

Obtaining of Hydrotalcite-based Ceramic Monoliths through Extrusion

The investigation of the effect of additives on the rheological behaviour of the ceramic pastes

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In this paper are presented the results of experimental research regarding the behaviour of ceramic pastes based on microcrystalline hydrotalcite $[M^{II}_{1-x}M^{III}_x(OH)_2]_x A_{m-x/n} mH_2O$, used for the preparation of monoliths with circular section through extrusion. The experimental studies regarding the rheological behaviour of hydrotalcite pastes lubricated with stearin shows that these materials have viscoplastic behaviour. Two rheological models are proposed (Bingham-Schwedoff and Herschel-Bulkley) for the correlation of experimental data and for the determination of rheological parameters (n and k). It is shown that Herschel-Bulkley model is more appropriate than Bingham-Schwedoff model to describe these ceramic mixtures and that stearin has a lubricating role, improving the flowing parameters. By using the bifactorial analysis of variance it was also investigated, from the statistical point of view, the influence of the studied factors (the content of the plasticizer agent and the shear rate $\dot{\gamma}$).

Keywords: hydrotalcite, ceramic pastes, extrudates, rheology

Hydrotalcite ceramic powders have the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]_x A_{m-x/n} mH_2O$, where M^{III} is a trivalent metallic ion, M^{II} a bivalent metallic ion, A a charge compensating anion, m the number of mols of intercalated water per quantity of components in the formula; $x \in 0.2-0.4$ is the number of mols of M^{III} per quantity of components in the formula [1]. Nowadays these powders are frequently used in many environmental applications, like the treatment of waste water or the cleaning of gaseous flows, due to special properties and characteristics: high specific area and porosity, high adsorption capacity, ionic exchange capacity etc. [2-15].

The idea of using hydrotalcite based materials as extruded monoliths resulted from the intention of combining the properties and characteristics of these powders with the opportunities offered by the architecture of porous ceramic monoliths, especially those modelled through extrusion techniques. It is envisaged that the procedure is going to lead to the obtaining of new materials with a high potential of use in various environmental applications.

In the recent decades, due to its practical importance, a considerable interest has been shown in the study and modelling of physical phenomena developed in the process of extrusion of materials, especially for ceramic materials [16, 17].

Most of the ceramic materials with modelling capabilities through extrusion show viscoplastic behaviour, meaning that they start to flow only after the shear stress overstep a value called characteristic stress or yield stress (τ_y, τ_0). The way viscoplastic fluids behave when they are submitted to deformation can be described thereby [18]: when $\tau \leq \tau_0$ the fluid suffers elastic deformation; the

structural units elongate towards stress, but do not slip one over each other due to molecular cohesion forces. At $\tau \geq \tau_0$, the shear forces overcome the cohesion forces and the flowing starts, in a newtonian way (for Bingham-Schwedoff fluids) or non-newtonian (for Herschel-Bulkley fluids).

The linear viscoplastic behaviour can be express by the Bingham-Schwedoff law [18-20]:

$$\tau = \tau_0 + \eta \cdot \dot{\gamma} \quad (1)$$

where:

τ_0 is the yield stress, the characteristic shear stress at which the flow begins;

η – the viscosity;

$\dot{\gamma}$ – the shear rate.

The non-newtonian viscoplastic behaviour, shear thickening (dilatant) or shear thinning (pseudoplastic) can be express with Herschel-Bulkley model:

$$\tau = \tau_0 + k \cdot \dot{\gamma}^n \quad (2)$$

where k (consistency index) and n (flowing index) are constants specific to a viscoplastic material, and are experimentally determinable.

By logarithmation of equation (2) it is obtained:

$$\lg(\tau - \tau_0) = \lg k + n \lg \dot{\gamma} \quad (3)$$

which represents the equation of a straight line with n as slope and $\lg k$ as intercept, whereby k parameter can be calculated:

$$k = 10^{\lg k} \quad (4)$$

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The modelling of hydrotalcite pastes by plastic deformation through extrusion is a novelty, literature data on their modelling as monoliths being scarce [21], mainly because of the difficult preparation techniques of monolithic forms, conditioned by the non-plastic nature of powder.

The modelling of microcrystalline powders of hydrotalcite by extrusion process, followed by post-modelling heat treatment rigorously controlled, is based on the concern of authors to contribute to the obtaining of new materials with improved, pre-established, surface and structural-adsorption properties, with a high potential of use in a wide range of environmental applications.

This paper shows the research results on rheological behaviour of mixtures based on hydrotalcite lubricated with stearin. The factorial dispersal analysis is used to highlight the influence of composition factors and shear rate on the plastic behaviour of pastes.

Experimental part

In order to give to non-plastic materials a plastic behaviour, a variety of additives can be used, as binders, plasticizers and lubricants [16]. The right selection of these additives is a key step in the preparation process.

Different methods can be used in order to study and anticipate the behaviour of different ceramic materials in the plastic deformation process. The most illustrative is rheometry, the applied measurements covering a wide range of techniques, from simple tests to complex determinations of the material properties, often used with the aim of increasing the performance of the plastic deformation process through extrusion and to improve the geometry of used matrix.

Two main criteria are always taken into account: a good deformability of the tested material, shown by the shape of the apparent flow curve, and a rather good stability of flow properties into crude mixtures.

The ceramic paste used in the experimental research is composed of a main component, over 73%, in a fine powder form (under 90 μ m particle size; Master Sizer 2000, Ver.5.31, Malvern, UK), based on hydrotalcite synthesized in laboratory from pure chemical reactives (advanced purity). The Mg/Al hydrotalcite with Mg²⁺/Al³⁺ = 2 molar ratio was synthesized at constant pH = 10 by co-precipitation at high supersaturation using Mg(NO₃)₂ · 6H₂O, Al(NO₃)₃ · 9H₂O, Na₂CO₃ and NaOH as raw materials. The resulting gel was aged under mild stirring at 70°C for 18 h. The hydrotalcite was then separated by filtration, washed with deionised water and dried at 90°C during 24 h under nitrogen flow.

For determining the chemical composition of hydrotalcite powder, the analysis methods included the following techniques: ICP, DCP, AAS.

The phase mineralogical composition analysis was performed through X-ray diffraction (XRD), Bragg-Brentano diffraction, $\Theta - \Theta$ coupling in vertical configuration, (using a BRUKER D8 ADVANCE diffractometer equipped with the DIFFRAC^{plus} XRD Commander Bruker AXS software).

To obtain the pastes, firstly the solid components were dry mixed for homogenization, and then the liquid components were added (additives for binding and plasticization, a part of them being water soluble). The mixing was continued till the complete homogenization of the material, which did not present fissures visible with the naked eye during deformation through flattening. The obtained paste was rheologically analyzed.

The equipment used for the rheological study of crude paste mixtures is a rheometer with coaxial cylinders, type Reotest 2, used for measurements at 25°C. The constant

corresponding to the measuring cylinder is $z = 296,7 \frac{g}{cm^3 s}$. The apparatus gives values for a parameter α_R , cm²/s necessary to calculate the shear stress τ , dPa with equation (5).

$$\tau = z \cdot \alpha_R \quad (5)$$

The viscosity, η , is calculated with equation (6), the dimensional analysis showing as units in this case the Poise P.

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (6)$$

During the measurements the following elements were considered:

- the composition variation of ceramic paste was obtained by modifying the amount of lubricating component, while keeping the humidity of mixtures constant;

- the friction between tested material and container surface was considered negligible;

- the material was considered a fluid with viscoplastic behaviour.

Measurements on the rheology of hydrotalcite pastes were performed (changing the amount of plasticizer / lubricant, weight percents), one measurement for each combination of factor levels, and the experimental results were displayed as graphics or tables.

The study results are filled in with bifactorial analysis of variance on the influence of the addition of plasticizer agent, as stearin additions in four base compositions (weight percents relative to dried substance) and on the effect of shear rate $\dot{\gamma}$ on the behaviour of material submitted to linear deformation. In order to verify the significance of the investigated factor levels (named A and B), the bifactorial dispersal analysis without replication (Two-Way ANOVA) [22 - 30] was applied. The quantity of lubricant / plasticizer was considered as A factor and the shear rate as B factor. The bifactorial analysis was applied on the values of the objective function Y_{ij} , obtained by measuring the dynamic viscosity of hydrotalcite paste mixture.

The study was performed for four composition levels of stearin added as plasticizer / lubricant (A factor has $l = 4$ variation levels: 0; 0.05; 0.1; 0.2 %) using 11 different levels for the shear rate variation (B factor has $m = 11$ variation levels: 0.17; 0.3; 0.33; 0.5; 0.6; 0.9; 1; 1.5; 1.8; 2.7; 3 s⁻¹). Specialized mathematical software Mathcad 14.0. was used for numerical computations.

Results and discussions

The chemical composition of the hydrotalcite paste prepared in laboratory includes as main elements: Mg (18.2-18.6%), Al (10.0-10.5%), H₂O (humidity) (0.7-0.8%), CO₃²⁻ (10.4-13.3%), PC₁₀₀₀ (LOI) (44.1-44.8%).

The mineralogical phase composition of hydrotalcite powder used as start material in the paste mixture includes: HT structure > 90% (089-0460 PDF reference) Mg_{0.667}Al_{0.333}(CO₃)_{0.167}(H₂O)_{0.5} Hydrotalcite syn; Q-2H structure (possibly 1-p%) (087-1138 PDF reference) Al₂Mg₄(OH)₁₂(CO₃)(H₂O)₃, Quintinite -2H [31].

Figure 1 presents the rheograms $\eta = f(\dot{\gamma})$ and figure 2 $\tau = f(\dot{\gamma})$ for all hydrotalcite pastes lubricated with stearin in various proportions. All mixtures have a shear thinning (pseudoplastic) behaviour, shown in particular by $\eta = f(\dot{\gamma})$ diagrams, in which it is visible that with the increase of shear rate $\dot{\gamma}$ the pastes become more fluid.

Compared to a Newtonian fluid, where the viscosity is constant for any share rate, it is observed that all four pastes have a significant variation of viscosity, the decreasing of

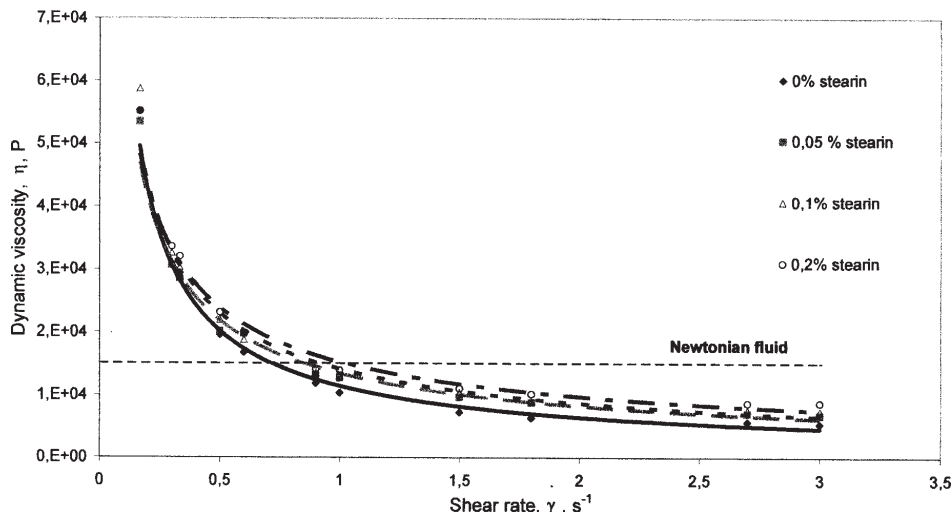


Fig. 1. The variation of dynamic viscosity η with the share rate γ for hydrotalcite pastes: without stearin and with 0.05%, 0.1% and 0.2% stearin.

this parameter with the increase of share rate being a proof of shear thinning behaviour. The fluidification phenomenon can be explained by the fact that, at big share rates, the individual flowing elements are oriented, gradually, to flowing direction, the apparent viscosity becoming smaller till a constant value η_{∞} , when the pastes behaviour became Newtonian. One remarks also the influence of stearin concentration which, apparently, increases the viscosity of pastes, idea that contravenes with the role as lubricating agent. Figure 2 explains the role of stearin as lubricant into ceramic pastes, at higher concentrations, because, as it will be noticed, the flowing parameters are significantly improved.

From figure 2 it can be seen the influence of stearin (lubricant) concentration on a very important flowing parameter, the yield stress τ_0 . Comparing the sample without stearin and the sample with the highest concentration of stearin (0.2%), it is observed that the value of the yield stress parameter decreases from 841 Pa to 825 Pa, suggesting a better fluidisation due to the lubricant.

Figure 2 reveals more information regarding the type of materials submitted to rheological study. All the pastes present a yield stress that situates these materials into viscoplastic fluids category. The τ_0 values for every paste can be determined by extending the lines until the intersection with the ordinate ($x = 0$).

On figure 2 a first discussion can be made regarding the rheological parameters of studied materials (n and k). The linear aspect of $\tau = f(\gamma)$ graphics suggests a close to Newtonian behaviour (after overstepping the yield stress τ_0). This is the case of Bingham fluid, for which the rheological parameters are $n = 1$ and k – the slope.

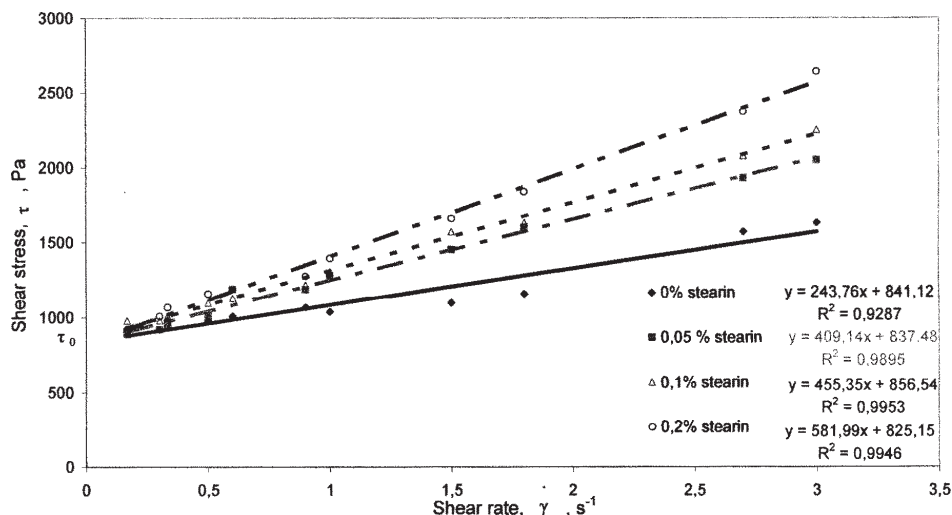


Fig. 2. The variation of shear stress τ with shear rate γ for hydrotalcite pastes: without addition of stearin and with 0.05%, 0.1% and 0.2% stearin.

The viscoplastic behaviour (with yield stress), combined with the pseudoplastic one, previously observed in $\eta = f(\gamma)$ diagram, indicates that the obtained pastes belong to Herschel – Bulckley category, and that for their study the equations (2), (3) and (4) must be used.

Figure 3 illustrates how the rheological parameters are determined for Herschel – Bulckley model.

For an easier comparison, in table 1 are presented the rheological constants (n and k), determined for the two rheological models from figures 2 and 3.

The Bingham-Schwedoff model is a simpler model than Herschel-Bulckley and presumes a Newtonian behaviour of pastes (flowing index $n = 1$) when the shear stress oversteps the yield stress (τ_0). The Herschel-Bulckley model is useful when the materials submitted to linear deformation do not behave in a Newtonian way ($n \neq 1$) over the yield stress. From table 1 it can be observed that, although a simpler model, the Bingham-Schwedoff model offers values for the k parameter close to those calculated with Herschel-Bulckley. This can be explained by the fact that the pastes (specially those well lubricated, with high amount of stearin) do not possess a strong shear thinning character ($n = 0.96$, so ≈ 1), approaching to Newtonian behaviour. However, the Herschel-Bulckley model describes more rigorously the rheological behaviour of the prepared pastes and is recommended for other similar materials. With the help of Herschel-Bulckley model it can be observed the lubricating role of stearin by looking at the values of flowing index n . For the paste without stearin (HT 1), the flowing index n is significantly different from the Newtonian value $n=1$. But as the lubricant

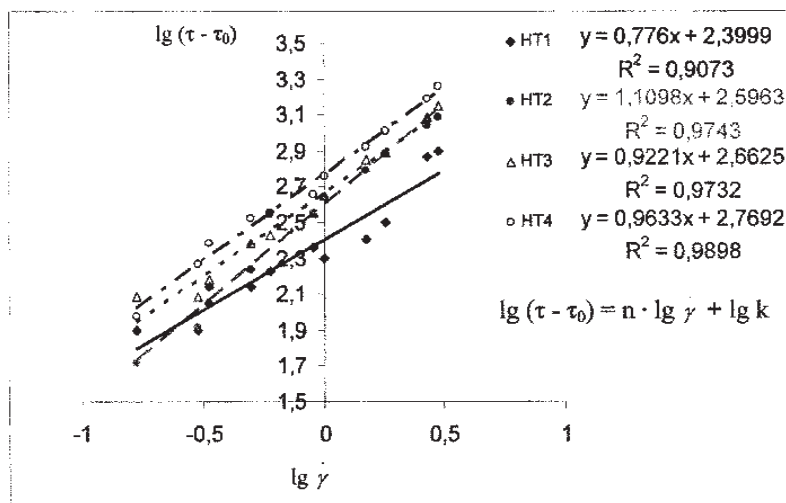


Fig. 3. The determination of rheological parameters (n and k) using the logarithmic form of Herschel-Bulckley equation (3)

Paste	τ_0 , Pa	Bingham-Schvedoff model		Herschel-Bulckley model	
		n	k	n	k
HT 1	841.1	1	243,8	0.78	251.1
HT 2	837.5	1	409.1	1.11	394.7
HT 3	856.5	1	455.3	0.92	459.7
HT 4	825.1	1	582	0.96	587.8

Table 1
RHEOLOGICAL CONSTANTS OF HYDROTALCITE PASTES, DETERMINED BY THE TWO RHEOLOGICAL MODELS

Factor	A, Amount of plasticizer/lubricant (weight %)				Sum on rows
	0	0.05	0.1	0.2	
B , shear strain rate, $\dot{\gamma}$, [s ⁻¹]	Dynamic viscosity, η , [Poise]				
0.17	53395.3	56955.0	58734.8	67634.0	236719.1
0.3	28671.0	32637.0	32637.0	38371.0	132316.0
0.33	24925.3	28486.0	30266.4	32937.0	116614.7
0.5	17208.6	19582.2	21955.8	23142.6	81889.2
0.6	19780.0	16813.0	18791.0	19780.0	75164.0
0.9	13186.7	11868.0	13516.3	14835.0	53406.0
1	12758.1	10087.8	13054.8	13945.0	49845.7
1.5	9692.2	6725.2	10483.4	10879.0	37779.8
1.8	8901.0	6428.5	9065.8	9890.0	34285.3
2.7	8241.7	7142.8	7692.2	8791.1	31867.8
3	7417.5	7318.6	7516.4	8604.3	97614.3
Sum of column	204177.4	204044.1	223713.9	248809.0	Overall sum 947501.4

Table 2
CALCULATED VALUES OF VISCOSITY FOR ALL 4 CERAMIC PASTES

Source of variance	Square sum	Degrees of freedom	Variance	F_c	F_{tab}
Factor A	$SS_A = S_2 - S_4 = 1,22 \times 10^8$	$(l-1)$ 3	$s_A = 4.08 \times 10^7$	9.548	2.92
Factor B	$SS_B = S_3 - S_4 = 9,72 \times 10^9$	$(m-1)$ 10	$s_B = 9.72 \times 10^8$	227.2	2.16
Experimental error	$SS_{rez} = SS_T - SS_A - SS_B = 1,28 \times 10^9$	$(l-1)(m-1)$ 30	$s_0 = 4.27 \times 10^6$	-	-
Sum	$SS_T = S_1 - S_4 = 9,97 \times 10^9$	$(lm-1)$ 43	-	-	-

Table 3
DISPERSIONAL BIFACTORIAL ANALYSIS

concentration rises (to 0.2% for HT4), the value of n parameter is approaching 1 (0.96), close to a Newtonian behaviour, with low viscosity, this remark being a confirmation for the lubrication role of stearin.

The values of viscosity, calculated with equation (6), are summarized in table 2 in order to apply the bifactorial dispersional analyse on experimental data.

Based on the data in table 2, the square sums $S_1 \div S_4$, SS_A , SS_B and SS_T were computed in a similar way as described in a previous article [32]. All these sums are

used to compute the variances s^2 . The results are centralized in table 3.

By comparing the dispersional reports F_c with the default values F_{tab} of F distribution (Fisher criteria), the following relations can be observed: $F_A > F_{tab(0.05;3;30)}$; $F_B > F_{tab(0.05;10;30)}$.

Because the dispersional reports are significant at the chosen significance level of 5%, it follows that both the shear rate $\dot{\gamma}$ and the amount of plasticizer / lubricant influences the rheology of crude pastes based on hydrotalcite. In other words, the two factors will act as variables in the mathematical model of extrusion process.

A Factor										
yA ₁			yA ₂			yA ₃			yA ₄	
1.855x10 ⁴			1.856x10 ⁴			2.034x10 ⁴			2.262x10 ⁴	
B Factor										
yB ₁	yB ₂	yB ₃	yB ₄	yB ₅	yB ₆	yB ₇	yB ₈	yB ₉	yB ₁₀	yB ₁₁
7.71x10 ³	7.97x10 ³	8.57x10 ³	9.44x10 ³	1.25x10 ⁴	1.34x10 ⁴	1.88x10 ⁴	2.05x10 ⁴	2.91x10 ⁴	3.31x10 ⁴	5.92x10 ⁴

Table 4
THE INFLUENCE OF PLASTICIZER AMOUNT (A FACTOR) AND OF SHEAR RATE (B FACTOR)

A Factor	2	3	4
N			
Rank	2,89	3,04	3,12
Lsr _A	2,98x10 ³	3,14x10 ³	3,23x10 ³

Table 5
RANK VALUES FOR A FACTOR (α = 0.05) AND FOR B FACTOR (α = 0.05)

B Factor	2	3	4	5	6	7	8	9	10	11
N										
Rank	2.89	3.04	3.12	3.20	3.25	3.29	3.32	3.35	3.37	3.38
Cmmrs _B	1.8x10 ³	1.89x10 ³	1.94x10 ³	1.99x10 ³	2.02x10 ³	2.05x10 ³	2.07x10 ³	2.9x10 ³	2.10x10 ³	2.11x10 ³

Plasticizer's level	Compared samples	Mean's difference	Lsr	Significance of difference
A ₄	Sample4 – Sample2	yA ₄ -yA ₁	lsr _{A4-1}	significant
	Sample4 – Sample1	yA ₄ -yA ₂	lsr _{A4-2}	significant
	Sample4 – Sample3	yA ₄ -yA ₃	lsr _{A4-3}	insignificant
A ₃	Sample3 – Sample2	yA ₃ -yA ₁	lsr _{A3-1}	insignificant
	Sample3 – Sample1	yA ₃ -yA ₂	lsr _{A3-2}	insignificant
A ₁	Sample1 – Sample2	yA ₂ -yA ₁	lsr _{A2-1}	insignificant

Table 6
SIGNIFICANCE DIFFERENCE TEST OF MEANS (THE EFFECT OF PLASTICIZER AMOUNT)

Shear rate level	Compared samples	Mean's difference	Lsr	Significance of difference
B ₈	Sample8 – Sample7	yB ₇ -yB ₇	lsr _{B8-7}	insignificant
B ₇	Sample7 – Sample6	yB ₇ -yB ₆	lsr _{B7-6}	insignificant
B ₆	Sample6 – Sample5	yB ₆ -yB ₅	lsr _{B6-5}	insignificant
B ₄	Sample4 – Sample3	yB ₄ -yB ₁	lsr _{B4-1}	insignificant
	Sample4 – Sample1	yB ₄ -yB ₂	lsr _{B4-2}	insignificant
	Sample4 – Sample2	yB ₄ -yB ₃	lsr _{B4-3}	insignificant
B ₂	Sample2 – Sample3	yB ₃ -yB ₁	lsr _{B3-1}	insignificant
	Sample2 – Sample1	yB ₃ -yB ₂	lsr _{B3-2}	insignificant
B ₁	Sample1 – Sample3	yB ₂ -yB ₁	lsr _{B2-1}	insignificant

Table 7
SIGNIFICANCE DIFFERENCE TEST OF MEANS (THE EFFECT OF SHEAR RATE)

Subsequently, the factor levels that differ significantly have been established, applying for this purpose the Duncan multiple rank test.

The arithmetic means were ordered ascending (table 4) and the mean square error was computed:

$$s_f = s_0 \cdot \frac{1}{\sqrt{n}} \quad (7)$$

From the tabulated values of Duncan test, [21,22], (l-1) rank values (for A factor) and respectively (m-1) rank values (for B factor) were extracted. The least significant ranks (Lsr) were determined, the differences being considered significant if they exceed the least significant values for the chosen significance level α = 0.05 (table 5).

In order to estimate the effect of plasticizer amount on the rheology of paste mixtures based on hydrotalcite, the difference between the C₁² (A factor) arithmetic means was computed, and they were compared to critical values (Lsr_A). The results were centralized in table 6.

In order to estimate the effect of shear rate on the rheology of paste mixtures based on hydrotalcite, the differences between the C_m² (B factor) arithmetic means were computed, and they were compared to critical values (Lsr_B). The majority of the obtained values for the 11 levels of shear rate were significant, excepting the ones from table 7.

The results of the dispersional analysis allowed the obtaining of valuable information for further development of the mathematical model in order to optimize the process using the so called base experiment. The two analyzed factors are parameters of the extrusion process of pastes;

the zero (base) levels for performing the external active experiment are A=A₄ and B=B₅; the variation intervals (Δz_i) have the following values: ΔA=A_{i+1} - A_i(i=2,3); ΔB ≥ B₇ - B₆.

Conclusions

All mixtures studied in this paper, containing hydrotalcite and lubricated with stearin, have a shear thinning (pseudoplastic) behaviour, showed in particular by η=f(γ) diagrams. To this remark is added the viscoplastic behaviour fluids with yield stress), so that the two combined observations situates the obtained pastes into Herschel – Bulckley category, and for their study were used specific equations.

The lubricating role of stearin is validated by two experimental observations.

As the concentration of stearin increases, the value of yield stress τ₀ decreases from 841 Pa to 825 Pa, suggesting a better fluidisation of pastes.

The increasing of lubricant concentration (to 0.2% for HT4) leads to values for the flowing parameter n close to 1 (0.96), so that the rheological behaviour is approaching to a Newtonian behaviour, with low viscosity.

Although a simpler model (because of the simplification that n is constant and equal to 1), the Bingham-Swedoff model offers values for the k parameter close to those calculated with Herschel-Bulckley. This can be explained by the fact that the pastes (especially those well lubricated, with high amount of stearin) do not possess a strong shear thinning character (n = 0.96, so ≈ 1), approaching to Newtonian behaviour. However, the Herschel-Bulckley

model describes more rigorously the rheological behaviour of the prepared pastes and with its help can be observed the lubricating role of stearin by looking at the values of flowing index n .

The amount of plasticizer / lubricant influences the rheological behaviour of pastes based on hydrotalcite at all concentration levels, with the note that a 0.05% variation in concentration produces a low effect on the rheology of studied pastes.

The shear rate influences as well the rheological behaviour of pastes with hydrotalcite at all shear rate levels, noting that in the range $0.2-0.5 \text{ s}^{-1}$ the effect is small, insignificant for the significance level $\alpha = 0.05$.

Acknowledgement: The work was performed with the financial support of ANCS and MEC, in the research contract no. 71-043/2007, National Programme PNCDI 2 –Partnerships 4.

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Manuscript received: 13.01.2011