Mineral composition and stone conservation of cultural heritage building materials studied by PXRD

B. Simionescu[1], M. Aflori[2,*], M. Olaru[2]

[1] University of Oviedo, Spain
[2] "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania
[*] maflori@icmpp.ro

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Abstract. For the present study two types of rock, from Spain and Romania, selected by regional significance, abundance and importance were characterized by powder X-ray diffraction (PXRD). The samples were prepared by casting the same amount of a silsesquioxane-based polymer obtained through sol-gel approach and radical polymerization of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) onto powder stones. Due to the distinct stones composition, the different polymer behaviour as regarding to these samples was evidenced through PXRD techniques. Conclusions concerning acid resistance, stone conservation and durability were revealed by using Match! Software and IUCr/COD/AMCSD database.

Introduction

The physico-chemical analytical techniques employed in the study of building materials provide very accurate qualitative and quantitative results on the alteration features, both related to the alteration layers and to the bulk chemistry of the exposed stone. The study of dolomitic sandstones evidenced the presence of weathering products inside the pores of sheltered parts after exposure to weathering conditions [1]. If a high amount of soluble salts is present in the stone structure, the local porosity is altered. Thus, the pore etching on the rain-washed side will allow pollutants to react on a greater surface area, and therefore will speed up the deterioration process. The petrography of the building material may also have an influence on the local porosity [2].

For the present study - two types of rocks, from Spain and Romania, were selected. The first type of rock is a bright white micritic dolomitic stone, typical from the Spanish region of Asturias, called Laspra (L) [3]. Important parts of Santa Maria del Naranco and San Miguel de Lillo churches, both listed in UNESCO's World Heritage List since 1985, were built by using L as building material. Due to the high level of L usage over the centuries, there is no quarry any more and in consequence, a small block of L arising from the Oviedo's cathedral portico was extracted for this study. The second selected stone is coming from Romania and it can be described as being a bioclastic oolitic stone, named Repedea (R). This type of stone

can be found in the east of Romania, along the Moldavian platform. Dobrovat monastery, one of the most important monasteries situated in the north-eastern part of Ro-mania, was built from R limestone.
The TMSPMA polymer was obtained by a combination of sol-gel and radical polymerization reactions, a common method for manufacturing mesoporous materials for stone conservation. Such type of products polymerize within the stone pores by means of a sol-gel process, thereby strengthening the material. Their low viscosity allows them to penetrate deeply into the porous material after polymerization, a process that occurs upon contact with environmental moisture, by the formation of a stable gel with a silicon-oxygen backbone. In the conservation product synthesis, the sol-gel transition occurs in the presence of a surfactant, an approach that provides an efficient means of avoiding cracking of the gel while it is drying inside the stone [4].

Experimental

Sample characterization
The samples were carefully grounded in an agate mortar in order to eliminate as far as possible any particle size effects during the measurements. XRD patterns were recorded with a D8 Advance Bruker AXS diffractometer (Bragg-Bretagno geometry) equipped with a scintillation detector. X-rays were generated using a CuKα source with an emission current of 40 mA and a voltage of 36 kV. A 0.6 mm fixed divergence slit was used for all samples to improve the signal-to-noise ratio. Scans were collected over the range 5 - 70 °2th using a step size of 0.01° and a count time of 0.5 s/step. The instrument calibration was carefully made by using the provided SRM1976 corundum sample.
The phase identification was first obtained by using the Match! Software version 1.9 together with IUCr/COD/AMCSD database. Match! performs a semi-quantitative analysis of the sample using the "Reference Intensity Ratio method" (RiR-method). The quantity of the phase in the phase mixture was measured by using the profile fitting of the complete pattern (for all accepted phases). Raw data processing included stripping of the alpha-2-radiation, data smoothing, background subtraction, peak searching, profile fitting and zero-point correction (specimen displacement) for errors. Quartz was the internal standard for all minerals.

Mixture preparation
Through radical polymerization of TMSPMA, that contains both methacrylate and silica phases, new hybrid materials can be obtained, in which the silica phase is dispersed in the form of domains with typical sizes of nanometers [5]. The complete process that develops the final silica phase takes place in three steps: the hydrolysis of the alcoxide groups of TMSPMA to form silanols, the condensation of the previously formed silanols to polymerize into silica polymers, and the aggregation of partially condensed silica macromolecules to build up the network [6]. The synthesis of the hybrid composite of polymethacrylate type implies the radical polymerization of TMSPMA in the presence of 2,2′-azobis(2-methylpropionitrile) and subsequent sol-gel reaction in the presence of dodecylamine. The schematic structure of the hybrid composite is presented in figure 1. Stone-polymer samples were prepared by mixing the same amount of TMSPMA with powder stones and dried at vacuum at 30° C.

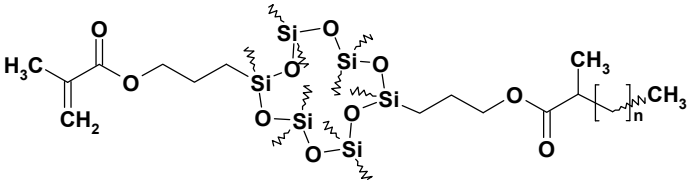

Figure 1. The structure of TMSPMA hybrid composite.

Results and discussions

L and R mineral composition

The PXRD peaks of L (figure 2) indicate the presence of four phases: dolomite, calcite, ankerite and quartz. Dolomite (D) and calcite (C) are the most abundant minerals in case of L, followed by ankerite (A) and a small amount of quartz (Q) (table 1). The peaks of R (figure 3) indicate the presence of calcite (C), magnesian calcite (MC), quartz (Q) and aragonite (Ar).

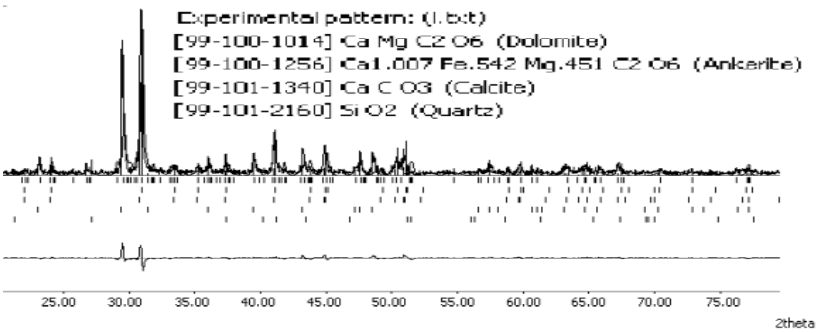

Figure 2. PXRD patterns of L sample using Match! R_p=51%.

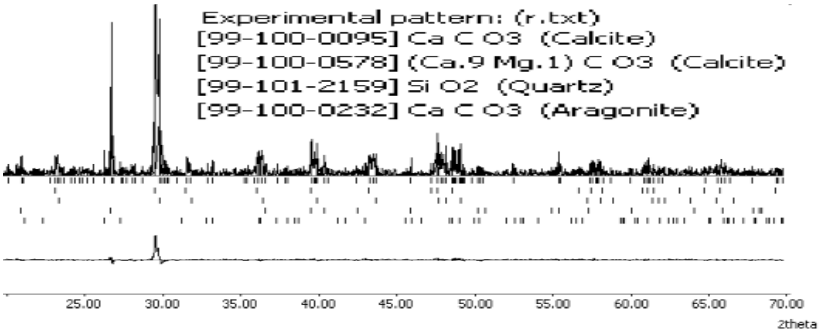

Figure 3. PXRD patterns of R sample using Match! R_p =61%.

Table 1. PXRD measurements results (wt %).

Sample	A	Q	C	D	Mc	Ar	$CaCl_2$	$MgCl_2$
L untreated	11	4	53	32				
R untreated		20	27		36	17		
L+TMSPMA	22	8	18	17			28	7
R+TMSPMA		29	19		28	13	6	5

The difference between the experimental data and the calculated profile studied by using Match! Software (figures 2, 3) appears on the bottom line, and the Bragg reflections are represented as vertical marks. The first row is represented by the experimental data, and the rest are the Bragg reflections of the selected mineral.

TMSPMA characterization

The X-ray diffraction patterns (figure 4) revealed the presence of three peaks, one sharp and two diffuse, which is somewhat different from the typical diffractograms of polysilsesquioxanes that exhibit two diffuse but rather intense peaks [7]. This behaviour excludes the formation of cage structures only (caged silsesquioxanes are normally crystallizable) and indicates the co-existence of crystalline and amorphous units, although crystallinity is not high. Also, in X-ray diffraction spectra, the peaks which appear at small Braggs' angles are particularly important for the elucidation of the nanocomposite structure of sol–gel materials. Such diffraction peaks stem from the silica clusters, which are linked via the non-hydrolyzable Si-C bond to the organic phase of the organic/inorganic hybrid network.

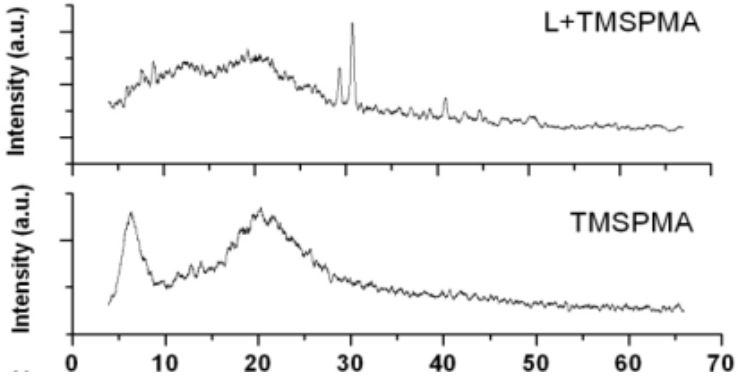

Figure 4. PXRD patterns of TMSPMA and L+TMSPMA samples.

Characterization of L+TMSPMA and R+TMSPMA mixtures

Due to the different stones compositions, the polymer addition has different effects. The structure of R is not affected by polymer addition, while L adopts a distinct amorphous configuration evidenced at angles from 5 to 25° (figures 5, 6). In both cases, a decrease of the relative intensities and peak areas is evidenced, more drastically in case of L+TMSPMA

mixture. The modification of cell parameters for L+TMSPMA (different cards from same database) is attributed to the existence of nanoscale order domains in polymer structure.

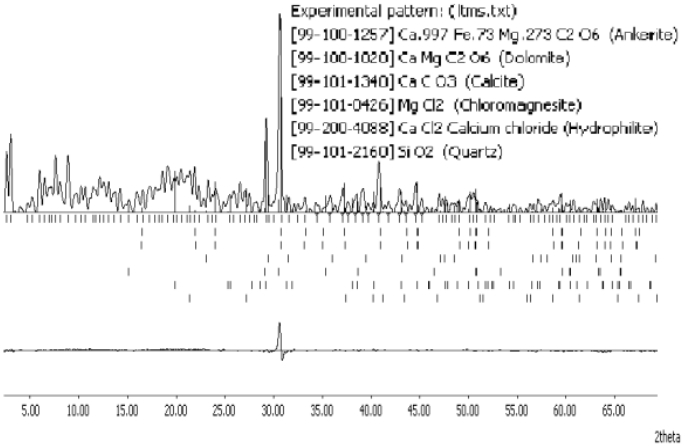

Figure 5. PXRD patterns of L+TMSPMA sample using Match! in the 2θ = 5-70° range, R_p = 45 %.

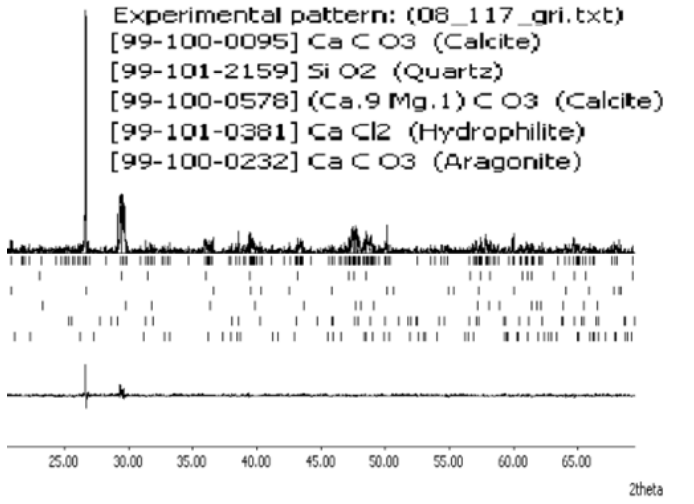

Figure 6. PXRD patterns of R+TMSPMA sample using Match! in the 2θ = 20-70° range, R_p = 50 %.

As a consequence of the presence of an acid medium (pH = 5), a dramatically reduction of dolomite and calcite weights is evidenced for L (table 1), this behaviour being attributed to the reaction of Ca^{2+} and Mg^{2+} with hydrochloric acid, with the formation of $CaCl_2$ and

$MgCl_2$ The percent of reaction products is of 35 % for L+TMSPMA, as compared to the value of 11 % for R+TMSPMA. This behaviour can be correlated with the high L stone porosity and high Ca^{2+} and Mg^{2+} concentrations [3, 8] as regarding to R one. It can be concluded that R is acid-resistant, a valuable information for the ranking of stones durability under the action of acid rains. The relative areas and intensities of the diffraction peaks in the XRD spectra can be related to the minerals crystallites size and stones degrees of crystallinity.

Concluding remarks

The relationship between intrinsic properties, such as mineralogy and microstructure, and functional and durability properties of stone and rocks used as construction materials is revealed. The PXRD technique is a valuable method to decide the applicability of a new conservation material for a certain type of stone. The conservation process of stone samples with the product under investigation modifies the carbonated area and is more efficient for Repedea. An additional examination of the contact angle, permeability and swelling behaviour of the products cast on stones surfaces is required, taking into account that such polymeric structures could function as water repellents and as crack-free conservation products for porous stones.

References

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