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Study of transition metal complexes used as catalysts for curing of unsaturated polyester resins

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REFERENCES

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ANNOTATION

The subject of this dissertation is the study of the siccative activity of transition metal complexes and their potential use as accelerators for curing of unsaturated polyester resins. The theoretical part presents the various types of processes for the preparation of unsaturated polyesters in general terms. Emphasis is also placed on the selection of raw materials that affect the properties and application of the final polyester. The main part is devoted to the curing process of unsaturated polyester, leading to unsaturated polyester resin. The studied process is feasible due to the involvement of an initiator and accelerator, brief introduction of which concludes the theoretical part. Based on the results of the tests, a logical evaluation of the findings, their development, confirmation, or refutation, takes place. The research line began with verifying the catalytic activity of individual complexes by measuring the gelation time, which was then confirmed and expanded with curing characteristics. Testing in a concentration series, focused on hardness, thickness, colour, coating adhesion, or chemical resistance provided important insights into possible optimal concentrations. The selected concentrations were then subjected to thermomechanical analysis on cast samples. Various types of these cast samples were used to expand the portfolio of characteristic properties necessary for the application of polyester resins, such as tensile and flexural properties. The perfection of the curing of individual formulations was assessed by determining the extractable fraction. For the selected optimal concentrations, physical-mechanical tests on steel panels were also supplemented.

KEYWORDS

catalytic activity, transition of metal salts, curing process, unsaturated polyester resins

ANOTACE

Předmětem této disertační práce je studium katalytické aktivity komplexů přechodných kovů a jejich potenciál k využití jako urychlovačů pro vytvrzování nenasycených polyesterových pryskyřic. V teoretické části jsou představeny jednotlivé typy procesů pro přípravu nenasycených polyesterů v obecné rovině. Důraz je také kladen na výběr vstupních surovin, které ovlivňují vlastnosti a použití finálního polyesteru. Stěžejní část je věnována vytvrzovacímu procesu nenasycených polyesterů vedoucí na nenasycenou polyesterovou pryskyřici. Proveditelnost námi sledovaného procesu je možná za účasti iniciátoru a urychlovače, jejichž stručné představení zakončuje teoretickou část. Na základě výsledků provedených testů dochází k logickému zhodnocení zjištěných faktů, jejich rozvoji, potvrzení či vyvrácení. Stručná linie výzkumu začala ověřením katalytické aktivity jednotlivých komplexů prostřednictvím měření doby gelace, následně byla potvrzena a rozšířena o vytvrzovací charakteristiku. Testování v koncentrační řadě, zaměřené na tvrdost, tloušťku, barevnost, adhezi nátěru či chemickou odolnost poskytlo důležité poznatky o možných optimálních koncentracích. Vybrané koncentrace byly následně podrobeny termomechanické analýze na odlitých vzorcích. Různé typy těchto odlitých vzorků byly použity pro rozšíření portfolia charakteristických vlastností potřebných pro použití polyesterových pryskyřic, jako jsou tahové a ohybové vlastnosti. Dokonalost vytvrzení jednotlivých formulací byla hodnocena stanovením extrahovatelného podílu. Pro vybrané optimální koncentrace byly doplněny testy na skleněných panelech o fyzikálně-mechanické testy na panelech ocelových.

KLÍČOVÁ SLOVA

katalytická aktivita komplexy přechodných kovů, vytvrzovací proces, nenasycené polyesterové pryskyřice

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Introduction

Unsaturated polyester resins (UPRs) are among the most widely used thermosets due to their low cost, ease of processing, and favourable properties [1]. Specifically, they consist of solutions of linear unsaturated polyesters in a reactive monomer, which are crosslinked through a curing process [2]. To initiate the curing process, the presence of free, highly reactive radicals is required. For this purpose, initiators are added to the system, which decompose to generate these radicals. However, only a limited number of such initiators are capable of initiating the reaction at ambient temperature [3]. One potential solution is the addition of accelerators, which are often complexes of transition metals [4]. These accelerators catalyse the curing process, thereby reducing the time required to solidify the polymer mixture.

A transition metal complex typically consists of a metal ion, which participates in the catalytic reaction, and an anionic component, which ensures solubility. To achieve sufficient accelerator efficiency, the complex must be soluble in the system [5]. For this reason, catalysts with branched carboxylic acids, such as octoates and naphthenates, are commonly used [6]. A significant advantage of accelerators is their effectiveness in small quantities and relatively low concentrations. Cobalt-based accelerators remain among the most widely used accelerators today. However, on October 1, 2021, the European Union proposed restrictions on cobalt salt compounds under the REACH regulation, as they were classified as carcinogens in category 1B [7–10]. For manufacturers, this represents the culmination of increasing pressure to find a suitable alternative to cobalt-based accelerators. UPRs are utilized across various industries, including construction, automotive, aerospace, and shipbuilding [11,12].

This dissertation focuses on the investigation and monitoring of the catalytic activity of transition metal complexes during the curing process of unsaturated polyester resins. The activity of selected metal ions is evaluated using both commercially available and *in-house* synthesized accelerators. A standard cobalt-based accelerator serves as a reference. The experimental section describes a stepwise process to determine the catalytic activity of these accelerators. Once catalytic activity is confirmed, the findings are further applied in tests involving both castings and thin-film coatings, followed by an evaluation of physical and physicochemical properties.

The results are presented in a logically structured sequence of tests to thoroughly examine and verify the influence of catalytic activity through accompanying physical and physic mechanical analyses. The objective is to determine the optimal concentrations of individual tested formulations with potential practical applications

1 Experimental methods

Due to limited range of thesis, the most important methods will be described in a short version

1.1 Preparation of Test Formulations

ChS Polyester 109 was treated with a given accelerator immediately before testing and homogenized in a SpeedMixer DAC 150.3 FVZ (Hamm, Germany) for 5 min (3500 rpm), degassed in an ultrasonic bath for 2 min, and tempered in a water bath (25 ± 0.5 °C) for 15 min. VO-T was dissolved in acetone immediately before use (20 μl of acetone was used on 1 g of UPR formulation). The other solid accelerators (Fe-H and VO-A) were used without predissolution.

1.2 Determination of Gelation Time

Test formulations (40 g) were treated with MEKP (339 μl) and mechanically stirred with a glass rod for 30 s. The gelation time was determined on a Techne Gelation Timer GT-5 (Cole-Parmer, U.K.) using a 22 mm stainless steel plunger according to ISO 2535. [13] We note that the time measurement started at a point when MEKP was added to the formulation.

1.3 Exothermic Behaviour

Test formulations (15 g) were treated with MEKP (127 μl), mechanically stirred with a glass rod for 30 s, and inserted into a thermally isolated installation. Temperature development in the central part of the curing formulation was followed by a K-type thermocouple temperature sensor (t_{99} = 7 s) using a multifunctional data logger Testo 435 (Testo, Lenzkirch, Germany). It is important to note that zero at the time scale corresponds to a point when MEKP was added to the formulation

1.4 REAL-Time NIR spectroscopy

Test formulations (5 g) were treated with MEKP (42.4 μl) and mechanically stirred with a glass rod for 15 s, and an appropriate amount of the sample was put between two glassy microscope slides with a 2 mm rubber seal used as the spacer to determine the sample thickness. The curing process was followed by real-time NIR spectroscopy with a Nicolet iS50 FTIR spectrometer (Waltham, MA, USA). The spectra were collected every 20 s (eight scans per spectrum, data spacing 0.5 cm^{-1}) at ambient temperature. The collected spectra were integrated by using a fixed two-point baseline in the regions 4840–4765 and 6187–6103 cm^{-1} to monitor the consumption of C═C double bonds of UP and STY, respectively. We note that zero at the time scale corresponds to a point when MEKP was added to the formulation.

1.5 Determination of the Film Hardness

Test coatings applied on glass plates (200 mm × 100 mm × 4 mm) were used for determination of the film hardness. Plates were degreased by chloroform and coated with a frame applicator of a 150 µm gap. Film hardness development was monitored for 100 days using a Pendulum Hardness Tester (Elcometer, Manchester, UK) with a König type of pendulum according to ISO 1522:2006 [14]. The measurements were performed under standard laboratory conditions (temperature 23 °C, relative humidity 50 %). This method is based on registering the number of pendulums swings it takes before the amplitude of the pendulum is damped to a certain extent. The measured values were related to the hardness of a glass standard and expressed as relative hardness. Each sample was measured three times on different positions; averaged values are reported.

1.6 Measurement of film colouration

The colour deviations of the applied and cured coatings on glass panels from the established standards were measured using the RM200QC colorimeter (X-Rite, USA). The transmission spectra were expressed in the CIELAB colour space with a standard illuminant “D65” and an observer at “2-degrees”. Data are reported as mean values ± standard deviation.

1.7 Measurement of solvent resistance and adhesion

The solvent resistance test was conducted on glass and steel panels in according to ASTM D4752-10 [15]. Testing on glass panels was performed approximately 120 days after coating application and subsequent curing, while testing on steel panels was carried out approximately 4 days after application and curing. Samples on steel panels were partially immersed in distilled water for 24 hours. As a result, the degree of chemical resistance was recorded as specified by the standard. Same samples were used for the adhesion and “wet adhesion” test. A knife with eleven blades, spaced 1 mm apart, was used for both wet and dry adhesion testing. According to the standard, the adhesion of the coating film was evaluated.

1.8 Thermomechanical analysis

The measurements of Thermomechanical analysis were carried out on a TMA CX04R device (RMI, Czech Republic). A suitable temperature range (- 20 °C – 180 °C) with a load of 50 mN was selected for the measurement of the test samples. The evaluation consisted of drawing tangents from the rubbery region and the glassy region from two points of the curve, the intersection of which indicates the glass transition temperature.

1.9 Dynamic thermomechanical analysis

Dynamic thermomechanical analysis was determined on DX045 device (RMI, Czech Republic) in single-fixed point configuration. Tested specimens (50 × 5 × 4 mm) were analysed in the single cantilever bending geometry (d = 11 mm) using deviation of -0.15 to 0.15 mm at 1 Hz frequency. The measurement was carried out in the temperature range -60°C to 250 °C, where linear termination of the measurements was always achieved. The temperature steps contain several phases. First, the sample was cooled from laboratory temperature of -60 °C at rate 10°C/min. It remained at this temperature for 10 minutes. This was followed by heating to 250 °C at rate of 3 °C/min. Then the measurement was terminated, and the sample was allowed to cool freely to ambient temperature.

1.10 Impact toughness

The Charpy impact test was performer on Pendulum Impact Tester with cured specimens of size 50 × 5 × 4 mm. The type of test specimens was according to standard 2b, so the jaw span was 40 mm according to ČSN 64 0612 [16,17]. The test specimens were tested in a number of 10 specimens. However, if the coefficient of variation was lower than 5%, it was sufficient to test 5 specimens, which was the minimum.

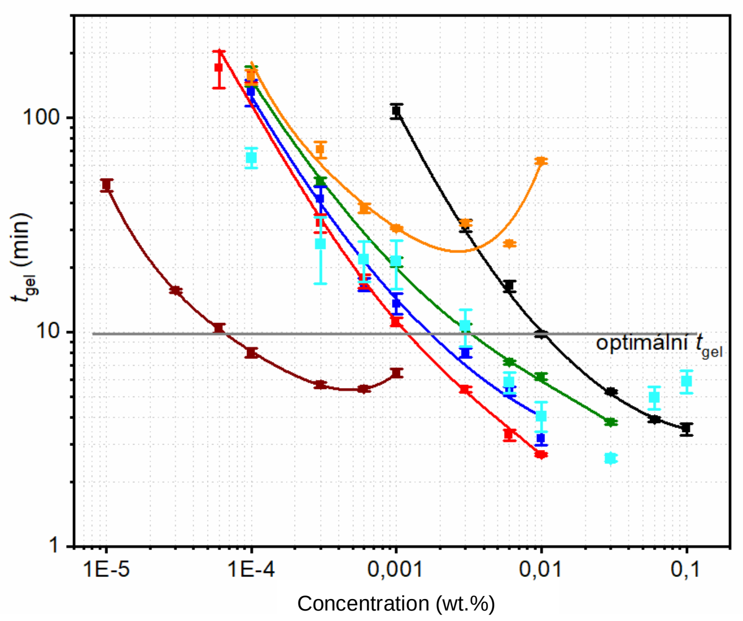
1.11 Measurement of tensile, flexural and compressive properties

The tests were performer on Shimadzu AGS-X (Shimadzu Corp., Japan). Measuring of tensile properties was performed according to the ČSN EN ISO 527-1 standard [18] on pre-cast and cured test specimens in the shape so-called „dog bone“. Measuring of flexural properties was performed according to the ČSN EN ISO 178 [19] standard on pre-cast and cured test specimens in the shape of prism. Measuring of compressive properties was performed according to the ČSN EN ISO 604 [20] standard pre-cast and cured test specimens in the shape of cylinder.

2 Results and discussion

2.1 Determination of Gelation Time

The gelation time was determined for formulations of unsaturated polyester resin with accelerators based on Co, Fe, and V. The resin formulation with the cobalt-based accelerator served as the reference sample. This accelerator remains one of the most widely used, making this comparison highly relevant for evaluating the potential for its replacement in the market.



Graph 1: *Resulting dependence of the effect of the accelerator used at given concentrations over time; Co-C (black), Fe-C (brown), Fe-S (red), V-C (orange), V-S1 (green), V-S2 (blue), V-S3 (torquese)*

The gelation time for the formulation with the cobalt-based accelerator (Co-C) was determined over a concentration range of $0.1–1\times10^{-3}$ wt % Co. The results indicate that the optimal concentration is 0.01 wt % Co, as is typically the case for cobalt-based accelerators.

For the formulation with the commercial iron-based accelerator (Fe-C), the gelation time was determined over a concentration range of $1\times10^{-3}–1\times10^{-5}$ wt. % Fe, i.e., up to two orders of magnitude lower than for the cobalt-based standard accelerator. The results show that the optimal gelation time, in this case tg=10.4 minutes, occurs at a concentration of 6×10^{-5} wt. % Fe. In the partial range of $1\times10^{-3}–1\times10^{-4}$ wt. % Fe, gelation times range from 5 to 8 minutes.

The *in-house* synthesized iron-based accelerator (Fe-S) was tested over a concentration range of $1\times10^{-2}–6\times10^{-5}$ wt. % Fe. The results indicate that the optimal concentration is 1×10^{-3}

wt. % Fe, which achieved gelation in 11.2 minutes. Very short gelation times (2.6 and 3.3 minutes) were observed at concentrations of 1×10^{-2} and 6×10^{-3} wt. % Fe, but these times were too short for further processing.

For the formulation with the commercial vanadium-based accelerator (V-C), the gelation time was determined over a concentration range of 1×10^{-2}–1×10^{-4} wt. % V. The optimal gelation time, according to our parameters, was not achieved.

In the case of the *in-house* synthesized vanadium-based complex (V-S1), the gelation time was determined over a concentration range of 6×10^{-2}–1×10^{-4} wt. % V. The optimal concentration was found to be 3×10^{-3} wt. % V, with a gelation time of 8 minutes.

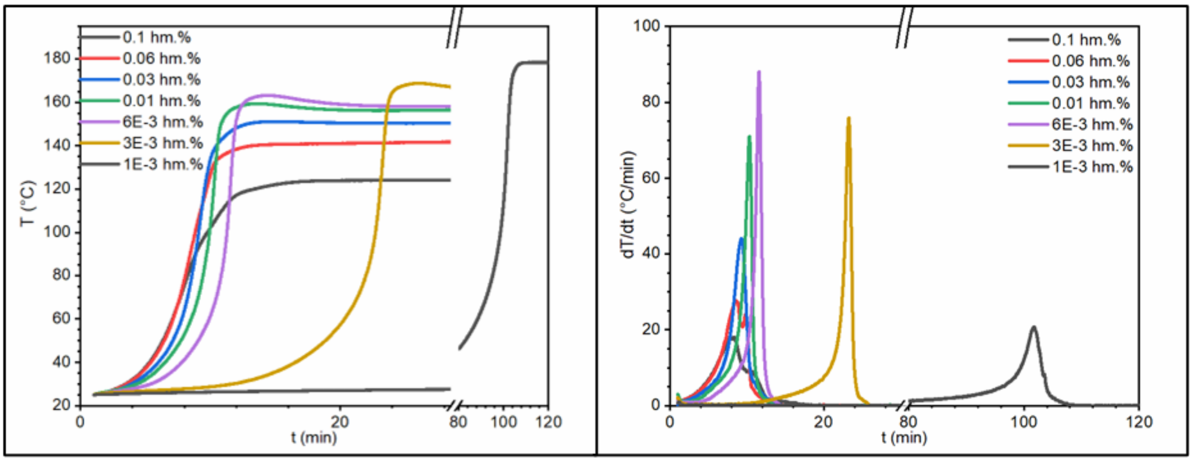
The formulation with another *in-house* synthesized vanadium-based complex (V-S2) was tested over a concentration range of 6×10^{-2}–1×10^{-4} wt. % V. The results for gelation time indicate that the optimal gelation time occurs at a concentration of 3×10^{-3} wt. %, with a gelation time of 10.35 minutes.

The catalytic activity of the *in-house* synthesized vanadium-based complex (V-S3) was studied over a concentration range of 0.1–1×10^{-4} wt. % V. The gelation time results for this formulation show that the optimal concentration is 3×10^{-3} wt. % V, with a gelation time of 10.67 minutes

2.2 Exothermic behaviour

Exothermic behaviours were determined for formulations of unsaturated polyester resins with accelerators based on Co, Fe, and V. The formulation with the cobalt-based accelerator again served as the reference sample. Additionally, commercial accelerators were compared with *in-house* synthesized ones. During the evaluation of adjusted curves measured under adiabatic conditions, both the reaction rate and the maximum achieved reaction temperature were monitored.

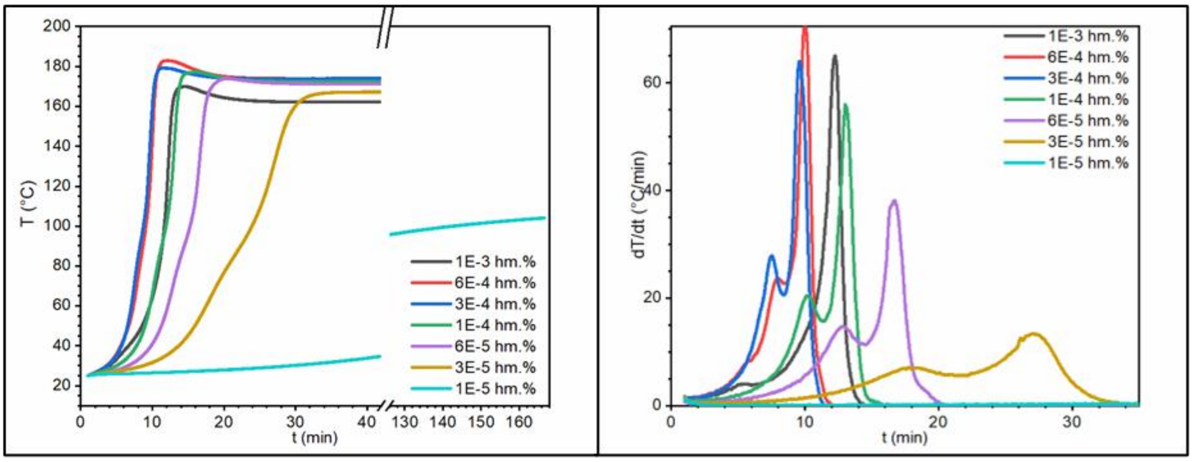
The exothermic behaviour of cobalt-based formulations was tested within a 0.1–1×10^{-3} wt. % Co concentration range (**Graph 2**). All formulations cured in under 100 minutes, with lower concentrations resulting in higher maximum reaction temperatures.



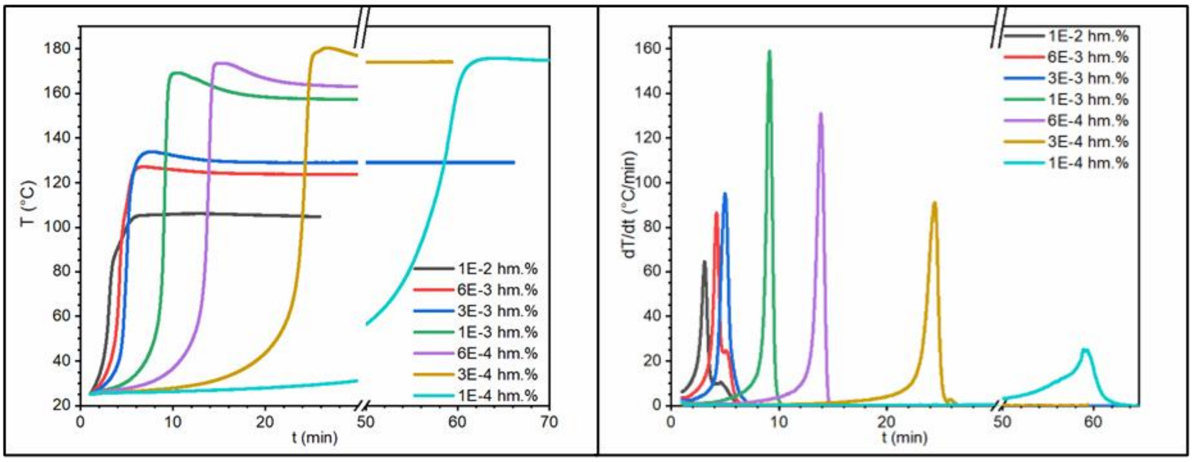
Graph 2: *Exothermic curves for the tested formulation with accelerator based on* ***Co-C***

At concentrations above 0.01 wt. .% Co, overdosing effects were observed, leading to reduced curing degrees and secondary maxima in exothermic curves. The optimal concentration was 6×10^{-3} wt. % Co, with a maximum temperature of 163.2 °C and a reaction rate of 88.0 °C/min, matching literature data [69]

When comparing the results of optimal concentrations from exothermic curves and gelation time, it can be stated that for the formulation with the commercial Fe-based accelerator (Fe-C), the optimal concentration was confirmed (1×10^{-3} wt. % Fe). In contrast, for the formulation with the accelerator (Fe-S), a higher optimal concentration was chosen (3×10^{-4} wt. % Fe) compared to the gelation time determination (6×10^{-5} wt. % Fe)

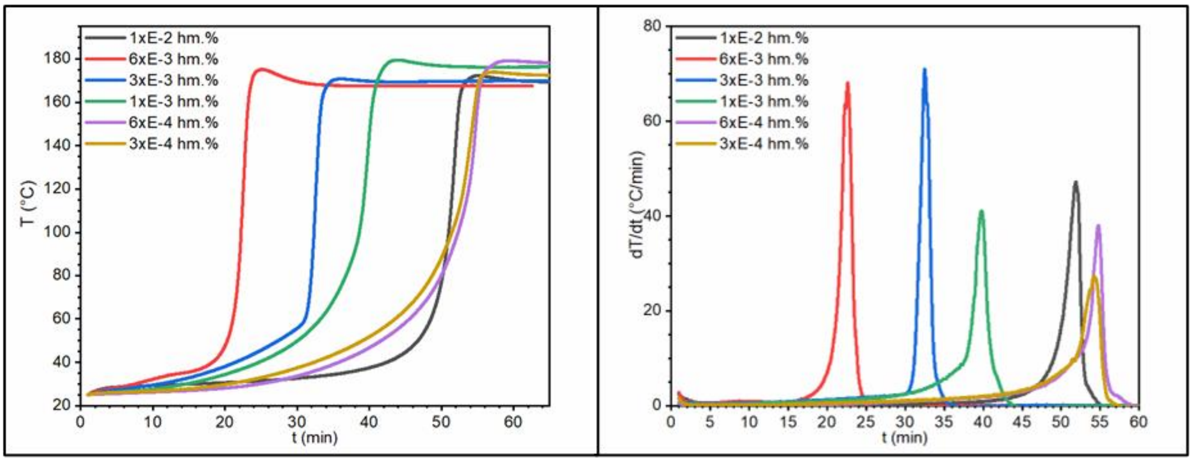


Graph 3:*Exothermic curves for the tested formulation with accelerator based on* ***Fe-C***

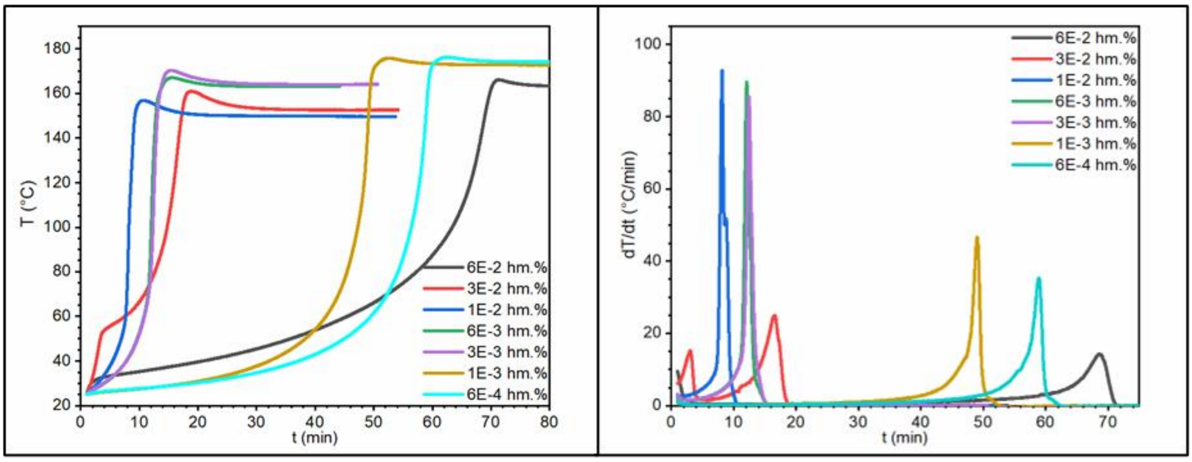


Graph 4: *Exothermic curves for the tested formulation with accelerator based on* ***Fe-S***

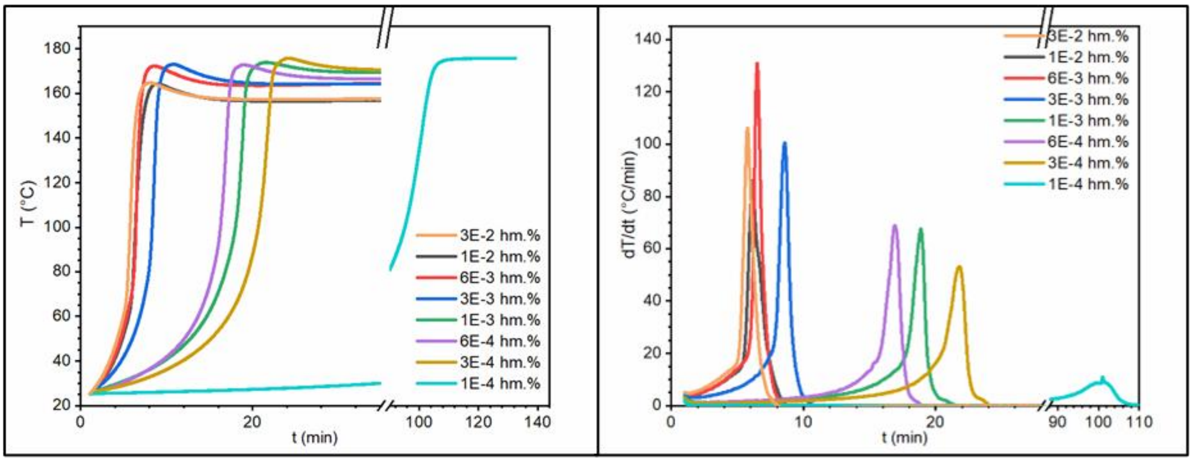
When comparing the results for the tested vanadium-based formulations, both commercial and synthesized, it is found that for V-C, high reaction temperatures close to T_{max}=180 °C are achieved, but in twice the time (t=20 min) compared to the synthesized ones. When comparing concentrations that reach the same temperature, the time to reach that temperature is around 10 minutes. For V-C and V-S1, the optimal concentrations determined from the gelation time results and subsequently from the curing characteristics are the same. For V-S2, the optimal concentration determined by gelation time (3×10^{-3} wt. % V) shifted to a higher concentration (6×10^{-3} wt. % V). The largest difference compared to the optimal concentration was found for V-S3, where according to the gelation time results, the optimal concentration was selected as 3×10^{-3} wt. % V, but from the curing characteristics monitoring, it was clearly indicated that 0.01 wt. % V is optimal.



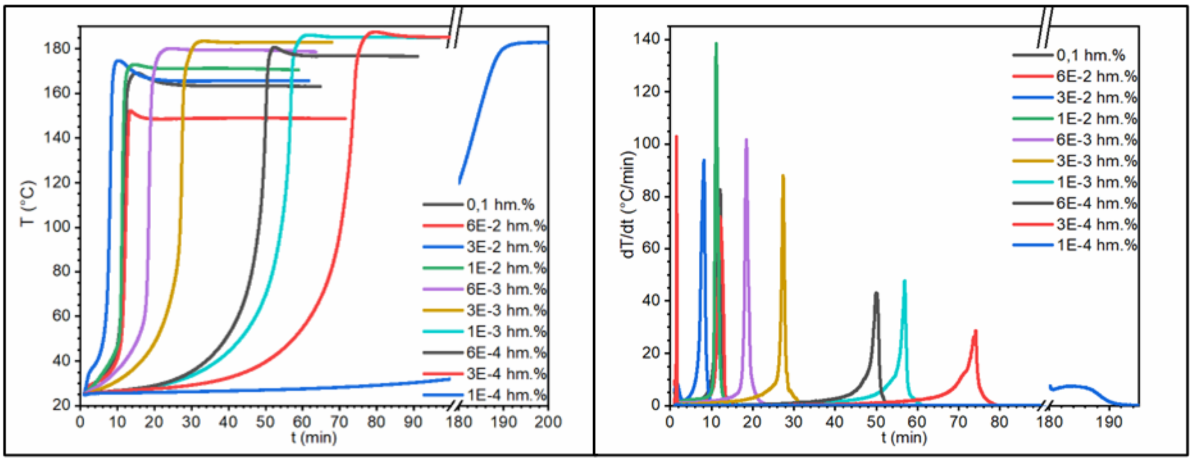
Graph 5:*Exothermic curves for the tested formulation with accelerator based on* ***V-C***



Graph 6: *Exothermic curves for the tested formulation with accelerator based on* ***V-S1***



Graph 7: *Exothermic curves for the tested formulation with accelerator based on* ***V-S2***



Graph 8: *Exothermic curves for the tested formulation with accelerator based on* ***V-S3***

From the comparison of results across the tested formulations with different types of accelerators, it can be observed that the formulations with commercial accelerators achieve lower reaction rates than those with newly prepared accelerators, as shown in **Table 1** and **Table 2**.

Table 1: *Overview of reaction speed for the tested formulation*

Accelerator	**Co-C**	**Fe-C**	**V-C**	**Fe-S**	**V-S1**	**V-S2**	**V-S3**
c [wt. % Me]	6×10^{-3}	6×10^{-4}	6×10^{-3}	1×10^{-3}	1×10^{-2}	6×10^{-3}	1×10^{-2}
$(\mathrm{d}T/\mathrm{d}t)_{\max}$	88.0	71.0	68.1	159.0	92.9	131.0	138.6

A common feature for all tested formulations with evaluated optimal concentrations is that the maximum temperature of the curing process falls within a relatively narrow temperature range of 160–175 °C.

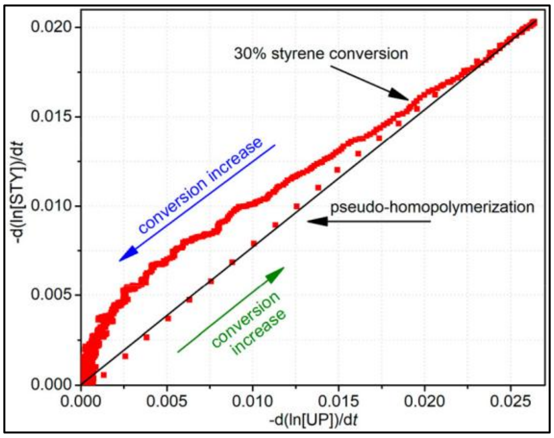
Table 2: *Overview of maximal reaction temperature*

Accelerator	**Co-C**	**Fe-C**	**Fe-S**	**V-C**	**V-S1**	**V-S2**	**V-S3**
c [wt. % Me]	6×10^{-3}	3×10^{-4}	1×10^{-3}	6×10^{-3}	3×10^{-3}	6×10^{-3}	1×10^{-2}
$T_{\max}$ **[°C]**	163.2	175.9	169.2	175.2	172.0	172.3	172.9

2.3 REAL-Time NIR spectroscopy

Based on the results of the curing characteristics, REAL-Time NIR spectroscopy was used to monitor the chemical processes occurring during the curing process. In this case, the consumption of double bonds was monitored, represented by absorption bands for unsaturated polyester at 4789 cm^{-1} and styrene at 6134 cm^{-1}.

The following **Graph 9** shows the reaction rate progression. The reaction rate initially increases until the point where the maximum reaction rate is reached. After reaching the peak, the reaction rate decreases, along with a deviation from pseudo-homopolymerization. This situation occurs due to the transition into the glassy state.



Graph 9: *Double bond C=C consumption*

The results indicate that the effectiveness of individual formulations varies depending on the type of accelerator used and its concentration. Cobalt-based formulations exhibit fast reactions at higher concentrations, but their activity decreases at lower doses, limiting their curing effectiveness. Iron-based formulations (Fe-C) show two peaks in the reaction rate, likely due to the presence of solvents, and are generally effective at lower concentrations, achieving fast reactions with 20–25% conversion. Vanadium-based formulations (V-C, V-S1, V-S2, V-S3) provide lower maximum reaction rates but are more effective in overall conversion, achieving higher levels of unsaturated polyester and styrene conversion, even at lower concentrations. Vanadium systems are the slowest, but due to their higher overall conversion and linear progression, they represent a gradual curing process

2.4 Hardness and colourfulness

The values of relative hardness will be discussed after 10 and 100 days post-application of the coating. To complete the overview of coating hardness, the dry film thickness measurements were also included. These provide information on how the film thickness changed from the initial application thickness (150 μm) to the final dry thickness measured 120 days after coating application. The formulations used for hardness and dry thickness measurements were then employed to measure the colour deviation from the established standards.

With decreasing concentration, the hardness of the coating also decreases, though a hardness of 53.1% is achieved even at lower concentrations after 100 days. The optimal concentration of 0.03 wt. % Co results in the highest hardness, supported by the lowest coating thickness. The expected trend of higher hardness with lower coating thickness is observed.

Regarding colour, increasing concentration leads to lower lightness (***L**** parameter), likely due to the higher presence of the intensively coloured accelerator.

At low concentrations (1×10-4 wt. % Fe and lower), the formulation was ineffective, with no increase in coating hardness and stickiness after 120 days. The optimal concentration for further use is 6×10-4 wt. % Fe, though hardness remained low (33.2%). Coating thickness results are relevant only for 6×10-4 and 3×10-4 wt. % Fe. The ***L**** parameter was similar for all concentrations, while the ***a**** (green) and ***b**** (yellow) parameters showed the lowest values for these formulations.

The highest tested concentration is also the optimal one. In other cases, complete curing of the coating was not achieved, as reflected in the relative hardness after 100 days, where the 3×10-3 wt. % Fe formulation reached only 16.4% hardness. Regarding colour parameters, the Fe-S formulation most closely matched the colour of the coating at the optimal concentration of the cobalt-based commercial accelerator (0.03 wt. % Co).

The optimal concentration is 3×10-3 wt. % V, which results in 81% relative hardness. The coating thickness ranges from 60 to nearly 90 µm. Regarding colour parameters, a shift of -1.4 ± 0.2 is observed for parameter a at this concentration. A higher shift is also noted for the 6×10-3 wt. % V concentration. Measurements for parameter ***b**** show minimal differences, although higher concentrations tend to shift more toward the b-axis, into the yellow region.

VS-1 -The concentration of 6×10-3 wt. % V (78.0%) can be considered optimal, as it achieves the highest relative hardness across the entire concentration range after 100 days of application. Although other concentrations also resulted in cured coatings, their final thicknesses were lower. The ***L**** parameter remained roughly the same across all concentrations. However, the selected optimal concentration stands out, showing the highest shift on the -a axis (-1.9 ± 0.3). The final evaluated parameter ***b****, shows a trend where the shift along the b-axis decreases with lower concentrations

It can be said that relatively consistent values of relative hardness were achieved across the entire concentration range after 100 days of application. Greater differences between concentrations are more noticeable when comparing thickness. In terms of colour parameters ***L****, ***a****, and ***b****, very similar results were obtained, making it difficult to determine the optimal concentration of the tested formulation in relation to colour.

The selected concentrations are most like the tested concentration series with the commercial cobalt-based accelerator. In the case of the highest concentration (0.03 wt. % V), a lower relative hardness was achieved after 100 days of application compared to the lower tested concentration (0.01 wt. % V). The **_L*_** parameter generally reaches the lowest values of all tested formulations. Similarly, the results for parameter a are unique, with the colour scale of this formulation extending to the boundaries of the +a and -a axes. On the other hand, the **_š_** parameter shows consistent results across almost the entire concentration range. An exception is the 6×10-3 wt. % V concentration, which is the only one to show a shift towards -b.

2.5 Chemical resistance to MEK

The tested cobalt-based formulations (Co-C) on glass panels exhibited lower adhesion at higher concentrations, while lower concentrations showed better adhesion. The same trend was confirmed for dry adhesion on steel panels, where lower concentrations achieved a 5B rating, indicating that the coating remained intact. Wet adhesion on steel averaged around 3B, with partial coating removal. The MEK resistance test showed consistent results across the entire concentration range.

Adhesion testing for the iron-based commercial accelerator (Fe-C) was challenging, with complete evaluation possible only for the highest concentration (6×10^{-4} wt. % Fe), where the coating was sufficiently cured. The lowest adhesion was observed on glass panels, while the highest, specifically for dry adhesion, was on steel panels. MEK resistance was tested only at the highest concentration, showing a decreasing trend. The highest chemical resistance (4) was recorded on glass panels with only surface polishing, while dry chemical resistance on steel reached - 3

The formulation with the *in-house* iron-based accelerator (Fe-S) was fully tested only at the highest concentration (6×10^{-3} wt. % Fe). Adhesion to glass was rated 3B, with up to 15% of the coating removed. Dry adhesion to steel was lower, classified as 2B, indicating up to 35% removal. Wet adhesion on steel was even lower, rated 1B.

Adhesion to glass for the formulation with commercial vanadium-based accelerator (V-C) was rated 0B across nearly the entire concentration range, indicating over 65% film removal. Similar results were observed for adhesion to steel panels. After immersion and wet adhesion testing, complete film removal was noted across all concentrations, also classified as 0B. In the chemical resistance test on steel panels, identical results were obtained for both wet and dry conditions, with maximum resistance and no visible surface degradation of the cured film.

In case of formulation with *in-house* vanadium-based accelerator (V-S1) was the result was rated 0B, with over 65% film removal. Identical results were obtained for wet adhesion on steel panels. Surprisingly, dry adhesion on steel panels showed significantly higher ratings, predominantly 4B to 5B across all concentrations. Chemical resistance testing exhibited consistent MEK resistance across the concentration range. On glass panels, a rating of 4 indicated only surface polishing. On steel panels, chemical resistance results were identical for both wet and dry conditions.

Adhesion testing on glass panels for the formulation with a vanadium accelerator (V-S2) showed the highest rating for the highest concentration (3×10^{-3} wt. % V), while the lowest concentration (3×10^{-4} wt. % V) had the lowest rating (0B). Dry adhesion on steel panels reached 3B to 4B. Chemical resistance testing has the same results as MEK resistance across all concentrations. On glass panels, a rating of 4 indicated only surface polishing. On steel panels, chemical resistance results were identical for both wet and dry conditions.

For the formulation with a vanadium accelerator (V-S3), adhesion testing on glass panels showed the same adhesion classification 0B across the entire concentration range. In contrast, relatively high adhesion was achieved in the dry adhesion test on steel panels. In wet adhesion testing, higher concentrations resulted in the lowest adhesion rating, leading to complete film detachment from the substrate. The chemical resistance test, conducted with the vanadium-based formulation, showed consistent MEK resistance results across all concentrations. Similarly, dry chemical resistance testing on steel panels yielded uniform results across the entire concentration range, with no film damage observed. Comparable results were obtained in the wet chemical resistance test on steel panels.

2.6 Results of Thermomechanical; Dynamic Thermomechanical analysis

Thermomechanical analyses were monitored for all tested formulation. The resin formulation with a Co-based accelerator served as a reference sample for the remaining tested formulations. The commercial Fe-C accelerator was used as a reference for comparison with the synthesized Fe-S. Similarly, V-C was selected as a reference for the remaining vanadium-based tested compounds. Based on the measured T_g values, formulations with commercial accelerators exhibit values within a close range of 82.1–87.2 °C. Among the synthesized formulations, Fe-S stands out with a T_g of 91.0 °C, whereas the lowest T_g of 73.3 °C corresponds to the V-S2 formulation. A key finding from the TMA measurements was that the recorded data reflect the long-term activity of the accelerators over time, as the measurements were conducted on samples that had undergone self-curing for two weeks.

Accelerator c [wt. % Me]	**Co-C 1×10^{-2}**	**Fe-C 6×10^{-5}**	**Fe-S 1×10^{-3}**	**V-C 3×10^{-3}**	**V-S1 3×10^{-3}**	**V-S2 3×10^{-3}**	**V-S3 3×10^{-2}**
T_g [°C]	87.8	86.2	91.0	82.1	86.7	73.3	84.9

Table 3: *Overview of glass transition temperature (T_g) for tested formulation*

The previously determined so-called optimal concentrations proved to be unsuitable for sample casting. One of the reasons was the necessity to introduce an additional step involving degassing using a centrifuge (1000 rpm). This step was added to minimize defects caused by air bubbles in the casting. Once the air content in the formulation was reduced, the processing time decreased approximately threefold—likely because the presence of air had an inhibitory effect. Therefore, concentrations were selected such that the gel time was approximately 30 minutes, which, after centrifugation, corresponded to a working time of about 10 minutes—thus representing our defined optimum which is shown in **Table 4** and **Table 5**.

Accelerator	**Co-C**	**Fe-C**	**Fe-C**	**Fe-S**	**Fe-S**
c [wt. % Me]	**3×10^{-3}**	**3×10^{-5}**	**1×10^{-5}**	**3×10^{-4}**	**1×10^{-4}**

Table 4: *Optimal concentration for formulation with tested accelerator*

Accelerator	**V-C**	**V-S1**	**V-S2**	**V-S2**	**V-S3**	**V-S3**
c [wt. % Me]	**1×10^{-3}**	**1×10^{-3}**	**6×10^{-4}**	**3×10^{-4}**	**6×10^{-4}**	**3×10^{-4}**

Table 5: *Optimal concentration for formulation with tested accelerator*

The results presented in **Table 6** demonstrate the catalytic activity of the accelerators, as evidenced by the higher T_g values, ranging from 119.7 to 131.9 °C. A comparison of these temperatures allows for several conclusions to be drawn. One of them is that Fe-C achieved higher T_g values in both tested formulations compared to Co-C, which served as the standard. Conversely, Fe-S reached lower T_g values than Co-C. It is therefore necessary to also consider the crosslink density, which provided insight into the extent to which the formulation was crosslinked during the curing process.

Acceler.	**c [wt. % Me]**	**T_g [°C]**	**Cross.density [mol/m^3]**	**Acceler.**	**c [wt. % Me]**	**T_g [°C]**	**Cross.density [mol/m^3]**
Co-C	**3×10^{-3}**	125.4	5.89	**V-C**	**1×10^{-3}**	121,4	16,85
Fe-C	**3×10^{-5}**	131.9	7.25	**V-S1**	**1×10^{-3}**	121,4	14,31
Fe-C	**1×10^{-5}**	130.1	18.82	**V-S2**	**6×10^{-4}**	127,2	43,11
Fe-S	**3×10^{-4}**	121.8	9.19	**V-S2**	**3×10^{-4}**	126,4	22,04
Fe-S	**1×10^{-4}**	119.7	2.59	**V-S3**	**6×10^{-4}**	124,5	24,62
-	-	-	-	**V-S3**	**3×10^{-4}**	123,6	28,70

Table 6: *Overview of the results by TMA and DMA*

2.7 Impact toughness

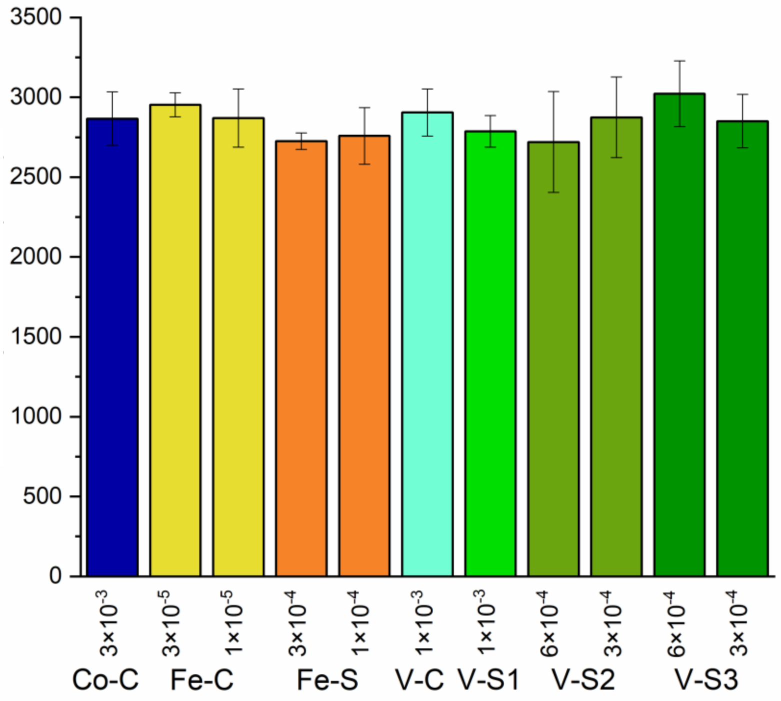
The tested concentrations were selected based on previous measurement results as suitable for use in cast forms. **Table 7** presents an overview of the impact toughness test results (a_{cU}), performed using the Charpy method, along with the standard deviation of the measurements. According to the measured and calculated a_{cU} values, the lowest toughness was observed in systems with commercial Co- and V-based accelerators. More than three times higher values were achieved by the Fe-S formulation (3×10^{-5} wt % Fe) and V-S2 (1×10^{-4} wt % V), in each case at the higher tested concentration. The highest impact toughness values were recorded for iron-based formulations, where the test specimens did not fracture during testing but only exhibited partial damage or bending. These materials were tacky on the surface and more flexible than those with lower a_{cU} values

Accelerator	c [wt. % Me]	a_{cU} [kJ×m^{-2}]
Co-C	3×10^{-3}	5.3 ± 0.8
Fe-C	3×10^{-5}	30.7 ± 3.5
Fe-C	1×10^{-5}	28.9 ± 0.5
Fe-S	3×10^{-4}	16.0 ± 1.6
Fe-S	1×10^{-4}	35.7 ± 4.9
V-C	1×10^{-3}	5.6 ± 0.7
V-S1	1×10^{-3}	7.7 ± 0.7
V-S2	6×10^{-4}	16.3 ± 0.7
V-S2	3×10^{-4}	27.5 ± 2.3
V-S3	6×10^{-4}	23.1 ± 2.8
V-S3	3×10^{-4}	27.5 ± 2.3

***Table 7:** Results of impact toughness for the tested formulation*

2.8 Measurement of tensile, flexural and compressive properties

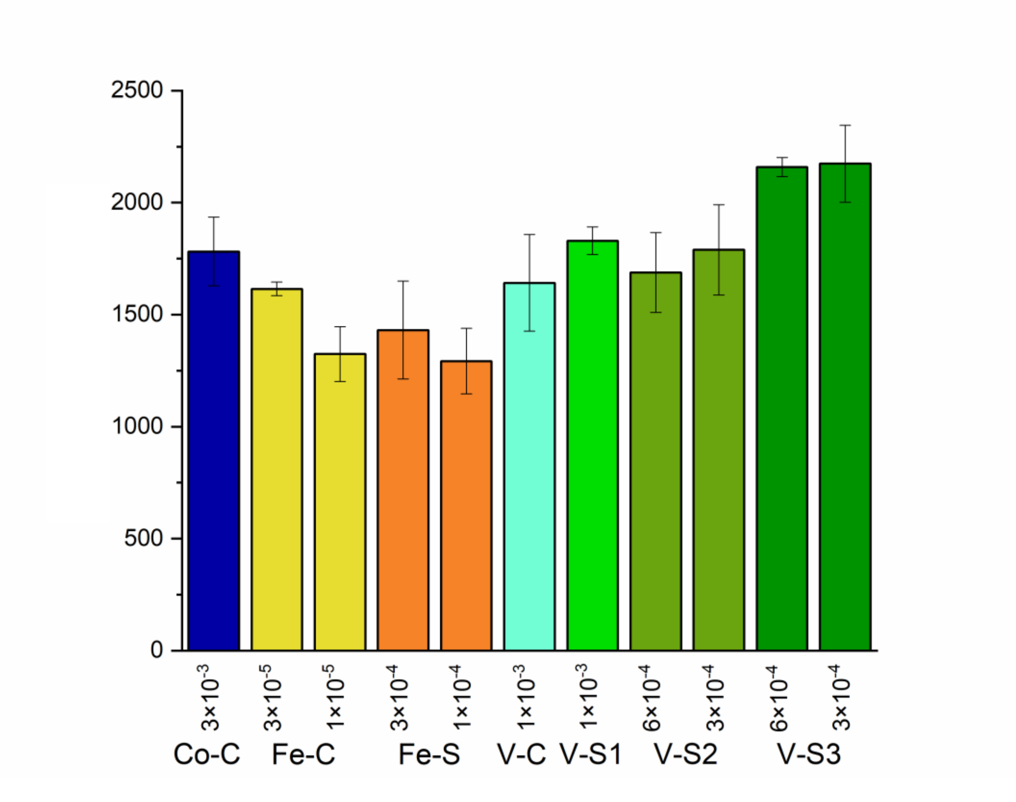
The tensile modulus of elasticity [MPa] reflects the stiffness of the given material. For polymeric systems, an increasing modulus generally correlates with an increase in material stiffness. Based on the measured values presented in **Graph 10**, it is evident that all tested materials exhibit very similar tensile modulus values, with no significant variations. The values range from approximately 2700 to 3000 MPa. The formulations at the lower end of this range include those based on Fe and the V-S2 accelerator. In contrast, the only formulation to reach the upper limit—3023 ± 206 MPa—was V-S3. Surprisingly high values were also recorded for the commercial vanadium-based accelerator (V-C), which was positioned near the upper boundary of the measured modulus range. An interesting trend was observed in the calculated standard deviations: the vanadium-based *in-house* synthesized accelerators showed higher deviations compared to the other tested formulations. This indicates greater variability in the tested material. In contrast, the standard deviations of the other groups were relatively consistent and closely aligned with those observed for the commercially used cobalt-based accelerator.



Graph 10: *Results for the tensile modulus of elasticity [MPa] for the tested formulation*

The tensile modulus of elasticity [MPa] was used to evaluate material stiffness. As with most polymeric materials, a higher modulus generally indicates greater stiffness. **Graph 11** shows that the tested formulations exhibited tensile modulus values ranging from 1292 to 2174 MPa. A notable trend is that some formulations with lower tensile strength now show higher stiffness, suggesting that materials requiring lower force to deform can still be relatively stiff.

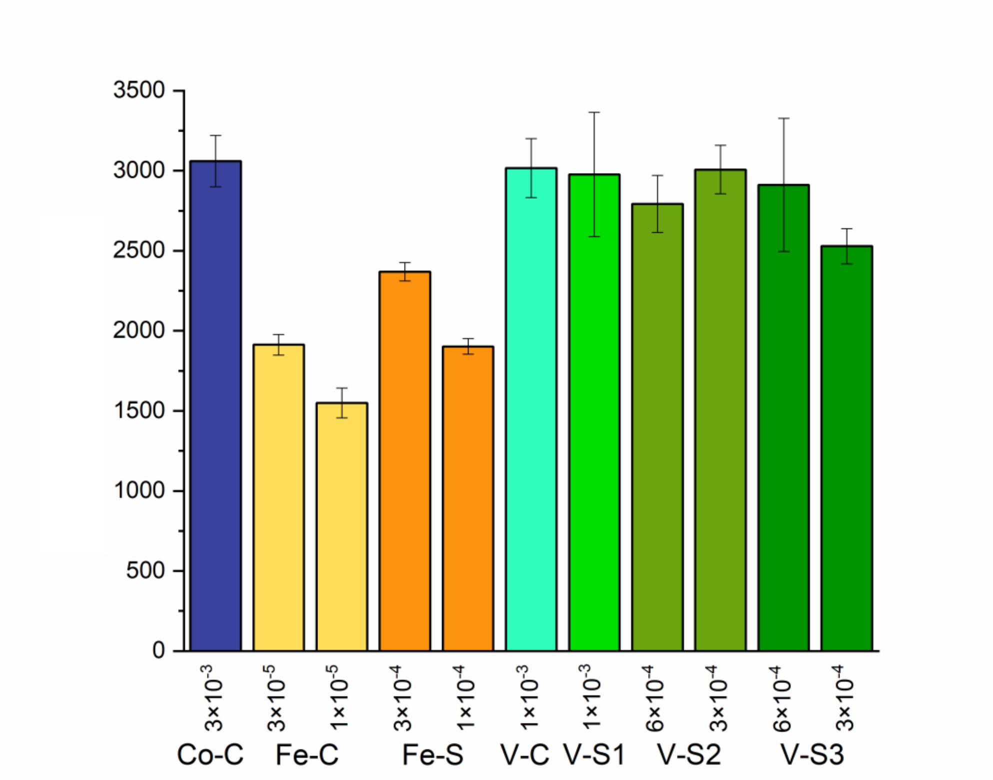
For iron-based formulations at lower concentrations, there was no significant difference between tensile strength and modulus. These materials require higher force for deformation, resulting in higher stress, but their stiffness increases only slightly. The most outstanding result was recorded for the vanadium-based formulation V-S3 at 6×10⁻⁴ wt. % V. It showed high tensile strength and the highest modulus among all tested materials, with minimal deviation demonstrating excellent consistency and mechanical stability.



Graph 11: *Results for the flexural modulus of elasticity [MPa] for the tested formulation*

The flexural modulus of elasticity [MPa] was used to assess the stiffness of the material. As with tensile properties, for polymeric materials, an increase in the modulus of elasticity corresponds to an increase in material stiffness. The measured values shown in **Graph 12** indicate that the tested formulations exhibited values in the range of 1560 to 3060

MPa. In this case, regarding flexural properties, the iron-based formulations had the lowest measured values. This holds true for both the commercial accelerator (Fe-C) and the *in-house* synthesized version (Fe-S). The remaining tested formulations exhibited similar flexural modulus values around 3000 MPa. Notably, the highest values were observed for the formulations with the commercial cobalt-based accelerator (Co-C) and the commercial vanadium-based accelerator (V-C).



Graph 12: *Results for the compressive modulus of elasticity [MPa] for the tested formulation*

3 Conclusion

Based on the conducted research focused on the catalytic activity of transition metal complexes used for curing unsaturated polyesters, it can be stated that the individual tests were approached with logical continuity. This approach allowed for the investigation of catalytic activity manifestations and subsequent validation of the results through related or complementary physical and physicomechanical tests.

The activity of selected metal ions was studied using commercially available and *in-house* synthesized accelerators. A standard cobalt-based accelerator served as a reference. The selected transition metal complexes intended for this research were first subjected to a gelation time test. The results of this test indicated that all the selected formulations could achieve gelation. Formulations with *in-house* synthesized accelerators based on iron and vanadium achieved significantly shorter gelation times compared to formulations using their commercial alternatives.

The obtained data were subsequently confirmed through curing characterization. By measuring complete concentration series and determining the maximum reaction rate along with the maximum reaction temperature, it was evaluated that formulations with *in-house* synthesized accelerators achieved up to twice the reaction rate compared to the use of commercial accelerators. Regarding the maximum reaction temperatures, it can be stated that no significant differences were observed between the compared accelerators that would challenge their catalytic activity. Additionally, initial optimal concentrations were identified for closer observation.

Based on the curing characterization results, real-time NIR spectroscopy was employed to monitor the consumption of double bonds. The evaluation was conducted for the conversion of both the unsaturated polyester and styrene. The results revealed that cobalt-based formulations achieved rapid reactions at higher concentrations but exhibited reduced efficiency at lower dosages. Iron-based formulations showed two peaks in reaction rates and were highly effective even at very low concentrations. Vanadium-based formulations, while reacting more slowly, achieved higher overall conversion rates, making them efficient systems even at lower concentrations.

For each formulation, an optimized concentration series was prepared and subsequently tested on glass panels. In terms of relative hardness results, the Co-C formulations and all tested vanadium-based formulations (V-C; V-S1; V-S2; V-S3) excelled. The most effective results were observed at higher concentrations within the tested series.

Surprisingly, the colour test provided unexpected outcomes, as no significant colour differences were observed, despite the logical expectation that different-coloured transition metal complexes might exhibit variations. Adhesion tests on the same films, assessing substrate adhesion, showed results at the lower boundary of substrate adherence. This observation applied to all tested formulations, whether the adhesion test was conducted under dry or wet conditions.

In contrast, very high chemical resistance to MEK (methyl ethyl ketone) was demonstrated across all tested formulations. During this test, only surface polishing occurred without substrate penetration.

The optimized concentrations were subjected to dynamic thermomechanical analysis. Vanadium-based formulations exhibited a relatively narrow glass transition temperature range and higher crosslink density compared to the other tested accelerators. The highest crosslink density was achieved with the V-S2 formulation at a higher concentration, making it the most effective accelerator in the test. Conversely, the lowest crosslink density was observed with the Fe-S formulation

The tested iron-based formulations, as well as V-S2 in terms of tensile properties, exhibited lower values of the elastic modulus. In contrast, the highest elastic modulus was achieved by the accelerator V-S3. Surprisingly high values were measured for the commercial vanadium-based accelerator (V-C), which reached the upper limits of the measured elastic modulus values. The compressive modulus confirmed the assumptions regarding vanadium-based formulations, indicating increased material stiffness as suggested by previous tests. On the other hand, problematic results were observed for V-C and V-S1 formulations, which did not even reach the average performance of the Co-C formulation. In terms of flexural modulus, the measured values for the tested iron-based formulations were the lowest. This statement applies to both the commercial accelerator (Fe-C) and the *in-house* synthesized one (Fe-S). The remaining tested formulations exhibited very similar values of the elastic modulus

Based on the results of this research, it can be assumed that the tested formulations with *in-house* vanadium-based accelerators have significant potential to replace cobalt-based accelerators and thus become an environmentally friendly alternative. Among the tested formulations, V-S2 and V-S3 achieved the most effective and stable results.

The potential for further research lies in addressing the need to replace cobalt-based accelerators with more eco-friendly alternatives, ideally in combination with the use of styrene-free solvents. Such a step would not only satisfy the market for unsaturated polyester resins but also reduce health and environmental issues associated with this topic, aligning with the objectives of the Green Deal.

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