussein, S., Petit, J., Churchman, B., Theng, D., Righi, D., Delvaux, Clay Miner., **2005,** *40*, 383-426
31. P. K., Nicolini, B. R. C., Fukamachi, F., Wypych, S. A., Mangrich, J. Colloid Interface Sci. **2009**, *338*, 474-479
32. H., Cheng, Q., Liu, J., Yang, J., Zhang, L. R., Frost, X., Du, J. Mol. Struct. **2011**, 990, 21-25
33. R. M., Carr, H., Chih, Clay Miner. **1971,** *9*, 153-166

34. A. F. M., Barton, Handbook of Solubility Parameters and Other Cohesion Parameters, **1983,** CRC Press, Boca Raton, Florida, USA

Captions

Fig. 1 Particle structure of aggregated halloysite nanotubes; a SEM micrograph.

Fig. 2 TEM micrograph taken from individual halloysite nanotubes.

Fig. 3 Correlation between the nominal and measured quercetin content of coated halloysite nanotubes.

Fig. 4 Dissolved quercetin plotted against the amount used for treatment. Effect of the time of dissolution; (○) 24 h, (□) 85 h.

Fig. 5 Typical dissolution curves presenting the amount of bonded quercetin as a function of the amount used for coating. Effect of solvent characteristics; (○) butanol, (□) ethyl-acetate.

Fig. 6 Correlation between the characteristic concentrations and the solubility of quercetin in the various solvents; (○) c_{100}, (□) c_{max}.

Fig. 7 Characteristic concentrations plotted against the dielectric constant of the solvents used for dissolution; (○) c_{100}, (□) c_{max}.

Fig. 8 Lose correlation between the acid-base characteristics of the solvents used in the experiments and the characteristic concentrations determined by the dissolution technique; (○) c_{100}, (□) c_{max}.

Fig. 9 Effect of ageing time and the amount of quercetin adsorbed on the surface of halloysite on the residual stability of PE; (□) 50 ppm quercetin, separately dispersed, (△) 50 ppm quercetin, adsorbed, (●) 250 ppm quercetin, adsorbed.

Table 1 Type, source and quality of the solvents used in the experiments as well as the solubility of quercetin in them

Solvent	Supplier	Purity (%)	Solubility of quercetin (g/cm^3)
Chloroform	Molar Chemicals	99.9	0.2
Diethyl-ether	Merck	99.5	0.2
Ethyl-acetate	Molar Chemicals	99.9	0.9
Butanol	VWR International	99.0	1.2
Methyl-ethyl-ketone	Molar Chemicals	99.8	6.0
Ethanol	Molar Chemicals	99.9	11.0
Acetone	Molar Chemicals	99.9	18.0
Tetrahydrofuran	Molar Chemicals	99.9	40.0

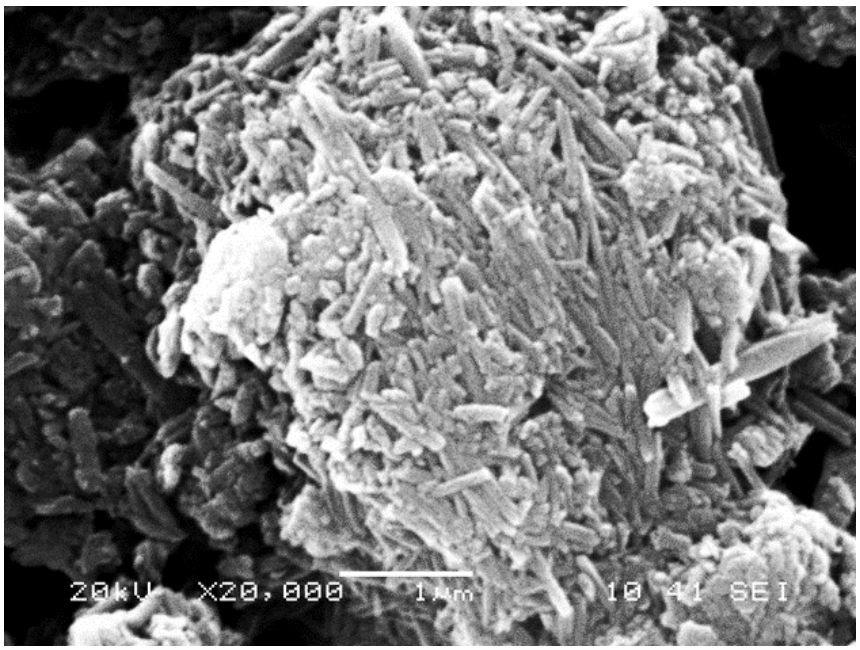
Table 2 Properties of the solvents used in the dissolution experiments and the characteristic concentrations determined

Solvent	δ $(MPa)^{1/2}$	μ (D)	ε	DN (kcal/mol)	AN* (kcal/mol)	Characteristic concentration (%)	
						c_{100}	c_{max}
Chloroform	19.0	1.04	4.80	0	5.4	2.2	6.5
Diethyl-ether	15.1	1.15	4.33	19.2	1.4	1.4	5.8
Ethyl-acetate	18.6	1.78	6.08	17.1	1.5	2.0	4.7
Butanol	23.3	1.66	17.84	–	9.1	1.1	3.7
Methyl-ethyl-ketone	19.0	2.78	18.56	–	–	1.2	3.1
Ethanol	26.0	1.69	25.30	20.0	10.3	0.8	4.0
Acetone	20.2	2.88	21.01	17.0	2.5	1.4	5.2
Tetrahydrofuran	18.6	1.75	7.52	20.0	0.5	1.5	4.5

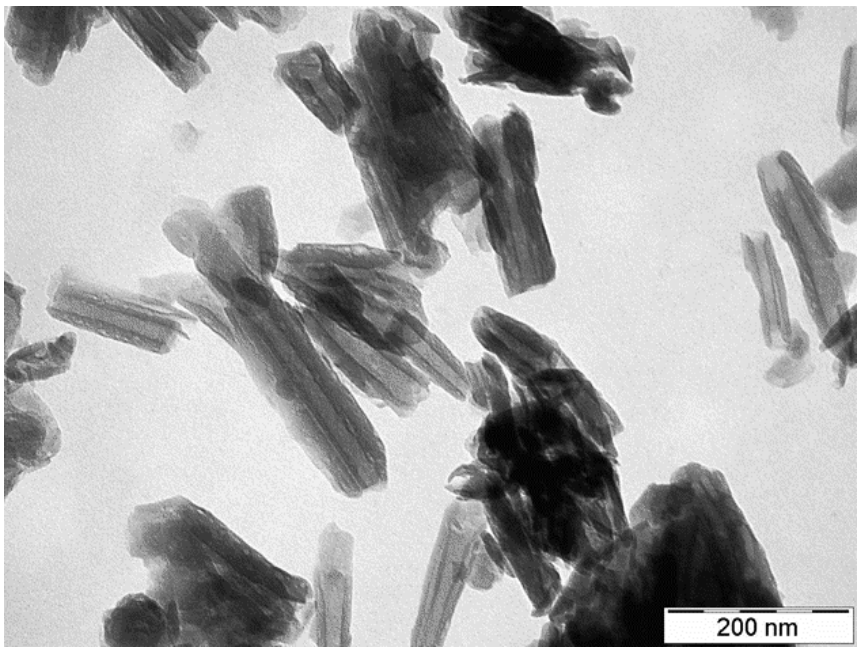
Table 3 Surface coverage of the halloysite with quercetin at the characteristic concentrations derived from the dissolution experiments

Solvent	c_{100} (wt%)	Surface coverage (%)	c_{max} (wt%)	Surface coverage (%)
Chloroform	2.2	62	6.5	184
Diethyl-ether	1.4	40	5.8	164
Ethyl-acetate	2.0	57	4.7	133
Butanol	1.1	31	3.7	105
Methyl-ethyl-ketone	1.2	34	3.1	88
Ethanol	0.8	23	4.0	113
Acetone	1.4	40	5.2	147
Tetrahydrofuran	1.5	42	4.5	127

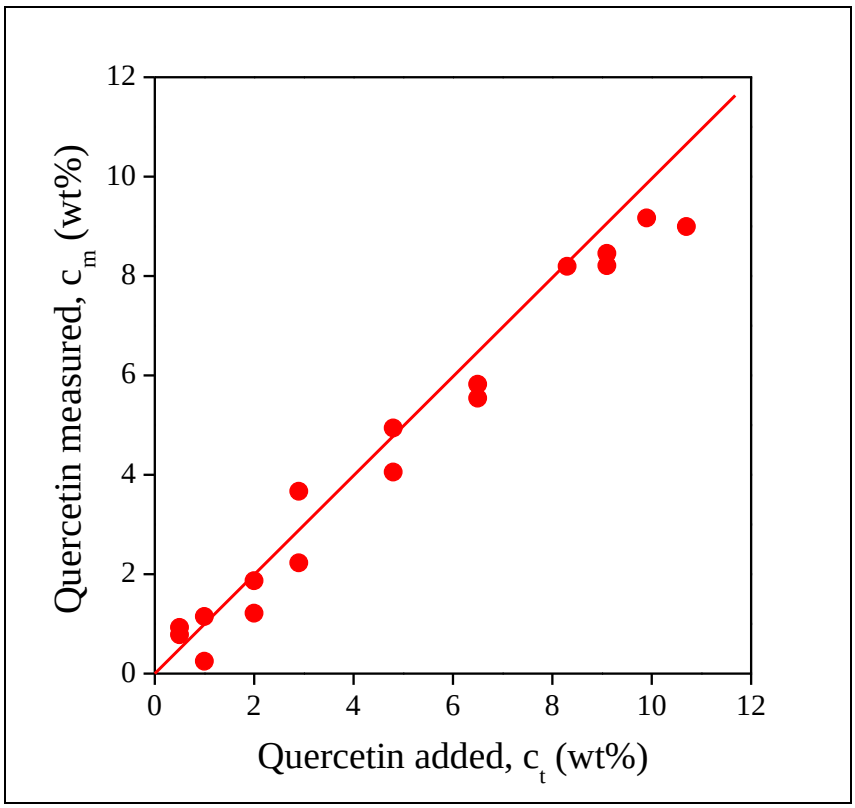
Hári, Fig. 1



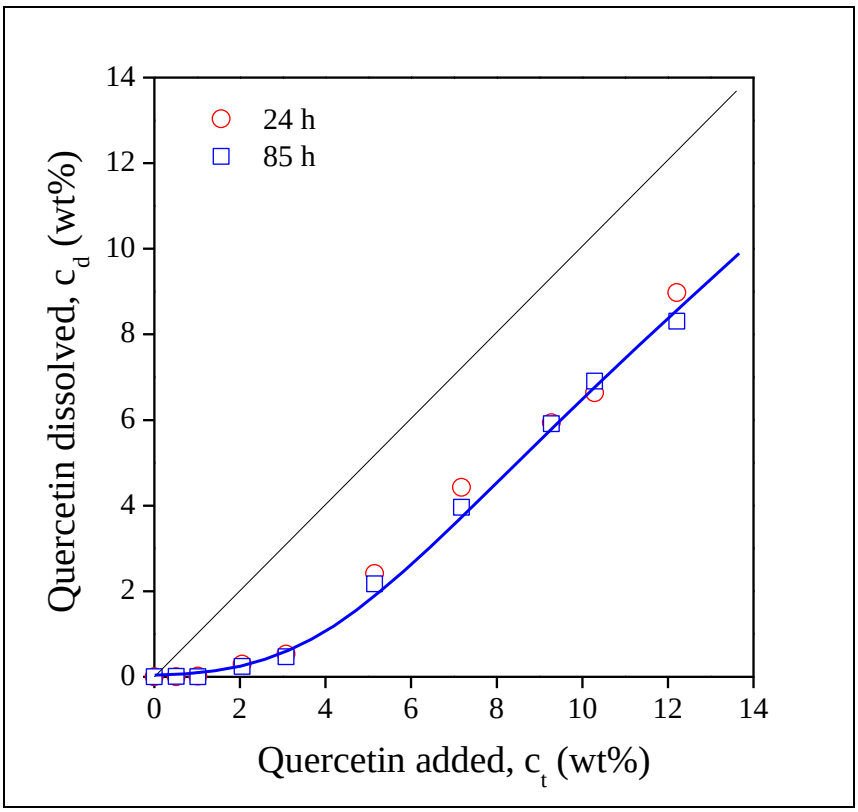
Hári, Fig. 2



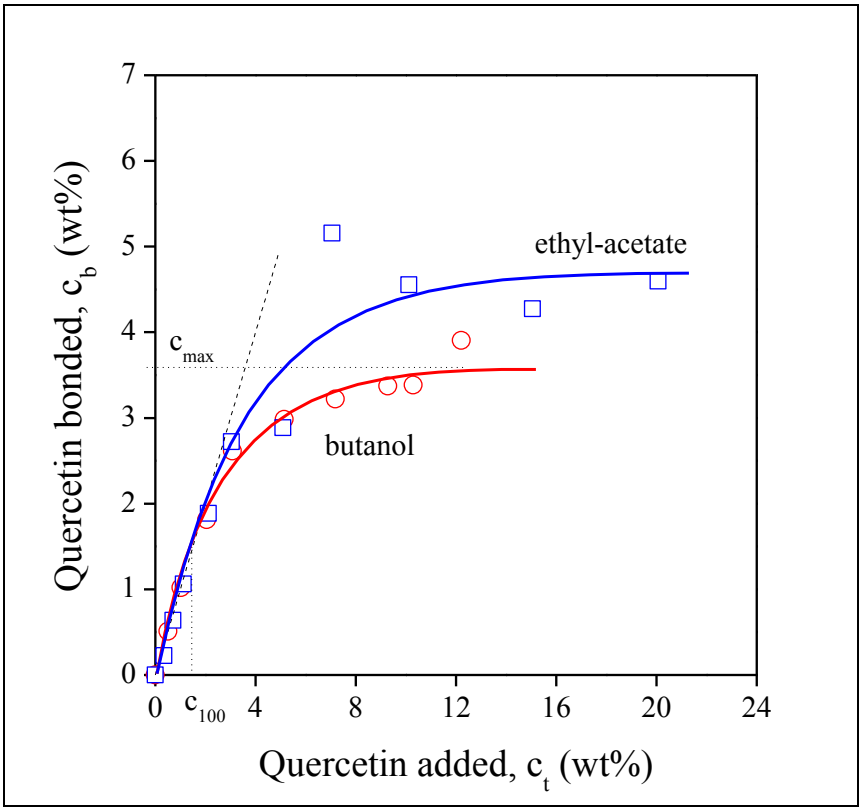
Hári, Fig. 3



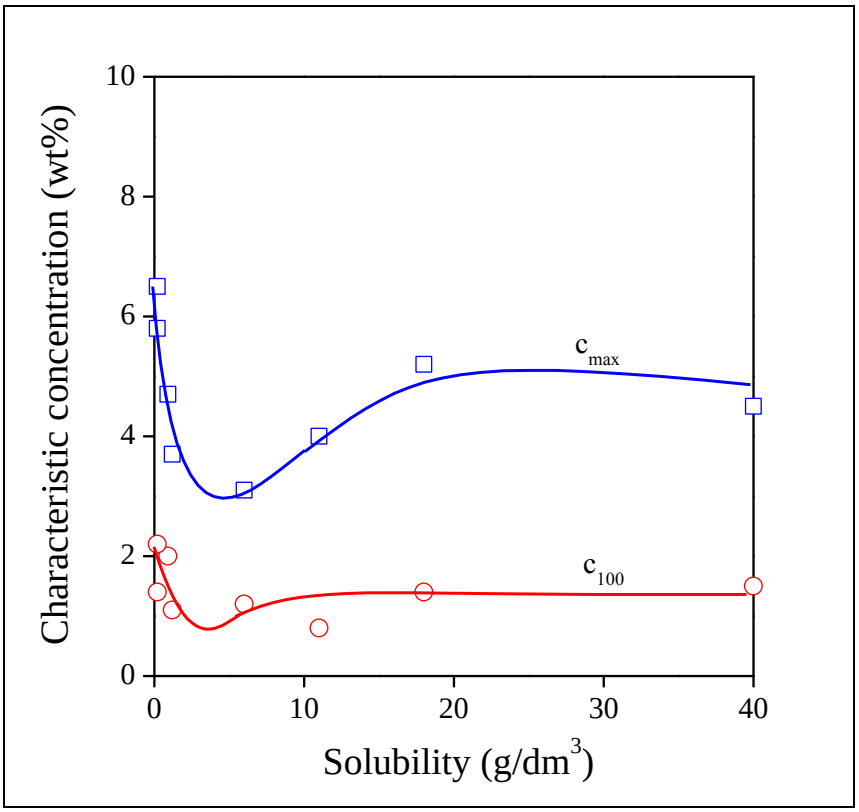
Hári, Fig. 4


24 h
85 h
Quercetin dissolved, c_d (wt%)
Quercetin added, c_t (wt%)
0
2
4
6
8
10
12
14

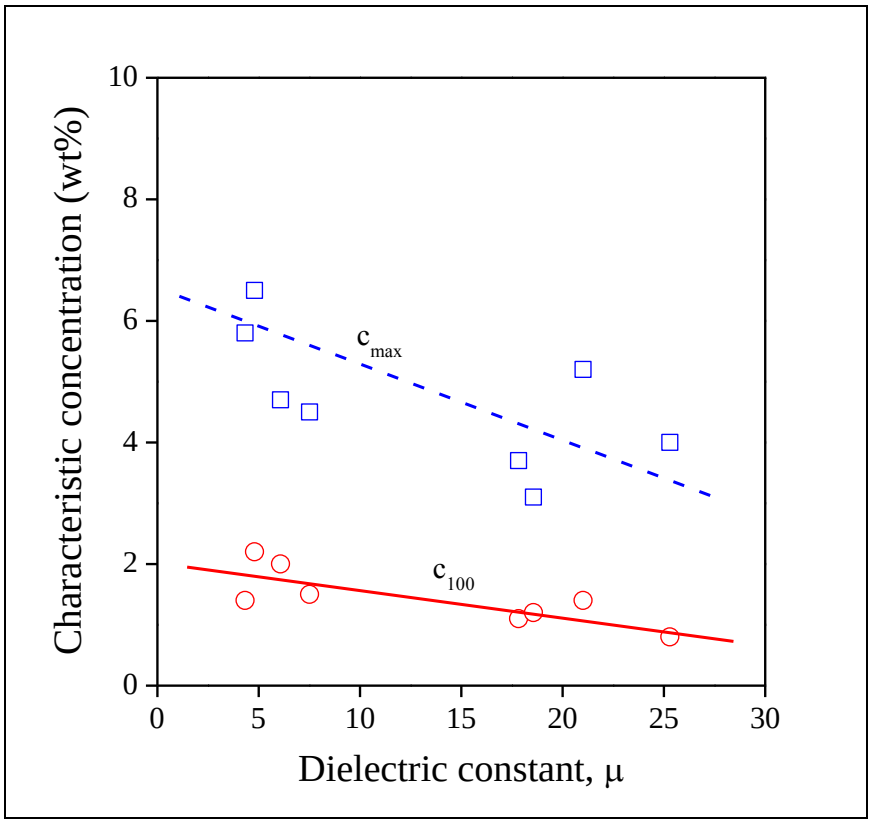
Hári, Fig. 5


Quercetin bonded, c_b (wt%)
Quercetin added, c_t (wt%)
ethyl-acetate
butanol
c_{max}
c_{100}
0
1
2
3
4
5
6
7
0
4
8
12
16
20
24

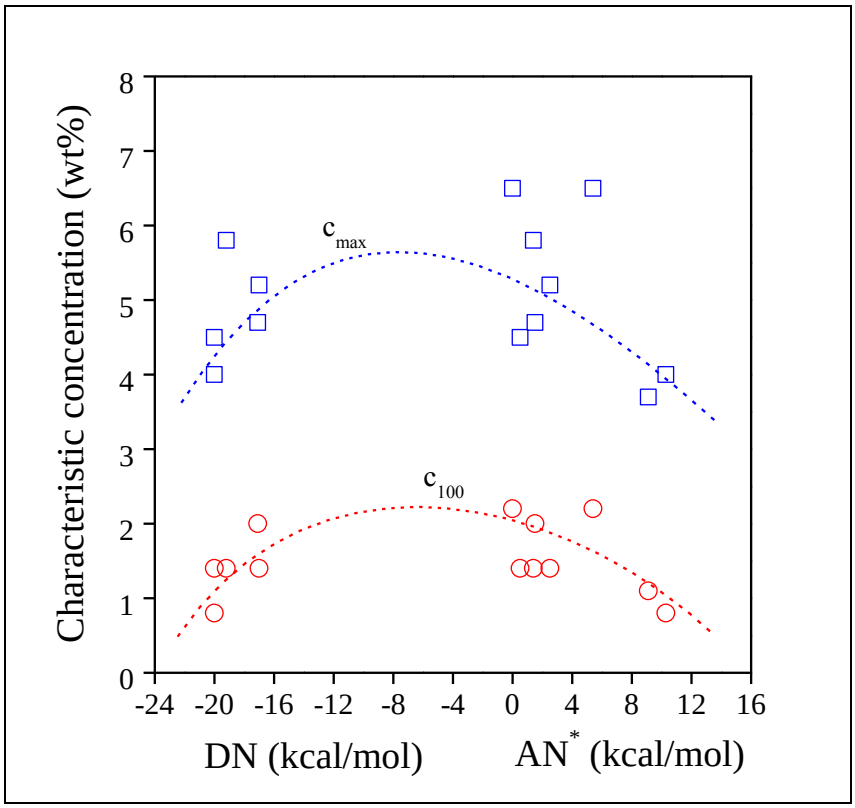
Hári, Fig. 6


Characteristic concentration (wt%)
Solubility (g/dm3)
cmax
c100
0
2
4
6
8
10
0
10
20
30
40

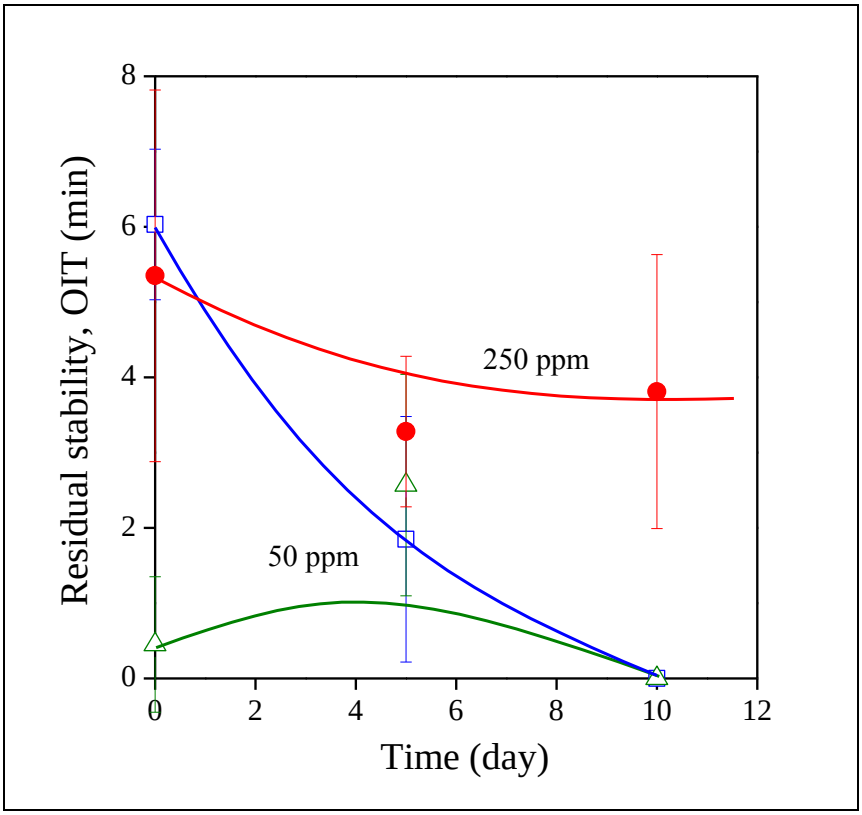
Hári, Fig. 7


Characteristic concentration (wt%)
Dielectric constant, μ
c_max
c_100
0
2
4
6
8
10
0
5
10
15
20
25
30

Hári, Fig. 8


Characteristic concentration (wt%)
8
7
6
5
4
3
2
1
0
c max
c 100
-24 -20 -16 -12 -8 -4 0 4 8 12 16
DN (kcal/mol)
AN* (kcal/mol)

Hári, Fig. 9


Residual stability, OIT (min)
Time (day)
250 ppm
50 ppm
0
2
4
6
8
10
12