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Ternary-mixture quantification of ceramic raw materials

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The mechanical properties of a ceramic are the favored criteria to measure its qualities. For this purpose, we present in this article a new technique which consists in improving the mechanical properties by strengthening the structure of the ceramic with polymers. The amount of incorporated polymer, in a kaolin reference, is used as a criterion for the optimization of the mechanical properties of a hybrid refractory ceramic. The formulation of the mixture, in ceramic, optimized rests on a new methodology of mixture calculation and a mathematical multiple linear regression analysis (MLRA). In conclusion, the optimal mechanical properties were recorded for the optimized formula giving a mixture of 80% of hybrid kaolin, 20% of by-products GW1 and GW2 and 16% of polyethylene glucose (PEG) (PEG1500 and PEG6000). This result was confirmed by various physical tests such as the X-ray Diffraction (XRD) and the mechanical tests.

Key words: Mixture calculation, Multiple linear regressions, Hybrid refractory ceramic, Rates PEG1500 & PEG6000, Mechanical properties.

Introduction

Nancomposites have been the focus of academic and industrial attention in recent years because the final composites often exhibit a desired enhancement of mechanical, barrier, thermal, and/or other properties relative to the original polymer matrix [1-4]. Normally, natural or organically modified clay is put in direct contact with the polymer matrix or its precursor monomers and the nanocomposites are subsequently obtained by one of several methods, including in situ polymerization, intercalation from solution, or melt intercalation [3]. For real nanocomposites, the clay layers must be uniformly dispersed in the polymer matrix (intercalated or exfoliated), as opposed to being aggregated as tactoids. A diverse array of matrix polymers have been used in nanocomposite formation, ranging from synthetic non-degradable polymers such as nylon [5-7], polystyrene [8-9], and polypropylene [10-11] to biopolymers such as polylactide [12-13] and starch [14-21].

The transversal approaches or molecular engineering are synergetically gathered and cover up the strategies of bio-inspired synthesis [22-25] in which the integration of different domains of competence allow the chemist to elaborate complex systems of varied forms with a perfect mastery on different scales of size, composition, function and morphology. The conditions of soft-chemistry are exactly those in which many reactions of organic, organometallic chemistry, supramolecular and polymers chemistry are realized [26-30]. The realization of complex hierarchical hybrid architectures involves transversal modes of synthesis and successfully illustrates the main role of integrative chemistry in the area of advanced materials [31, 22-23]. The judicious choice of metallic cations possessing d or f orbitals partially fulfill their confer of additional electronic functions allowing the generation of magnetic or optic proporties [32-33]. Materials elaborated with the presence of tensioactives present a strong degree of organization and possess porosity that remains accessible for a second functionalization through a graft post [34-35].

For many applications, ceramic is in competition with other materials. The much properties of kaolin based ceramic sought after [36-37] are: their temperature resistance (mullite, cordiérite, magnesia) generally greater than 1500 °C, their resistances to the creep (because of their structure, ceramic tends to suffer less from dislocations), their chemical resistances (acids aggressive environment, basic or in the humidity), their hardness is higher than that of some metals, excellent dimensional stability as the body of a sensor of strength or pressure, and their electric insulations (very big range of dielectric constants) [38-39]. Nevertheless, these materials often present a low mechanical resistance [40]. To improve this very important property, in the case of materials intended for the construction and for the surface, it is necessary to add reinforcements such as polymers [41], to increase their resistance in flexion and in compression and improve the micro hardness of materials. In this optics, we wanted to create a new refractory hybrid ceramic, in matrix of kaolin strengthened by the polyethylene glycol 1500 and 6000 [42-44].

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Experimental techniques and Methodology

Experimental techniques

XRD analyses were done thanks to a PANAlytical diffractometre. The chemical compositions were obtained by X fluorescence (XF). The used KT3B was beforehand treated with the peroxyde of hydrogen in 20 V. We obtain KR, the kaolin reference which will be added for the hybrids preparation by insertion of the PEG. The tests of micro Vickers hardness were realised using an indenteur of Zwick brand endowed with a point of diamond in pyramidal shape of a 360° basal angle.

Raw materials

The 99% pure reagents such as polymer PEG1500 and PEG6000 are from PROLABO. The diméthylesulfoxyde DMSO, the acetone and the ethanol are of BIOCHEM origin. The finished products of kaolin KT3B as well as by-products (fine sand) GW1 and GW2 are supplied by the complex SOALKA of El Milia. The by product (GW1 and GW2) are very rich in muscovite; they were added as clay exhilarating, for their recycling and the improvement of the fusion of raw materials during the cooking. Their considerable contents in alumina (21 in 25%) allow to obtain refractory materials meeting the American standard for the manufacturing of the ceramic (45% Al₂O₃ 25%). The chemical compositions of the by-products samples GW1 and GW2, the whitened kaolin (KT3B), kaolin reference (KR), as well as hybrids are presented in Tables 1 and 2 [39].

Methodology

The aim of this study is to quantify and optimize the three proportions (Cj) forming the mixture according to the ceramic standards. The optimization of this latter will allow the improvement of the mechanical resistances of the hybrid ceramic materials. The creations of mixtures are among the most widely corresponding tools for the formulation of the product. The best mathematical approach in the modeling of the physic-chemical phenomena is the use of the general linear model (GLM) [45-49] which is in the following form:

$$y = \sum_{j=i} C_j f_j(X) \tag{1}$$

The procedure of elaboration of the model which describes

Table 1. Chemical composition of by-products

Dr. masduata				%	oxide	es			
By-products	Al_2O_3	SiO_2	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	PF
GW1	25.17	65.06	0.06	0.29	0.03	0.01	0.05	0.01	8.00
GW2	21.42	64.02	0.96	0.12	0.04	0.04	2.20	0.01	4.00
Kaolin (KT3B)	33.90	48.60	0.90	0.21	0.06	0.80	2.70	0.08	10.80

the evolution of the chemical composition of the mixture according to the chemical composition of the three raw materials is determined by the multiple linear regressions (MLR-method of the least squares). It consists in minimizing the quantity:

$$e = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2$$
(2)

The obtained linear system is in the following form

$$\sum_{j=1}^{m} a_{kj} * c_j = b_k \tag{3}$$

With :

$$a_{kj} = \sum_{i=1}^{k} f_i(X_{(i,i)}) * f_k(X_{(k,j)})$$
(4)

$$b_k = \sum_{i=1} y_i * f_k(X_{(k,j)})$$
(5)

An additional constraint was added to the linear system:

$$\sum_{i=1}^{m} c_i = 100\%$$
 (6)

The resolution of the obtained system is ensured by the algorithm of GAUSS. The validity of the chosen model is ensured by statistical criteria such as: the coefficient of correlation (R^2), the residual variance, the STUDENT test and the FISHER SNEDECOR test.

Algorithm of calculation of mixture

The proportions calculation of the three raw materials was made from the data of the oxides contents and loss on ignition, respectively the by-products GW1 and GW2 (Table 1), hybrids (Table 2) the chemical composition of the mixture meet the requirements of the American standard. The progress of the algorithm (Fig. 1) consists in varying continuously the chemical composition of the mixture in oxides in a standard interval. The realization of a phase shift on oxides from a minimal value to a maximal value, always remaining in the standard interval, gives place to several variants (solutions). The choice of the optimal solution is dictated by the statistical criteria (Table 3).

Elaboration of hybrid refractory ceramic

The execution of the mixture calculation program allowed to quantify and optimize the proportions of three raw materials to be used in the formulations of hybrid refractory ceramic. Generally, the constituent of the three optimized raw materials given by the calculation program corresponds to 80% of KT3BH, 10% of GW1 and 10% of GW2.

Uribuida	DEC 1500					% oxides				
nybrids	PE01300 -	SiO ₂	Al_2O_3	Fe_2O_3	CaO	MgO	Na ₂ O	K ₂ O	MnO	PF
KR0	0	45.14	31.86	0.83	0.056	0.48	0.076	0.216	0.0350	07.27
KH4	10	42.02	29.41	0.71	0.051	0.228	0.068	0.210	0.0019	17.30
KH5	12	41.62	27.45	0.64	0.049	0.199	0.062	0.186	0.0009	18.20
KH6	14	40.30	26.79	0.61	0.047	0.192	0.059	0.179	0.0007	18.85
KH7	16	38.99	25.86	0.59	0.046	0.180	0.055	0.172	0.0006	19.80
KH8	18	38.22	25.17	0.57	0.043	0.177	0.051	0.160	0.0005	20.25
KH9	20	37.53	24.54	0.52	0.039	0.173	0.048	0.132	0.0004	20.87
Hybrids	PEG6000									
KH10	10	42.51	31.17	0.68	0.054	0.207	0.065	0.126	0.0023	15.33
KH11	14	40.56	28.95	0.55	0.049	0.195	0.063	0.109	0.0013	16.89
KH12	16	39.98	27.58	0.54	0.042	0.187	0.057	0.105	0.0010	17.18
KH13	20	36.92	24.54	0.54	0.042	0.170	0.053	0.083	0.0009	18.29
					-	-				

 Table 2 Chemical composition of hybrids KT3B

Table 3. Proportion of raw materials and statistical criteria

% raw materials								S	tatistical	l criteria		
Polymer PEG1500		КТ3ВН	GW1	W1 GW2	$GW2 R^2$	2 residual	Calculated STUDENT test		Tabulated Ca STUDENT I	Calculat-ed	Tabulat-ed	
						variance	C ₁	C ₂	C ₃	test	TISTILK	FISHER
CRU4	10	80.09	09.99	09.95	0.999	7.116e ⁻⁴	237	8.06	9.04		1499200	
CRU5	12	80.00	10.00	09.96	0.999	$1.202e^{-3}$	177	6.03	6.52		864113	
CRU6	14	80.07	09 .98	09.95	0.999	$4.010 e^{-4}$	309	10	12		2477604	
CRU7	16	79.96	09.98	10.05	0.999	$7.832 e^{-5}$	729	23	28		$1.21 e^{+7}$	
CRU8	18	89 .00	5.52	5.44	0.999	$1.168 e^{-3}$	217	3.69	3.98		758910	
CRU9	20	85.88	9.00	6.00	0.999	$1.163 e^{-3}$	217	5.77	4.40	$T(n-m., \alpha/2) = 2.36$	761839	$f(n-m.m-1, \alpha) = 4.74$
Polymer Pl	EG600	00								2.50	//	α) 1.71
CRU10	10	80.11	09.93	09.95	0.999	$5.942e^{-4}$	280	9.52	10.72		1845010	
CRU11	14	80.24	10.00	09.94	0.999	1.508 e ⁻⁴	507	17	18		6711768	
CRU12	16	79.95	10.00	09.95	0.999	$3.830 e^{-3}$	94	3.5	4		256514	
CRU13	20	79.91	10.08	10.00	0.999	$1.068e^{-3}$	180	6.84	7.50		842254	

According to this, we prepared a series of raw mixtures containing a proportion of 80% in hybrids KHi (i = 1 in 13), and 20% in by-products. We realize first pieces in the shape of pastilles of small dimensions $(13 \times 4 \text{ mm})$ pressed under a pressure of 3 to 4 tons, in a hydraulic press, using stainless steel cylindrical moulds (mussels). Pastilles about 1 g, are then dried in 105 °C during 24 hours then weighed (the loss in weight is bound to the rate of absorbed humidity and consequently to the capillary porosity of pastilles) and their dimensions are measured with a precision of ± 0.01 mm. The different samples are then cooked in two maximal temperatures 1200 °C and 1500 °C. The test tubes of bigger dimensions (2 cm \times 8 cm \times 3 mm) were pressed in stainless steel rectangular moulds (mussels) under a 5-6 tons pressure, to realize mechanical Vickers micro hardness and flexion tests, after cooking in 1200 °C and in 1500 °C.

Results and Discussion

Raw materials

Chemical composition

We record a decrease of the contents of the minor elements and to the state of trace (Table 2) when the rate in polymer increases from 0% to 20%. In particular, we shall notice a considerable stepping down in the K_2O contents in the hybrids (approximately10 times less than the content of KT3B and GW2) due to the insertion of the PEG into the kaolinite, the muscovite and into their exfoliation as well. This is raising from potassium exchange and substitution phenomenon which comes after the fixation of the OH groupings and from oxygen's of the ethers functions on the clay site containing initially the potassium element.



Fig. 1. Summarized organization chart of calculation program progress and ternary mixtures simulation.

Mineralogical composition

The analyses by X diffraction (XRD) gave us the diffractogrammes of the powder samples ground until 50 μ m, the by-products GW1 (Fig. 2(a)) and GW2 (Fig. 2(b)), the finished product of kaolin KT3B (Fig. 3). The obtained crystallized mineralogical phases, as show in the Fig. 2 and 3, are: the muscovite (Mu); the kaolinite (K); the albite (Ab); the quartz (Q); the orthose (gold) and the potassium tecto-aluminotrisilicate (PTA). Analyses by diffraction with X-rays of the hybrids samples are obtained according to the sol-gel process, after drying in 50 °C to eliminate the solvent (ethanol) during at least 24 hours, were weighed, finely ground then analyzed by the powder diffractomètre. The obtained diffractogrammes (Fig. 4) show the influence of the rate of PEG1500 on the intensities of peaks and on their positions, in particular the peaks of diffraction of the kaolinite ($2SiO_2$, Al_2O_3 , $2H_2O$) which is the main mineralogical phase of kaolin. This latter decrease in hybrids, in particular the most characteristic peak of this mineral, situated at $2\theta = 12.31^{\circ}$ and related to diffraction maps (001), corresponding to the basale distance d001 estimated at 7.15 Å, without addition of polymer. This one tends to increase with the insertion of the PEG1500 in the space inter foliair of the kaolinite, and can reach a value of 11.04 Å



Fig. 2. X diffractogrammes of by products, a) GW1; b)GW2.



Fig. 3. X diffractogrammes of the finished product of kaolin KT3B.



Fig. 4. X diffractogrammes of hybrids of KT3B-PEG1500 with different polymer rates.

 $(2\theta = 8^{\circ})$, for certain hybrid samples (in 14 and in 16% of PEG1500) by insertion of the polymer, and 11.77 Å after addition of the DMSO (5%) by insertion of the molecules of the diméthyle sulfoxyde at the end of 4 hours of agitation in the space inter leaf. The increase of the basale distance of the kaolinite provokes a decrease of the diffraction angle 20 to approximately 7.5°. The most obvious decreases of the intensities of the peaks characteristic of the kaolinite as well as the muscovite (6SiO₂, 3Al₂O₃, K₂O, 2H₂O) which is a minor phase of the kaolin, Show the existence of a practically total exfoliation of clays after insertion of the DMSO and the polymer in inter- foliairs spaces. The two main peaks at 2 θ : 20.83° and 26.59° attributed respectively





Fig. 5. X diffractogrammes of hybrids of KT3B-PEG6000 with different polymer rates.

to the maps of diffraction (100) and (011) of the quartz tend to disappear by considerable decrease of their respective intensities. This fact that highlights the formation of an amorphous phase by dissolution of the quartz after dispersion of the polymer, under the chemical effect of the PEG1500 by fixing of the hydroxyle grouping of this last one on the octaédrique site. The substitution with the PEG6000 of length of chain and higher weights (approximately 4 times the weight of PEG1500) ended at hybrids of the same type and the cristallographiques characteristics (Fig. 5). On the (Fig. 6), we represented both X diffractogrammes powder of the samples of PEG1500 (Fig. 6(a)) and PEG6000 (Fig. 6(b)) corresponding to similar semi-crystalline structures. We shall note the existence of the same main peaks of diffraction successively at 20 about 19° and 23.2°, of respective intensities 100 and 86%. However, we observe additional considerable peaks, on the X diffractogramme of the PEG6000 situated at angles 2θ equal to 18.9° and 23.4° much more intense, and characteristics of a chain longer than that of the PEG1500. This is explained by a more important increase of the crystal lattice of the PEG6000 by giving crystallites of more important dimensions.



Fig. 6. X diffractogrammes of polymer powder, a) PEG1500; b) PEG6000.



Fig. 7. Ternary diagram of raw materials with ceramic.

Selection of the optimal variants from a software mixture calculation

The theoretical calculation of the chemical compositions (Table 4) and proportions of raw materials in ceramic was made from the data of the contents in oxides and loss on ignition, respectively the by-products GW1 and GW2 (Table 1) and hybrids (Table 2) previously mentioned. Generally, after carrying out the calculation program of the elaborated mixture, several solutions were obtained. The choice of optimal solution is concerned with the variant giving the proportions of hybrid kaolin (80%), of GW1 (10%) and GW2 (10%), Fig. 7(a), with a rate of 16% PEG. This choice is dictated by the statistical criteria (Table 3) and the mechanical resistances. On one hand, we record Fisher calculated values superior to its tabulated value which confirms to us the whole model. On the other hand, all the coefficients of the elaborated models are accepted because the calculated Student test values are at least superior to its tabulated value. On the whole, the obtained solutions (Fig. 7(a)), for each case constituted an area of mixture in which each solution is optimal except for the rates of PEG1500 superior to 16% where we record a decrease of the mechanical resistance of the prepared hybrid ceramic (experimentally obtained) Fig. 7(b). In general, and according to the obtained results, the optimal general empirical model that raises from this simulation is in the following form:



 Table 4. Theoretical chemical compositions of hybrids refractory ceramics mixture

Polymer			% oxides										
PEG15	00	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K_2O	PF				
CRU4	10	46.32	28.15	0.6673	0.0477	0.1877	0.0565	0.3837	15.06				
CRU5	12	46.01	26.64	0.6111	0.0462	0.1652	0.0519	0.3585	16.25				
CRU6	14	44.95	26.06	0.5907	0.0446	0.1592	0.0492	0.3654	16.31				
CRU7	16	43.90	25.24	0.5740	0.0437	0.1486	0.0459	0.3655	16.97				
CRU8	18	41.48	25.17	0.5665	0.0424	0.1614	0.0468	0.2660	18.82				
CRU9	20	41.47	24.55	0.5085	0.0385	0.1517	0.0427	0.2481	18.86				
Polymer PEG60	00				% 0	xides							

CRU10	10 46.58	29.50	0.4620	0.0500	0.1706	0.0540	0.3102	13.45
CRU11	14 44.92	27.71	0.5354	0.0460	0.1611	0.0525	0.2942	14.72
CRU12	16 44.58	26.52	0.5345	0.0402	0.1531	0.0472	0.3001	14.83
CRU13	20 42.85	24.43	0.5348	0.0408	0.1410	0.0444	0.2936	15.86

$$\hat{\mathcal{Y}} = C_1 * X(1,i) + C_2 * X(2,i) + C_3 * X(3,i),$$

(C₁=80; C₂=10; C₃=10) (7)

The theoretical chemical composition of refractory ceramic

is obtained by the following mathematical expression (Table 5):

$$CR(i) = \frac{Cru(i)}{100 - PF} *100$$
(8)

Hybrid refractory ceramic materials

The obtained samples of ceramic were subjected to several tests such as the thermal shock resistance, the refractoriness (for 1500 °C which is the minimal pyroscopique temperature according to the standard relative to refractories), their holding to cooking (we shall note the absence of deformations and fissuring), their retreats, their losses in weight as well as their chemical resistances to acids (H₂SO₄ in 70%) and to bases (NaOH), assessed according to the French standard AFNOR. Retreats are low for the hybrid refractoriess. The thing that shows in spite of the increase of the rate of polymer, few variations of the dimensions. Consequently, the addition of a considerable amount in GW1 and GW2 improves the aspect and the holding to the cooking of ceramics by increasing their resistance to thermal shocks. The aspect, such as the color and the state of the surfaces of ceramics, change according to the cooking temperature and the composition of the initial mixtures. We will note that the color is light pink to 1200 °C and the surfaces are smoother to the hybrid ceramics in particular. While the color becomes light grey and the surface more rough to 1500 °C, with appearance of pores on the materials surface.

Chemical composition of hybrid refractory ceramic

The obtained values show that these decrease when the rate of polymer increases from 10% to 20%. These estimations allow us to anticipate the global contents in oxides

 Table 5. Theoritical chemical compositions of hybrids refractory ceramics

<i>Polyn</i> PEG1:	<i>ier</i> 500	% oxides									
		SiO ₂	Al_2O_3	$\mathrm{Fe}_2\mathrm{O}_3$	CaO	MgO	Na ₂ O	K_2O			
CH4	10	54.51	33.17	0.80	0.06	0.23	0.07	0.43			
CH5	12	54.91	31.86	0.78	0.05	0.16	0.07	0.41			
CH6	14	53.70	31.17	0.68	0.05	0.20	0.06	0.45			
CH7	16	52.87	30.41	0.68	0.05	0.17	0.06	0.45			
CH8	18	51.11	31.01	0.70	0.05	0.19	0.05	0.37			
CH9	20	51.09	30.25	0.63	0.05	0.19	0.05	0.31			
<i>Polyn</i> PEG6	<i>1er</i> 000			%	oxide	5					
CH10	10	53.83	34.09	0.74	0.06	0.20	0.06	0.36			
CH11	14	52.68	32.49	0.63	0.05	0.19	0.06	0.34			
CH12	16	52.26	31.22	0.58	0.04	0.19	0.06	0.35			
CH13	20	50.90	29.10	0.65	0.05	0.13	0.06	0.36			

as well as the loss on ignition, the various mixtures of the raw before the cooking, to control in particular those of the major oxides such as the silica and the alumina, and those of the minor oxides that represent generally the coloring impurities such as the hematite Fe₂O₃ and the oxide of manganese. For this latter, the values are non negligible and consequently do not intervene in the calculations of chemical compositions. The real chemical compositions of ceramic (Table 6) after cooking at 1500 °C, were made with several methods. The dosage of the main elements such as the silica, was made by gravimetric and by UV-visible spectrophotométry, the contents of the alumina were obtained by colorimetric with the aluminon. While the contents of the minor elements were determined by the SAA, such as oxides of iron, Manganese, some lime CaO, the magnesia MgO, oxides of sodium and potassium. The results show that the contents depend on initial chemical compositions of mixtures of the raw and in this particular case on the rate of polymer in hybrids. The values tend not only to decrease when the rate in PEG increases, but also they are for the majority of oxides superior to the theoretical values (mixtures of the raw) of the Table 4, respectively for ceramic of reference and hybrids. We record low differences between the experimental and theoretical chemical composition of hybrid refractory ceramic. The existence of the fluctuations in the values between those of the mixture and ceramic, brings to light the influence of the temperature of cooking (1500°C) on the chemical compositions of ceramic that tend to make increase the contents of oxides SiO₂, Al₂O₃ and CaO because of their refractoriness. On the other hand, the contents of the other oxides (Fe₂O₃, K₂O, Na₂O, MgO) that liquefy at temperatures mainly lower than 1500 °C, decreased because of their low temperature resistance.

Table 6. Chimical Compositions of hybrid ceramics after cooking at 1500 $^{\circ}\mathrm{C}$

Polymer				%	oxides			
PEG15	500	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na ₂ O	K ₂ O
CRU0	10	54.00	33.00	0.79	0.05	0.20	0.06	0.45
CRU4	12	54.50	31.50	0.75	0.04	0.18	0.06	0.40
CRU5	14	53.20	31.00	0.65	0.04	0.17	0.05	0.42
CRU6	16	52.30	30.10	0.63	0.04	0.15	0.05	0.43
CRU7	18	49.80	29.50	0.62	0.03	0.13	0.04	0.32
CRU8	20	48.50	28.30	0.59	0.02	0.11	0.03	0.29
<i>Polym</i> PEG60	er 000			%	oxides			
CRU10	10	53.30	33.90	0.70	0.05	0.22	0.05	0.38
CRU11	14	52.29	32.10	0.61	0.04	0.20	0.05	0.36
CRU12	16	52.00	31.06	0.52	0.03	0.18	0.05	0.34
CRU13	20	49.50	28.90	0.59	0.04	0.15	0.05	0.33

Mineralogical composition

The previous results of the chemical analysis are in correlation with XRD analyses of represented ceramics by the Fig 8, obtained from mixtures of raw in (80% of hybrid with 16% of PEG + produced 20% of the byproduct GW1 and GW2) respectively with PEG1500 and PEG6000. The examination of the lines of X diffractions of both different X diffractogrammes show that the signals are the same in 2 diagrams and correspond to a practically unique phase of mullite. The background noise makes appear a wide signal and more or less flatten relating to an amorphous phase of quartz associated with a carbon phase.

Mechanical properties

The technique of the micro indentation is widely spread; it is used to characterize the mechanical properties of a material. Such as its hardness, its module of elasticity or still its resistance to the fissuring. This test was realized on a series of ceramic hybrid cooked samples at 1200 °C and 1500 °C. The obtained results are presented in the Table 7.

The obtained results show that the increase of the hardness of Vickers (HV) is proportional to the rate of polymer added until the 16% rate for PEG1500 and then beyond this value, the hardness of Vickers decreases. For this reason, the rate of optimized polymer is 16%.

Infrared analysis (FTIR)

According to the Fig. 9 at the first sight, we notice the appearance of two strips of asymmetric and symmetric elongation of CH_2 in 3000-2900 cm⁻¹. The intensities increase of the elongation strips of OHoct of the octahedral site of the kaolinite was observed in 3600 and 3700 cm⁻¹. This phenomenon is due to the presence of the polymer



Fig. 8. Comparison between X diffractogrammes of ceramics in (80% kaolin + 10% by-product) in 1500 °C of hybrids with. 1) 16% of PEG1500; 2) 16% of PEG6000.

Table 7. Micro hardness of hybrid ceramic and the reference cooked at $1500 \,^{\circ}\text{C}$

ceramic	CR ₀ (reference)	CH12	CH16	CH18	CH20
PEG 1500 (%)	0	12	16	18	20
HV (Kg/mm ²)	17.14	20.51	62.13	26.16	22.37



Fig. 9. Infrared specters (FTIR) of hybrid ceramic at 1500 °C.

in the clay which becomes fixed by hydrogen connections in octahedral site. For this reason, the results obtained by XRD are confirmed by the infrared (specter IRFT).

Conclusion

The aim of this study was to find a more resistant ceramic material which is harder and high performant, which corresponds to the required standards. Our preference is lean towards the synthesis and the manufacturing of hybrid refractory ceramic from the kaolin (KT3B) of the deposit of Emilia of TAMAZERT-Algeria and two polymers PEG 1500 AND PEG6000. These two last ones are used as materials of reinforcement. Generally speaking, the results pulled through this study are essentially:

• The loss on ignition of kaolin hybrids (KT3BHi) increases with the increasing levels of polymer. This increase is due to the decomposition of polymer incorporated into the kaolin reference to residual organic matter and mineral volatiles (sulfides, heavy metals etc..). For the same rate in PEG1500 and PEG6000, we record a loss on ignition high of hybrids with PEG6000. This difference is mainly due to the molecular weight and to the size of PEG6000. This latter decompose less than the PEG1500 with high temperature (1050 °C). But reinforce more the effect of intercalation and exfoliation.

• The results of chemical analysis show us a decrease of contents of the major and minor elements when the rate of polymer increases from 0% to 20% for the both types of hybrids (PEG1500 and PEG6000).

• Characterization of hybrids by XRD has shown that the dispersion of kaolin in DMSO for 4 hours of agitation made the clay more organophilic in order to facilitate the intercalation of polymer by an increase in the sheets of kaolinite. The intensity of the most characteristic peak is observed at a rate of 16% PEG1500 & PEG6000.

• The made hybrid ceramic refractory presents excellent electrical resistances and provide very good insulation. We record a high ultimate bending strength for a rate of 16% PEG1500 & PEG6000. Further testing by micro Vickers indentation has led to optimum values. These provide high creep rupture strength and improved plasticity.

• Attenuation of a share of the intensities of peaks of X

diffraction of the mullite and moreover the more less rounded form of micro grain making up the hybrid ceramic at 1200 °C bring to light the formation of a new amorphous phase and meso-porous composite, containing an appreciable rate of carbon, resulting from the pyrolytic decomposition of PEG. This result is in direct increase of mechanical strength of ceramic hybrid.

Abbreviations List

- X (j.i) : Proportion of oxide (i) in the material (j)
- $\hat{y}(i)$: Proportion of oxide (i) in the mixture
- CR (i) : Percentage of oxide (i) in the hybrid ceramic refractory
- Cru (i) : Percentage of oxide (i) in the ceramic mixture
- Error between the chemical composition of the e: mixture (y(i)) and that determined by the general model $(\hat{y}(i))$
- $f_j(X)$: Chemical composition of oxides of the three raw materials (KT3BH. GW1 and GW2)
- PF : Loss on ignition

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