RESSALVA

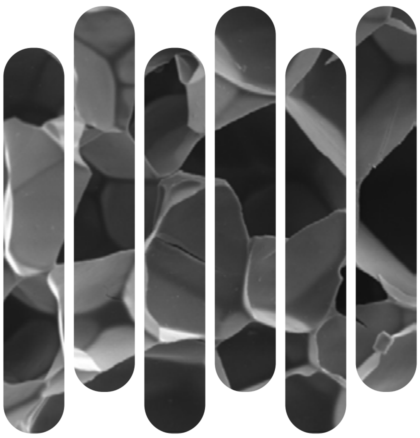
Atendendo solicitação do autor, o texto completo desta tese será disponibilizado somente a partir de 29/07/2023.

UNIVERSIDADE ESTADUAL PAULISTA "JÚLIO DE MESQUITA FILHO"
FACULDADE DE ENGENHARIA
CAMPUS DE ILHA SOLTEIRA

ADHEMAR WATANUKI FILHO

"PHYSICAL AND MECHANICAL CHARACTERIZATION OF CEMENT-MORTARS INTERNALLY CURED WITH HYBRID NANOCOMPOSITES BASED ON HYDROGEL AND NANOCLAY"

Ilha Solteira, SP
2021



Ph.D. Thesis

“Physical and mechanical characterization of cement-mortars internally cured with hybrid nanocomposites based on hydrogel and nanoclay.”

Ph.D. thesis presented to the School of Engineering Ilha Solteira/SP as part of the requirements to obtain the Ph.D. degree in Materials Science.

Concentration area: Materials Science and Engineering.

Adhemar Watanuki Filho
Advisor: Prof. Dr. Fauze Ahmad Aouada

FICHA CATALOGRÁFICA
Desenvolvido pelo Serviço Técnico de Biblioteca e Documentação

W324p

Watanuki Filho, Adhemar.

Physical and mechanical characterization of cement-mortars internally cured with hybrid nanocomposites based on hydrogel and nanoclay / Adhemar Watanuki Filho. -- Ilha Solteira: [s.n.], 2021

146 f. : il.

Tese (doutorado) - Universidade Estadual Paulista. Faculdade de Engenharia de Ilha Solteira. Área de conhecimento: Ciência e Engenharia dos Materiais, 2021

Orientador: Fauze Ahmad Aouada
Inclui bibliografia

1. Hydrogel. 2. Absorbent polymer. 3. Hybrid nanocomposite. 4. Civil construction. 5. Internal curing. 6. Cloisite Na+.

Raiane da Silva Santos

UNIVERSIDADE ESTADUAL PAULISTA

Câmpus de Ilha Solteira

CERTIFICADO DE APROVAÇÃO

TÍTULO DA TESE: Physical and mechanical characterization of cement-mortars internally cured with hybrid nanocomposites based on hydrogel and nanoclay

AUTOR: ADHEMAR WATANUKI FILHO
ORIENTADOR: FAUZE AHMAD AOUADA

Aprovado como parte das exigências para obtenção do Título de Doutor em CIÊNCIA DOS MATERIAIS, área: Ciência e Engenharia dos Materiais pela Comissão Examinadora:

Prof. Dr. FAUZE AHMAD AOUADA (Participaçao Virtual)
Departamento de Física e Química / Faculdade de Engenharia de Ilha Solteira - UNESP

Prof. Dr. MAURO MITSUUCHI TASHIMA (Participaçao Virtual)
Departamento de Engenharia Civil / Faculdade de Engenharia de Ilha Solteira - UNESP

Prof. Dr. JORGE LUIS AKASAKI (Participaçao Virtual)
Departamento de Engenharia Civil / Faculdade de Engenharia de Ilha Solteira - UNESP

Prof. Dr. JOÃO VICTOR FAZZAN (Participaçao Virtual)
Departamento de Construção Civil / Instituto Federal de Educação, Ciência e Tecnologia de São Paulo - IFSP

Prof. Dr. EDUARDO RADOVANOVIC (Participaçao Virtual)
Departamento de Química / Universidade Estadual de Maringá - UEM

Ilha Solteira, 29 de julho de 2021

Faculdade de Engenharia - Câmpus de Ilha Solteira -
Av. Brasil, 56, 15385000, Ilha Solteira - São Paulo
http://www.feis.unesp.br/#!/dfq CNPJ: 48.031.918/0015-20.

Dedication

*Dedico esta tese a meus pais, **Rosária** e **Adhemar** por estarem sempre ao meu lado me apoiando em todas as minhas decisões pessoais, pelas palavras de incentivo, por serem meu exemplo de perseverança e por todo o amor incondicional que me foi concedido.*

*Dedico também a minha amada e companheira **Cássia** pela paciência e amor por toda esta jornada.*

Acknowledgments

A cada ciclo que se encerra ou se inicia devemos ser gratos a tudo que nos conduziu durante esta jornada, por isso, faço uso da palavra "Obrigado" de tamanho singelo, contudo de nobre significado para expor toda minha gratidão:

À Deus, pelo dom da vida, bençãos concedidas, conhecimentos e ser meu refúgio espiritual em todos os momentos.

Aos meus pais Rosária e Adhemar, pelo exemplo de caráter, honestidade, perseverança e amor incondicional. Por serem meu porto seguro e sempre me incentivar a novos desafios, ir além, desbravar o desconhecido e ter coragem para seguir com humildade e bondade nos caminhos da vida. A vocês todo meu amor e gratidão!

Aos meus irmãos Eduardo e Elys, pelo amor e incentivo! Pela torcida e admiração recíproca, mesmo que as vezes distante. E a toda minha família que sempre ficou na torcida.

Aos meus "pequenos" José Eduardo, Felipe e André, meu afilhado e sobrinhos queridos, que tornaram essa trajetória mais leve, através de um simples sorriso, uma palavra de carinho ou um abraço apertado. A vocês meu orgulho de tê-los como sobrinhos e todo meu amor.

À Cássia por entender minhas ausências neste período, pelo carinho, atenção, amor e parceria. Agradeço a você por me ensinar o verdadeiro sentido do amor e do respeito, por estar ao meu lado em decisões importantes da minha vida, sempre me apoiando com muita delicadeza e acolhimento junto a sua família, ao qual estendo todo meu carinho, respeito e gratidão.

Aos meus amigos de outrora, Adimitri, Fernando, Leticia Nascimbem, Paula Amed, Nilton Pimenta, Rosemeire, Fatinha, Renata Nassar pela torcida e por estarem ao meu lado para o der e vier.

Aos "amigos irmãos" que a pesquisa me presenteou Ana Paula, Elaine, Danilo, Fabricio, Kely, Renan, Uilian, Vanessa Solfa, muito obrigado pelos "cafés com ciência" regados à sorrisos e lágrimas, pela convivência diária, ensinamentos sobre a vida e ciência, e por permitir sonhar, compartilhar e viver tudo isso junto com vocês. Muito obrigado!

Aos alunos de iniciação científica Sabrina, Vitor, Murillo, Giovanna e Lais pela amizade e contribuições. Enfim, ao nosso "nanogrupo" de pesquisa, obrigado.

Ao Prof. Dr. Fauze Ahmad Aouada, por toda orientação, confiança e parceria estabelecida durante esses anos. Obrigado por todas as orientações nos caminhos da Química, vida acadêmica e científica. Agradeço por contribuir na minha formação sem hesitar em compartilhar conhecimento. Ao professor externo toda minha admiração e profunda gratidão!

A todos integrantes do grupo de pesquisa Grupo de Compósitos e Nanocompósitos Híbridos (GCNH) pelo apoio e companheirismo. E a Prof.ª Dr.ª Marcia Regina de Moura Aouada pelo apoio e parceria.

Aos professores Prof. Dr. Mauro Mitsuuchi Tashima e Prof. Dr. Jorge Luís Akasaki por todo apoio dado durante a realização desta pesquisa. Por disponibilizar, laboratórios, equipamentos e acima de tudo tempo, para que esta pesquisa se concretizasse. Aos professores muito obrigado.

Ao Grupo de Polímeros (GPol) pela utilização do laboratório para as análises de difração de raios-X (DRX), em especial ao professor Dr. José A. Malmonge.

A Universidade Estadual Paulista "Júlio de Mesquita Filho" (UNESP), Faculdade de Engenharia de Ilha Solteira (FEIS), Programa de Pós-Graduação em Ciência dos Materiais (PPGCM), pela oportunidade.

Aos professores e funcionários do Departamento de Física e Química (DFQ) da Faculdade de Engenharia de Ilha Solteira (FEIS).

Aos professores e funcionários do Departamento de Engenharia Civil da Faculdade de Engenharia de Ilha Solteira (FEIS), por disponibilizar acesso a toda infraestrutura de laboratórios do departamento. Em especial, aos técnicos de laboratório Gilson, Flávio e Natália por todo apoio na execução de alguns ensaios.

Aos professores e funcionários do Departamento de Engenharia Elétrica da Faculdade de Engenharia de Ilha Solteira (FEIS), em especial ao Prof. Dr. Ricardo Tokio pelo apoio nas medidas e análises de ultrassom.

Ao Instituto Federal de Educação, Ciência e Tecnologia de São Paulo (IFSP) pelo apoio concedido durante todo o período de afastamento. E ao programa de formação doutoral docente (PRODOUTORAL) pelo incentivo. Aproveito ainda para agradecer ao Prof. Dr. João Fazzan (campus Ilha Solteira) pelo apoio e atenção de sempre!

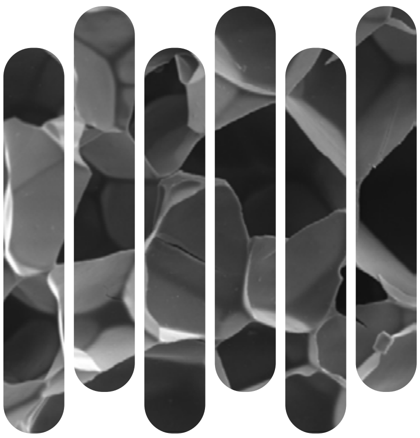
A Embrapa Instrumentação, São Carlos, pela ajuda e apoio científico prestado ao GCNH.

À Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) pelo incentivo para realização desta pesquisa.

O presente trabalho foi realizado com apoio da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - ***Código de Financiamento 001***.

"Descobri como é bom chegar quando se tem paciência.
E para se chegar, onde quer que seja, aprendi que não é preciso dominar a força, mas a razão. É preciso, antes de mais nada, querer" [Amyr Klink].

"Existe um limite na mente das pessoas sobre quão longe é seguro ir. Após cruzar essa linha é impossível voltar atrás" [Fiódor Dostoiévski].



SCIENTIFIC

PRODUCTION

BOOK CHAPTER

FERNANDES, R. S.; TANAKA, F. N.; ANGELOTTI, A. M.; F JUNIOR, C. R.; YONEZAWA, U. G.; **WATANUKI FILHO, A.**; MOURA, M. R. de ; AOUADA, F. A. Properties, synthesis, characterization, and application of hydrogel and magnetic hydrogels: A concise review. Advances in Nano-Fertilizers and Nano-Pesticides in Agriculture, 1 (2021), 437-457, https://doi.org/10.1016/B978-0-12-820092-6.00017-3 (**Published)**

PAPERS

CILLI, S. L., SILVA, H. C., **WATANUKI FILHO, A.**, AOUADA, M. R. D. M., AOUADA, F. A., Otimização de metodologia de obtenção de pastas cimentícias contendo hidrogéis. J. Exp. Tech. Instrum. 2, 1 (2019), 1-9, DOI: 10.30609/jeti.2019-7474. **(Published).**

SIQUERI, V. A., **WATANUKI FILHO A.,** MOURA, M. R. de, AOUADA F. A., Effect of hydrogel nanocomposites on the fresh and hardened properties of cementitious pastes, Macromol. Symp., 394, 1 (2020), 2000047, doi.org/10.1002/masy.202000047 **(Published).**

CALESCO, M. A. F., **WATANUKI FILHO A.,** MOURA, M. R. de, AOUADA F. A., Melhoria das propriedades dos estados frescos e endurecido de argamassas cimentícias ocasionada pela presença de nanocompósito híbridos baseados em hidrogéis de polissacarídeos e nanoargila, Cerâmica (2021) **(Under review/ Accepted)**

PUBLICATIONS IN EVENTS

WATANUKI FILHO, A., CILLI, S. L., AKASAKI, J. L., TASHIMA, M. M., DE MOURA, M. R., AOUADA, F. A., Obtenção de argamassas cimentícias com a inserção de hidrogéis de poliacrilamida (PAAm), carboximetilcelulose (CMC) e nanoargila do tipo Cloisita Na^{+}. In: IV Encontro de Pesquisadores em Ciência e Engenharia de Materiais – EPCEM, Ilha Solteira: UNESP, 2018.

CILLI, S. L., COLLETI SILVA, H., **WATANUKI FILHO, A.,** DE MOURA, M. R., AOUADA, F. A., Otimização de compósitos obtidos a partir de hidrogéis e cimento Portland: investigação mecânica e morfológica. In: IV Encontro de Pesquisadores em Ciência e Engenharia de Materiais – EPCEM, Ilha Solteira: UNESP, 2018.

WATANUKI FILHO, A., DE MOURA, MARCIA R; AOUADA, F. A. Propriedades mecânicas de argamassas produzidas com nanocompósitos híbridos baseados em hidrogéis e cimento Portland. In: 23º CBECIMAT – Congresso Brasileiro de Engenharia e Ciência dos Materiais, Foz do Iguaçu, 2018.

CILLI, S. L., **WATANUKI FILHO, A.,** DE MOURA, M. R., AOUADA, F. A., Analysis of the physical properties of cement pastes containing hydrogels. In: 1º SPIMF – Simpósio de Pesquisa e Inovação em Materiais Funcionais - SPIMF, São Carlos, 2019.

SIQUERI, V. A., **WATANUKI FILHO A.,** MOURA, M.R. de, AOUADA F. A., Effect of the application of nancomposites on the bulk density and slump test of cement pastes. In: 1º SPIMF – Simpósio de Pesquisa e Inovação em Materiais Funcionais - SPIMF, São Carlos, 2019.

WATANUKI FILHO, A., DE MOURA, MARCIA R; AOUADA, F. A. Water absorption, kinetic and structural characterizations of polymeric hydrogels containing Cloisite Na^+ using cement Portland and water as swelling medium. In: V Reunião Anual sobre Argilas Aplicadas, Franca: UNIFRAN, 2019.

CALESCO, M. A. F., **WATANUKI FILHO, A.**, MOURA, M. R.; AOUADA, F. A. Efeito da relação água/cimento sobre as propriedades mecânicas de nanocompósitos baseados em hidrogel polimérico e argamassas cimentícias. In: 61. Congresso Brasileiro do Concreto - IBRACON, Fortaleza, 2019.

WATANUKI FILHO, A., MOURA, M. R., AOUADA, FAUZE A. Efeito da aplicação de nanocompósitos híbridos baseados em hidrogéis e nanoargila nas propriedades mecânicas de argamassas. In: 15º Congresso Brasileiro de Polímeros - CBPOL, Bento Gonçalves, 2019.

CILLI, SABRINA L., **WATANUKI FILHO, A.**, MOURA, M. R.; AOUADA, F. A., Efeito de hidrogel polimérico sobre as propriedades mecânicas e índice de consistência de pastas cimentícias. In: 15º Congresso Brasileiro de Polímeros - CBPOL, Bento Gonçalves, 2019.

SIQUERI, V. A., **WATANUKI FILHO, A.**, DE MOURA, MARCIA R.; AOUADA, F. A., Efeito de nanocompósito sobre as propriedades no estado fresco e endurecido de pastas cimentícias. In: 15º Congresso Brasileiro de Polímeros - CBPOL, Bento Gonçalves, 2019.

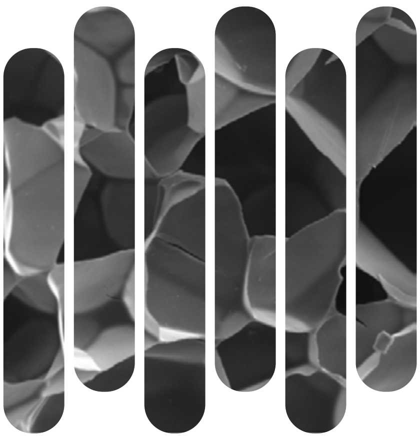
WATANUKI FILHO, A., MOURA, M. R., AOUADA, FAUZE A. Application of hybrid biodegradable nanocomposites based on hydrogel and nanoclay in cement mortars. In: II Encontro de Polímeros Naturais, Ilha Solteira (on line), 2020.

OLIVEIRA, A. P. S., **WATANUKI FILHO, A.,** MOURA, M. R., AOUADA, F. A., Translucent cementitious composites based on mortars and polymeric optical fiber as sustainable alternatives for energy saving. In: II Encontro de Polímeros Naturais, Ilha Solteira (on line), 2020.

BONFIM, K. S., **WATANUKI FILHO, A.,** AOUADA, F. A, MOURA, M. R. Effect of oxidation reaction time on water retention properties (WRV) of bacterial cellulose nanofibers. In: II Encontro de Polímeros Naturais, Ilha Solteira (on line), 2020.

CILLI, SABRINA L., **WATANUKI FILHO, A.,** MOURA, M. R.; AOUADA, F. A. Technological potential of hydrogels in cementitious pastes: a possible application as an internal curing agent. In: II Encontro de Polímeros Naturais, Ilha Solteira (on line), 2020.

TANAKA, F. C., **WATANUKI FILHO, A.,** MOURA, M. R.; AOUADA, F. A. Influence of morphology and Ph on the swelling degree and diquat released properties from methylcellulose-based nanocomposite hydrogels. In: II Encontro de Polímeros Naturais, Ilha Solteira (on line),2020.



ABSTRACT

Cement-based materials are the most produced in civil construction due to their versatility and durability. However, new admixtures have been widely studied and applied for better performance, especially when it comes to curing processes. The hybrid nanocomposite hydrogels, characterized by their hydrophilic characteristics of water absorption and release, stand out as promising agents for internal curing in cementitious matrices. This study proposed to analyze the physical, chemical, and morphological properties of hydrogels based on polyacrylamide, carboxymethylcellulose, and three different concentrations of Cloisite Na^+ in two different swelling media (distilled water and filtered solution of water+Portland cement) and to evaluate the effect of applying 0.5% (wt/wt_{cement}) of these presoaked hydrogels on the fresh and hardened state properties of cementitious mortars (1:2.16 and 0.40 w/c ratio). The results showed that the hydrogels provided reductions in slump flow of up to 4.8% for AHN20 mortars and exudation rate for the fresh state. These observations allowed us to evaluate that the increased concentration of nanoclay in the polymer interferes directly in the kinetic parameters of hydrogels and contributes to greater water retention, which may reflect better hydration and reduction of pathologies. As for the results in the hardened state, it was possible to evaluate that the type of curing of the samples was an important factor since there were no variations in densities (2.18 ± 0.02 g/cm^3) of all samples, indicating that the hydrogels were partially or fully swollen during the tests. Loss of mechanical strength was observed, but at 28 days for AHN20 mortars, the results were similar to the control, which corroborates the percentage of voids found. In this case, both mortars had a lower rate of voids when compared to AHN0 and AHN10 mortars and consequently better performances in their mechanical properties. The concentration of nanoclay in the hydrogel controls water release, as observed from the results of mass loss and plastic shrinkage that reduced as this concentration increased. The SEM images allowed us to evaluate that the more uniform matrices with higher mechanical properties, with few pores or micro-cracks. It is concluded that hybrid hydrogel nanocomposites can be applied as internal curing agents, especially those produced with 20% (wt/wt of CMC+AAm) nanoclay. Because its more controlled release allowed reducing porosity, water absorption, shrinkage, and significantly acting on the mechanical properties thus, this type of polymeric additive can be an innovative material for water control improvements in cementitious materials technology.

Keywords: Absorbent polymer, hybrid nanocomposite, civil construction, Cloisite Na^+, internal curing.

RESUMO

Os materiais de base cimentícia são os mais produzidos na construção civil devido a sua versatilidade e durabilidade. Contudo, para melhores desempenhos, novos aditivos vêm sendo amplamente estudados e aplicado, principalmente ao que se refere aos processos de cura. Destacam-se então os hidrogéis nanocompósitos híbridos caracterizados por suas características hidrofílicas de absorção e liberação de água, como promissores agentes de cura interna em matrizes cimentícias. Este estudo se propôs analisar as propriedades físicas, químicas e morfológicas de hidrogéis baseados em poliacrilamida, carboximetilcelulose e três concentrações diferentes de Cloisita-Na^+ em dois meios diferentes de intumescimento (água destilada e solução filtrada da mistura de água+cimento Portland), e avaliar o efeito da aplicação de 0,5% (m/$m_{cimento}$) destes hidrogéis pré-intumescido nas propriedades do estado fresco e endurecido de argamassas cimentícias (1:2,16 e relação a/c=0,40). Os resultados demonstraram que para estado fresco os hidrogéis proporcionaram reduções no *slump flow* de até 4,8% para argamassas AHN20, além de menor taxa de exsudação. Estas observações permitiram avaliar que o aumento da concentração de nanoargila no polímero interfere diretamente nos parâmetros cinéticos dos hidrogéis e contribui para maior retenção de água, o que pode refletir em melhor hidratação e redução de patologias. Quanto aos resultados no estado endurecido, foi possível avaliar que o tipo de cura das amostras interferiu nos resultados, já que não ocorreram variações nas densidades (2,18 $\pm$ 0,02 g/cm³) de todas as amostras, indicando que os hidrogéis encontravam-se parcialmente ou totalmente intumescidos durante a realização dos ensaios. A perda de resistência mecânica foi observada, contudo aos 28 dias para as argamassas AHN20 os resultados foram similares ao controle, o que corrobora com a porcentagem de vazios encontrada. Neste caso, ambas argamassas tiveram menor porcentagem de vazios, em relação as argamasssa AHN0 e AHN10, e consequentemente melhores desempenhos em suas propriedades mecânicas. Destaca-se também, que a concentração de nanoargila no hidrogel controla a liberação de água, sendo observado a partir dos resultados de perda de massa e retração plástica que reduziam à medida que esta concentração aumentava. As imagens de SEM permitiram avaliar que as matrizes com maiores propriedades mecânicas são mais uniformes, com poucos poros ou microfissuras. Conclui-se que os hidrogéis híbridos nanocompósitos podem ser potencialmente aplicados como agentes de cura interna, em destaque para os produzidos com 20% (massa/ massa de CMC+AAm) de nanoargila, uma vez que sua liberação mais controlada permitiu reduzir aspectos como porosidade, absorção de água, retração e atuar significativamente nas propriedades mecânicas. Assim, este tipo de aditivo polimérico pode ser um material inovador no para melhorias no controle de água na área da tecnologia de materiais cimentícios.

Palavras-chaves: Polímero absorvente, nanocompósito híbrido, construção civil, Cloisita Na^+, cura interna.

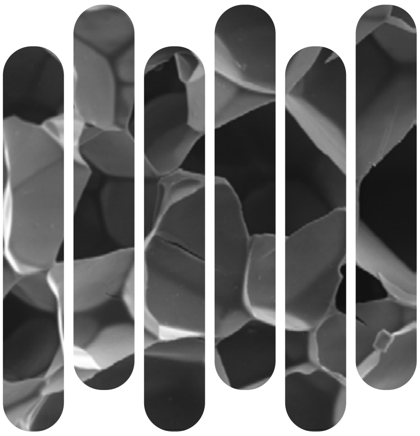
List of figures

List of tables

List of abbreviations and symbols

AAm	Acylamide
C_2S	Calcium disilicate or belite
C_3A	Tricalcium aluminate or aluminate
C_3S	Calcium trisilicate or alite
C_4AF	Tetracyclic iron or ferrite
$Ca(OH)_2$	Calcium hydroxide
CMC	Carboxymethylcellulose
C-S-H	Hydrated calcium silicate
EDX	Energy Dispersive X-Ray Analysis
FTIR	Fourier-transform infrared spectroscopy
k	Diffusion coefficient
KBr	Potassium bromide
MBAAm	N'-N-Methylenebisacrylamide
MMT	Montmorillonite
MW	Molecular Weight
n	Diffusion exponent
N_2	Elemental nitrogen gas
$Na_2S_2O_8$	Sodium Persulfate
PAAm	Polyacrilamide
RH	Relative Humidity
SAP	Superabsorbent Polymer
SD	Sweeling degree
SEM	Scanning Electron Microscopy
TEMED	N,N,N',N'-tetramethyl-ethylenediamine
w/c	water/cement ratio
wt	weight
XDR	X-Ray Diffraction
XRF	X-Ray fluorescence
θ	Incidence angle between the incident beam and sample plane
λ	Wavelength of the beam incident on the sample
Ø	Diameter

Contents



CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Cement-based materials are defined as some products obtained from the use of a cementitious medium [1]. These are generally characterized by the basic mixture of a hydraulic binder with the presence or not of aggregates [2], whose chemical reactions of setting and hardening occur in water presence [3-5].

Portland cement is widely used as a binder [6], confirmed by the high global production of approximately 4100 Mt in 2019 [7]. Recent data showed that cement production in Brazil was about 4.7 Mt in February 2021, representing an increase of around 14% compared to the same period in 2020 [8]. Thus, it is important to know that cement production is complex. It involves four main stages, such as crushing and grinding of raw materials, homogenization of the materials (limestone, clay, iron oxides, etc.) [9] in the correct proportions, burning the prepared mix in a rotary kiln at 1450 °C [9], and grinding clinker together with gypsum.

Calcium sulfate or gypsum is added to the clinker in small concentrations (~5%) to control the setting time due to the high clinker reactivity with water [8]. Elemental clinker chemistry composition presents around 67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3, and 3% other compounds. Four phases are denominated calcium trisilicate or alite (C_3S), calcium disilicate or belite (C_2S), tricalcium aluminate or aluminate (C_3A), and tetracyclic iron or ferrite (C_4AF) are formed. They are responsible for the hardening and strength increase because of the reaction these with water [10].

Thus, C_3S and C_2S silicates are important compounds for cement materials because their contact with water is responsible for forming hydration products, such as hydrated calcium silicate ($C_3S_2H_3$) or C-S-H gel. In addition, some amounts of crystalline calcium hydroxide $Ca(OH)_2$ or portlandite [1], whose chemical reactions are expressed by Equations 1.1 and 1.2 [6, 10]:

$$2(3CaO.SiO_2) + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2 \quad \text{Equation 1.1}$$

$$2(2CaO.SiO_2) + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 \quad \text{Equation 1.2}$$

C_3A presence in Portland cement contributes poorly to strength development, but it can be beneficial in manufactured types of cement where they facilitate silica and limestone combinations [11]. It should be noted that C_3A reactions with water (Equation 1.3) are fast and could cause a quick hardening that can be prevented with the gypsum addition to the clinker [6].

$$3CaO.Al_2O_3 + 12H_2O + 3Ca(OH)_2 \rightarrow 3CaO.Al_2O_3.Ca(OH)_2.12H_2O \quad \text{Equation 1.3}$$

Its reaction with the gypsum results in ettringite crystals, as presented by Equation 1.4 [10].

$$3CaO.Al_2O_3 + 10H_2O + CaSO_4.12H_2O \rightarrow 3CaO.Al_2O_3.SO_4.12H_2O \quad \text{Equation 1.4}$$

C_4AF is also present in cement in small quantities compared to the other three compounds, and it does not significantly affect the cement-paste behavior. However, C_4AF reacts with the gypsum resulting in calcium sulfoferrite that can accelerate the hydration of silicates [1, 11]. C_4AF reactions with water (Equation 1.5) are slower concerning C_3A, and these can result in a final compound based on iron (III) oxide or hydroxide.

$$4CaO.Al_2O_3.Fe_2O_3 + 10H_2O + 2Ca(OH)_2 \rightarrow 6CaO.Al_2O_3.Fe_2O_3.12H_2O \quad \text{Equation 1.5}$$

Although the chemical reactions involved in the hardening and strength gain are complex, aspects such as easier handling, good mechanical properties, and durability, performance satisfactory [12] of pastes, mortars, or concretes, depending on their combination or not with aggregates [13], make Portland cement the second material most used in the civil construction world rank [14].

Pastes, mortars, and concretes as main cement products are widely researched to obtain materials with satisfactory properties in their fresh and hardened states [15]. The main purpose is to develop cementitious composites to reduce pathological manifestations such as plastic shrinkage, cracking, increased permeability and porosity, and improve their durability and performance [16] over time. In this way, the development of new admixtures contributes to the insertion of chemical concepts in the construction industry to produce special cementitious materials [17] with better physical properties, such as increased setting time, reduced water/binder ratio, porosity, and shrinkage reduction [18].

Several mitigations strategies to avoid pathologies are based on the use of admixtures. Thus, these are most frequently applied to aid in controlling the dosage of water, once it is one of the elements that can change the properties of cementitious materials in their fresh and hardened states. Water control in cementitious materials is important because the hydration degree changes the mechanical behavior since effective cement particles' hydration results in a homogeneous microstructure [19, 20] and, consequently, a denser matrix.

In this way, hydrogels acting as a polymeric additive can contribute to the internal hydration of cement-matrix and act as small reservoirs of slow-release water.

1.2 HYDROGELS

Hydrogels are also known as hydrophilic absorbent polymers. They are three-dimensional (3D) cross-linked chain materials [21, 22] synthesized from synthetic, semi-synthetic, or natural raw materials whose main function is to absorb large amounts of water or other fluid [23] and release it later. Some authors define hydrogel as polymeric systems capable of swelling in water and retaining a significant fraction (>20%) of water inside their 3D structure without dissolving in this medium [21, 24]. The water storage of the hydrogels occurs from polymeric chain expansion due to the repulsion from the hydrophilic groups present on polymeric chains such as -OH-, $-NH_2-$, -COOH-, $-CONH_2-$, $-SO_3H-$ [25, 26].

The interaction between chain networks and water is through capillary, osmotic, and hydration forces causing expansion of these chains [21, 27]. Thus, when the osmotic and hydration forces are counter-balanced with the elastic forces, the hydrogel no absorbs more water, reaching its swelling equilibrium [28, 21]. Such equilibrium state of these absorbent polymers determines some properties, such as internal transport, diffusion characteristic, and mechanical strength [29].

Hydrogels can be classified from the chemical nature of their side groups, the type of the chemical crosslinking, the type of raw material, etc. According to the side groups, hydrogels can be neutral when the side groups have no electrical charge or ionic, when side groups dissociate and they interact with other elements, i.e., they have positive (anion) or positive (cation) charges [30-33]. Classification from the crosslinking process is based on the type of three-dimensional networks established by polymer synthesis, which allows these to be denominated chemical, physical [34], or biochemical hydrogels [35]. Chemical-type hydrogels are characterized by chemical cross-links (covalent bonds). They can no longer be undone [36, 37] because the covalent bonding introduces mechanical integrity and degradation resistance to the hydrogel. While physical hydrogels are formed by physical interactions such as van der Waals forces and hydrogen bonds, their networks can be undone through a change in environmental conditions such as pH changes, temperature, or saline solution [38, 39]. In biochemical hydrogels, biological agents like enzymes or amino acids participate in the gelation process [35]. As mentioned, another important classification of hydrogels is about the constituent raw material of their matrices, which can be based on natural, semi-synthetic, or synthetic polymers. Natural hydrogels are synthesized from biodegradable materials such as polysaccharides [40], alginate [41], cellulose and their derivatives, pectin, gelatin, chitosan [42], etc., and they are considered as ‘ecologically-friendly products due to their renewable and non-toxic sources [43]. All of these materials are naturally abundant. They present satisfactory characteristics to their synthesis, such as biocompatibility [41, 44], water-solubility, a high swelling degree that permits a wide range of chemical structures [45]. On the other hand, this hydrogel type presents a low mechanical resistance, but the association with synthetic raw materials during the synthesis process can improve it [45].

Remarkably, some natural hydrogel applications are in drug delivery systems, tissue engineering [46], and agricultural field due to their unique characteristics such as satisfactory hydrophilic network and adsorption capacity [47], low-cost and straightforward synthesis, non-toxicity of the final material, and easy application [48].

Synthetic hydrogels are materials commonly applied in numerous fields due to their interesting properties, such as large water absorption capacity and reasonable strength and cost [21]. Typically, synthetic hydrogels are obtained from raw materials like poly(hydroxyalkyl methacrylates), polyacrylates, poly(acrylic acid), polyacrylamide, and polymethacrylamide and its derivatives as poly(N-vinyl-2-pyrrolidone) and poly(vinyl alcohol), among others [21]. In addition, these polymers are applied in effluents treatment [42], as drug release systems, and medical field [49].

Sometimes, it is necessary to develop blends using natural and synthetic materials to obtain polymeric matrices that include the properties of natural and synthetic polymers simultaneously. First, however, it is important to understand the interaction between the two components so that the semi-synthetic hydrogel obtained can satisfy the application needs [50].

1.3 HYBRID HYDROGELS

Hybrid hydrogels are polymers composed of chemically, functionally, and morphologically distinct blocks, including natural, synthetic raw materials or nano/microstructures interconnected via physical or chemical means. In this way, the type-hydrogel has been developed to improve existing formulations and to expand the range of applications [51]. Thus, this research is based on applying nanocomposite hybrid hydrogel based on polyacrylamide (PAAm), carboxymethylcellulose polysaccharide (CMC) Cloisite Na^+ nanoclay in cementitious matrices. The choice for this hybrid hydrogel was based on the properties of each component to obtain a hybrid nanocomposite with appropriate characteristics to be applied as an internal curing agent for cementitious materials.

Firstly, it is important to understand the contribution of each raw material used in hydrogel formulations and its impact on the final behavior of the polymer obtained. Hydrogels based on polyacrylamide (PAAm) have been applied frequently in several areas (agricultural, biomedical, pharmaceutical area) [52] due to their properties, such as high hydrophilicity and good mechanical behavior. They are synthetized from synthetic acrylamide (AAm) monomer (Figure 1.1).

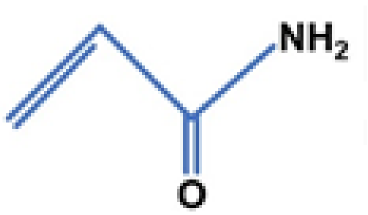


Figure 1.1 – Representative chemical structure of acrylamide (AAm) monomer.

Polyacrylamide hydrogels consist of a covalent polymer network and water; under ordinary conditions, the polyacrylamide network is stable, and water is mobile into the polymer network [53]. Because of their mechanical properties and hydrophilicity, this type-hydrogel has been widely used as the main base in developing new types of absorbent polymers [54].

Another interesting type of absorbent polymer widely researched is the polysaccharide-based hydrogel due to its biocompatibility, biodegradability, high water absorption capacity, and production from renewable raw materials [55,56]. Carboxymethylcellulose (CMC) (Figure 1.2) is a cellulose derivative [57], and its main properties are water-soluble anionic polysaccharide, non-toxicity, biodegradability [58], and owning its features, CMC is used in various areas such as food packaging [59], drug delivery [60] and tissue engineering.

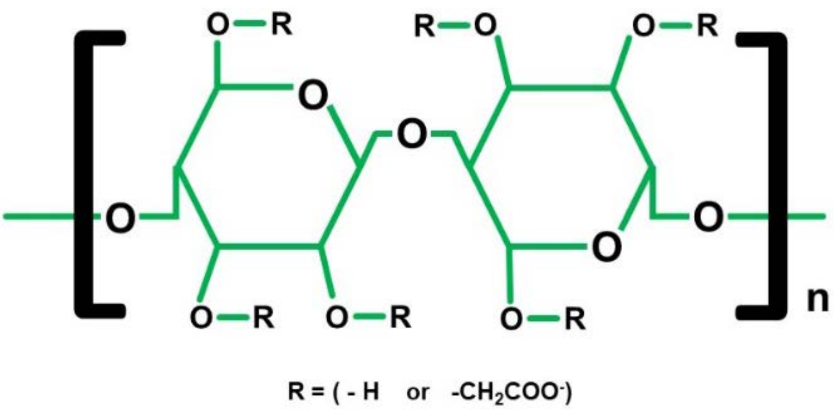


Figure 1.2 – Representative chemical structure of carboxymethylcellulose.

Moreover, CMC can be obtained by reacting cellulose with sodium hydroxide [61] and monochloroacetic acid. This procedure is necessary because cellulose is hydrophilic but insoluble in water due to the polymeric chain more crystalline. Their derivatives such as methylcellulose (MC), carboxymethylcellulose (CMC), hydroxypropylcellulose (HPC) acquire high water solubility because there is a partial substitution of the hydroxyl groups present in the cellulose chains by methyl, carboxyl, and hydroxypropyl groups, respectively, reducing the dense packing and causing physicochemical changes compared to cellulose [62].

CMC-based hydrogels have a high degree of swelling in water due to the repulsion of the functional carboxylate groups (COO^-). However, to improve the mechanical stability of these hydrogels, it is common to synthesize them with synthetic raw materials [63] and to add reinforcing agents such as clay minerals.

Combining these natural and synthetic materials with mineral clay allows the development of hybrid nanocomposites, as reported in the literature [64]. A mineral clay-type often used in nanocomposite hydrogels synthesis is the Cloisite Na^+ [65-67], a type of montmorillonite (MMT) sodium nanoclay.

Cloisite Na^+ nanoclay has a chemical structure compound by an octahedral alumina sheet between two tetrahedral silica sheets [68], as shown in Figure 1.3, and it can be used due to their excellent cation-exchange capacity, high specific surface area, functional swelling capacity, high platelet aspect ratio, and easy surface modification [69].

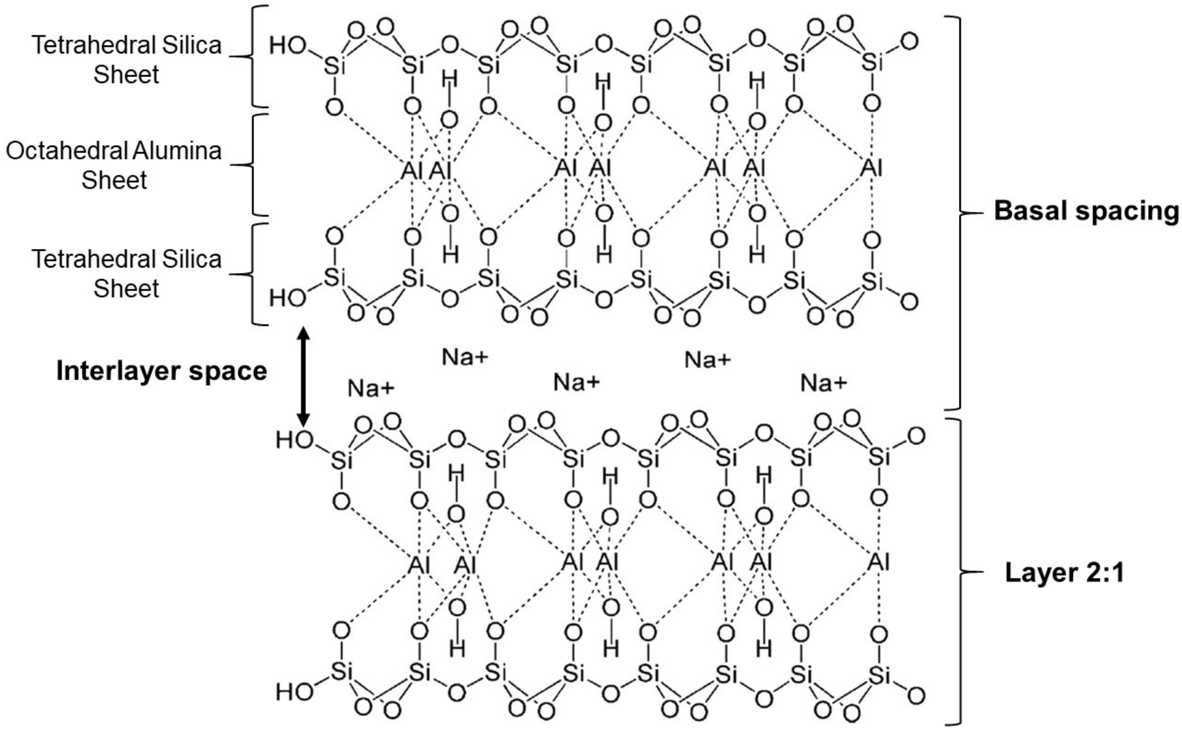


Figure 1.3 – Structure of MMT Cloisite-Na^+ nanoclay, adapted from Bao et.al, 2015. [70]

During the nanocomposite synthesis, three different configurations can be obtained concerning the dispersion of clay nanostructures into hydrogel (Figure 1.4): (i) Intercalated, in which the hydrogel chains are penetrated among the clay platelets, without affecting its structure [69, 71]; (ii) Exfoliated, when the clay platelets are completely dispersed in the polymeric matrix [72, 73]; (iii) Intercalated-exfoliated: junction of both [74, 75]. The most interesting dispersion to nanocomposites is the exfoliated configuration because its increases the polymer-clay interactions.

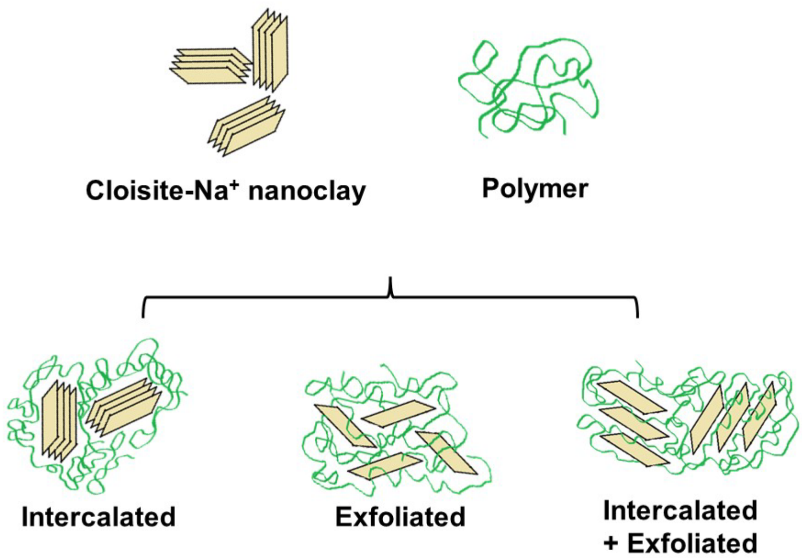


Figure 1.4 – Type of mineral clay dispersion in the hydrogel, adapted from Bensadoun et al. [76]

Notably, the manner as the clay is dispersed in the hydrogel matrix can modify the behavior of these nanocomposites. For instance, Cloisite Na^{+} nanoclay in the polymer demonstrated that it releases kinetics slower while its concentration increases in the polymer matrix [77]. Thus, the nanoclay presence on the polymeric matrix provides an increase in physical crosslinks, reducing both the amount of water released over time and the release time of the hydrogels [78]. In addition, mineral clay, when is associated with a polysaccharide, as carboxymethylcellulose (CMC) or others [79], can also improve the hydrophilic properties of these systems [80].

In this way, semi-synthetic hydrogel modified with nanoclays is a technological and innovative material for future application in construction civil, whereas their good properties of water retention and release are very interesting to the internal curing process in cement materials.

1.4 MOTIVATIONS AND JUSTIFICATIONS

The construction industry is an essential economic field that continues to grow worldwide due to housing shortages and population growth [81]. This expansion allows new materials to be developed to improve aspects such as durability and building performance.

Noteworthy is the high consumption of cement in pastes, mortars, and concretes since these are materials present good mechanical properties and easy handling and application. In this aspect, mortars as heterogeneous composite materials [82] can have multiple applications, either as a binding material for sealing elements (blocks, bricks, and stones) or as surface coatings and ceramic tile bases [83].

However, this cementitious composite has some characteristics that compromise its mechanical performance, such as low resistance to cracking, small deformation, and low flexural strength compared to compressive strength [84]. Some mortars can present porous microstructure, facilitating the transport of water inside and thus cause chemical damage to the structure due to the transport of some ions [82]. Thus, new materials have been developed and applied to improve the physical and mechanical properties and therefore ensure the reduction of pathologies of these cementitious materials [16].

One of the strategies to overcome these disadvantages is applying chemical additives as an integral part of the dosages of these materials [12]. Because one of its advantages lies in the fact that its use can alter the water/binder ratio without modifying the dosage of the other constituent materials to improve the mechanical properties and maintain its workability [18, 85].

The purpose of developing and applying an auxiliary alternative to the traditional curing procedures of cementitious materials, commonly performed externally, through the application of coatings or wet curing by immersion [20] is one of the justifications for applying this type of hydrogel in cementitious matrices. Furthermore, the application of hydrogels as a component of cementitious materials is a way to ensure that part of the dosage water is stored in its polymeric matrix to be later released, besides increasing the internal moisture and assisting in the hydration of cement particles.

Several studies [25, 85, 86] in the literature indicate the application of commercial superabsorbent polymers (SAP) in cementitious matrices. The innovation of this thesis is in developing a semi-synthetic hybrid nanocomposite based on a polysaccharide and a mineral clay with hydrophilic, biodegradable, and mechanical characteristics suitable for more controlled release kinetics [86].

The application of polysaccharides like carboxymethylcellulose (CMC) is a good option for the preparation of hydrogels because it has ionizable carboxylic groups in its chemical structure, increasing the hydrophilicity [47] of the polyacrylamide (PAAm)-based nanocomposite.

Clay minerals in nano and micro scale are commonly present in the constitution of nanocomposites because they provide high thermal stability, good gas barrier properties [87], good mechanical resistance, high degree of swelling, and adsorption capacity [47]. Thus, these nanoclays can improve the water release process [87] inside the cement matrix due to its improvements in the hydrogel's hydrophilic properties [88].

The motivation for this study is because the semi-synthetic hydrogels based on PAAm, CMC, and Cloisite Na^+ nanoclay may present similar or better behaviors to commercial synthetics when applied in cementitious matrices, which make these polymers technology attractive to the construction industry, as smarties internal curing agents. For this, the analysis of the behavior in the fresh and hardened states of mortars produced with these hybrid nanocomposite hydrogels was performed and discussed in detail in this thesis.

As hydrogels can absorb and release water as an internal curing agent, this can lead to the swelling of the polymer particles, which causes changes in the porous structure of the cementitious materials, affecting their properties in the hardened state. In this sense, the synthesis of the hybrid nanocomposite hydrogel took into account three different concentrations of Cloisite Na^+ nanoclay to verify the influence of this component in the process of water release by the polymer in aspects such as hydration of the cement and the changes of the mechanical properties of the mortar.

Thus, the guarantee that cementitious composites can have good physical and mechanical properties throughout their useful life, such as improvements in water retention [89], modifications in workability [16], reduction of shrinkage and cracking by water evaporation [90] from adequate hydration of the cement particles, assumes that it is necessary to establish greater control over the availability of water in the cement matrix [91], and this condition can be remedied with the application of a controlled release absorbent polymer.

1.5 OBJECTIVES

The general objective of this study was to evaluate the effect of the application of hybrid nanocomposites based on hydrogel and Cloisite Na^+ nanoclay on the properties of cementitious mortars in fresh and hardened states. For this, the following specific objectives were proposed:

- ✓ To analyze the physical, chemical, and morphological properties of hybrid hydrogels containing different concentrations of Cloisite Na^+ nanoclay, having two different swelling media, i.e., distilled water or in solution from the filtrate of the water+cement mixture.
- ✓ To develop cement mortars (dosage 1:2.16 and w/c ratio = 0.40) based on cement, sand, water, and 0.50% (wt/wt concerning cement) of the pre-soaked hydrogels their hybrid nanocomposites. Remarkably, 4 different systems have been used: - reference system or only cement mortar; - mortars containing different concentrations of Cloisite Na^+ nanoclay (0, 10 and 20% wt/wt acrylamide + CMC) in their polymeric matrices;
- ✓ To determine the effect of the different types of hydrogels, in the proposed systems, on the physical, mechanical and structural properties of the mortars, in their fresh (workability, density, incorporated air, water retention, exudation index) and hardened state (strength compressive, tensile and flexural, bulk density, dynamic and estatic elastic moduli, voids, capillarity index, water absorption, loss, and mass variation);
- ✓ To verify the effect of hydrogels, as potential agents of internal cure, in the control of plastic shrinkage and morphology (SEM) of the microstructure of the cement matrix.

1.6 THESIS STRUCTURE

For a better presentation and discussion of the results, this thesis was structured into 7 chapters:

CHAPTER 1: Overview of the main concepts of the thesis, besides the presentation of justifications and proposed objectives.

CHAPTER 2: Material and methodology for hydrogel synthesis and mortar productions.

CHAPTER 3: Main definitions and analyses about water absorption behavior, kinetic properties, and structural characterizations of polymer hydrogels containing Cloisite Na^+ nanoclay, using distilled water and solution filtered of Portland cement + water as swelling media, will be presented.

CHAPTER 4: At this moment, the properties in the fresh state of cement mortars produced with the addition of hybrid nanocomposites based on hydrogel and nanoclay will be analyzed. The results obtained for the physical properties of workability, the density of the mortar in the fresh state, incorporated air, water retention, and exudation index will also be discussed.

CHAPTER 5: This chapter will present the mechanical properties of cementitious mortars cured internally with hybrid nanocomposites based on hydrogel and nanoclay. The approach is based on discussing the results obtained for the properties of compressive strength, tensile and flexural, density in the hardened state, dynamic and elastic moduli.

CHAPTER 6: The effect of applying hybrid nanocomposites based on hydrogel and nanoclay will be presented as a potential application for shrinkage reduction, water absorption in cementitious materials, and its effect on capillarity properties, water absorption by immersion, mass loss and variation, and scanning electron microscopy (SEM);

CHAPTER 7: Finally, the most relevant final considerations on the application of these hydrogels as internal curing agents of cementitious mortars and their effect on the properties of the fresh and hardened states will be exposed in this chapter.

1.7 REFERENCES

[1] F. A. Neville, J. J. Brooks, Tecnologia do concreto. Bookman, Porto Alegre, RS, Brazil, 2013.

[2] S. Tang, J. Huang, L. Duan, L., P. Yu, E. Chen, A review on fractal footprint of cement-based materials. Powder Technol., 230 (2020), 237-250.

[3] American Society for Testing and Materials (ASTM), Standard Terminology Relating to Hydraulic and Other Inorganic Cements, ASTM C219-20a, ASTM International, West Conshohocken, PA, 2020.

[4] H. Zhang, Y. Xu, Y. Gan, Z. Chang, E. Schlangen, B. Šavija, Microstructure informed micromechanical modelling of hydrated cement paste: Techniques and challenges, Constr. Build. Mater., 251 (2020), 1-20.

[5] H. Cheng-Yong, L. Yun-Ming, M. M. A. B. Abdullah, K. Hussin, Thermal Resistance Variations of Fly Ash Geopolymers: Foaming Responses. Sci. Repor., 7 (2017), 1-11.

[6] M. S. Mamlouk, J. P. Zaniewski, Materials for civil and construction engineers. Upper Saddle River, NJ: Pearson Prentice Hall, 2006.

[7] International Energy Agency, Global cement production, 2010-2019, IEA, Paris, France, 2020. https://www.iea.org/data-and-statistics/charts/global-cement-production-2010-2019. (accessed 15 August 2020).

[8] Associação Brasileiro de Cimento Portland, Indústria do cimento mantém vendas em alta, ABCP, São Paulo, Brazil, 2021. https://abcp.org.br/imprensa/industria-do-cimento-mantem-vendas-em-alta/ (acessed 4th April 2021).

[9] W. Kurdowski, Cement and concrete chemistry. Springer Science & Business, Kraków, Poland, 2014.

[10] H. F. Taylor, Cement Chemistry, Thomas Telford, London, UK, 1997.

[11] G. C. Bye, Portland cement – Third Edition, ICE Publishing: Thomas Telford Limited, London, UK, 2011.

[12] P. K. Mehta, P. J. Monteiro, Concrete microstructure, properties and materials, McGraw Hill, USA, 2017.

[13] A. Mignon, D. Snoeck, P. Dubruel, S. Van Vlierberghe, N. De Belie, Crack mitigation in concrete: superabsorbent polymers as key to success? Mater. 10, 3 (2017), 237-262.

[14] Á. Salesa, J. A. Pérez-Benedicto, D. Colorado-Aranguren, P. L. López-Julián, L.M. Esteban, L. J. Sanz-Baldúz, D. Olivares, Physico–mechanical properties of multi–recycled concrete from precast concrete industry. J. Clean. Prod., 141 (2017), 248-255.

[15] J. J. Biernacki, J. W. Bullard, G. Sant, K. Brown, F. P. Glasser, S. Jones, T. Prater, Cements in the 21st century: Challenges, perspectives, and opportunities. J. Am. Ceram. Soc., 100 (2017), 2746–2773.

[16] V. Mechtcherine, E. Secrieru, C. Schröfl, Effect of superabsorbent polymers (SAPs) on rheological properties of fresh cement-based mortars—Development of yield stress and plastic viscosity over time. Cem. Concr. Res. 67, 1 (2015), 52-65.

[17] SAP, RILEM TC. Application of Superabsorbent Polymers (SAP) in Concrete Construction. RILEM State-of-the-Art Report Prepared by Technical Committee, 1 (2012), 165.

[18] L. G. Li, A. K. Kwan, A. K. Effects of superplasticizer type on packing density, water film thickness and flowability of cementitious paste. Constr. Build. Mater., 86 (2015), 113-119.

[19] M. Valcuende, C. Parra, E. Marco, A. Garrido, E. Martínez, J. Cánoves, J. Influence of limestone filler and viscosity-modifying admixture on the porous structure of self-compacting concrete. Constr. Build. Mater., 28 (2012), 122-128.

[20] X. Y. Liu, C. H. Huang, C. H. Zhuang, K. C. Hsu, C. H. Huang, An amphoteric hydrogel: Synthesis and application as an internal curing agent of concrete, J. Appl. Polym. Sci.,132 (2015), 1-9.

[21] K. Varaprasad, G. M. Raghavendra, T. Jayaramudu, M. M. Yallapu, R. Sadiku, A mini-review on hydrogels classification and recent developments in miscellaneous applications. Mater. Sci. Eng. C. 79, 11 (2017), 958-971.

[22] F. Wahid, X. J. Zhao, S. R. Jia, H. Bai, C. Zhong, Nanocomposite hydrogels as multifunctional systems for biomedical applications: Current state and perspectives. Compos. B. Eng., 1 (2020), 108208.

[23] F. Ullah, M. B. H. Othman, F. Javed, Z. Ahmad, A. M. Akil, Classification, processing, and application of hydrogels: A review. Mater. Sci. Eng. C, 57 (2015), 414–433.

[24] M.J. Zohuriaan-Mehr, K. Kabiri, Superabsorbent polymer materials: a review, Iran. Polym. J. 17 (2008), 451.

[25] M. T. Hasholt, O. M. Jensen, K. Kovler, S. Zhutovsky, Can superabsorbent polymers mitigate autogenous shrinkage of internally cured concrete without compromising the strength? Constr. Build. Mater., 31 (2012), 226-230.

[26] C. R. F. Junior, M. R. de Moura, F. A. Aouada, Synthesis and characterization of intercalated nanocomposites based on poly(methacrylic acid) hydrogel and nanoclay Cloisite-Na^+ for possible application in agriculture. J. Nanosci. Nanotechnol. 17 (2017), 5878-5883.

[27] S. Sharma, S. Tiwari, Shachi. A review on biomacromolecular hydrogel classification and its applications. Int. J. Biol. Macromol., 162 (2020), 737-747.

[28] W. E. Roorda, H. E. Bodde, A. G. De Boer, H. E. Junginger, Synthetic hydrogels as drug delivery systems. Pharm. Weekbl., 8 (1986), 165-189.

[29] U. G. Yonezawa, M.R. de Moura, F.A. Aouada, Hybrid bionanocomposites formed from polysaccharide hydrogels and nanoclay II: incorporation in substrate to seedling improving. Cult. Agron. 26 (2017), 82-94.

[30] S.J. Buwalda, K.W.M. Boere, P.J. Dijkstra, J. Feijen, T. Vermonden, W.E. Hennink, Hydrogels in a historical perspective: from simple networks to smart materials, J. Control. Release, 190 (2014), 254.

[31] N. A. Peppas, P. Bures, W. Leobandung, H. Ichikawa, Hydrogels in pharmaceutical formulations. Eur. J. Pharm. Biopharm., 50 (2000), 27-46.

[32] G. R. Bardajee, Z. Hooshyar. One-pot synthesis of biocompatible superparamagnetic iron oxide nanoparticles/hydrogel based on salep: Characterization and drug delivery. Carbohydr. Polym., 101 (2014), 741–751.

[33] F. N. Tanaka, C. R. F. Junior, M. R. de Moura, F. A. Aouada, F.A. Water absorption and physicochemical characterization of novel zeolite-PMAA-co-PAAm nanocomposites. J. Nanosci. Nanotechnol. 18 (2018), 7286-7295.

[34] P. Liu, et al. Synthesis of covalently crosslinked attapulgite/poly (acrylic acid-co-acrylamide) nanocomposite hydrogels and their evaluation as adsorbent for heavy metal ions. J. Ind. Eng. Chem., 23 (2015), 188-193.

[35] S. B. Majee, Emerging concepts in analysis and applications of hydrogels. BoD–Books on Demand. 1 (2016).

[36] F. A. Aouada, L. H. C. Mattoso, Hidrogéis biodegradáveis: uma opção na aplicação como veículos carreadores de sistemas de liberação controlada de pesticidas. Embrapa Instrumentação-Boletim de Pesquisa e Desenvolvimento (Infoteca-E), 2009.

[37] C. Ghobril, M. W. Grinstaff, M. W. The chemistry and engineering of polymeric hydrogel adhesives for wound closure: a tutorial. Chem. Soc. Rev., 44 (2015), 1820–1835.

[38] R. S. Fernandes, R. S., F. N. Tanaka, M. R. de Moura, F. A. Aouada, Development of alginate/starch-based hydrogels crosslinked with different ions: Hydrophilic, kinetic and spectroscopic properties. Mater. Today Commun., 21 (2019), 100636.

[39] J. A. F. Garcia, M. R. de Moura, F. A. Aouada. Efeito do pH, espécie e concentração iônica na absorção de água de hidrogéis bionanocompósitos constituídos de CMC/PAAM/LAPONITA RDS. Quim. Nova, 42 (2019), p. 831-837.

[40] D. Pasqui, M. de Cagna, R. Barbucci. Polysaccharide-based hydrogels: the key role of water in affecting mechanical properties. Polymers, 4 (2012), 1517-1534.

[41] R. da Silva Fernandes, M. R. de Moura, G. M. Glenn, F. A. Aouada, F. A. Thermal, microstructural, and spectroscopic analysis of Ca^{2+} alginate/clay nanocomposite hydrogel beads. J. Mol. Liq., 265 (2018), 327-336.

[42] Y. Zhou, S. Fu, L. Zhang, H. Zhan, M. V. Levit. Use of carboxylated cellulose nanofibrils-filled magnetic chitosan hydrogel beads as adsorbents for Pb (II). Carbohydr. Polym., 101 (2014), 75-82.

[43] W. Xu, X. He, M. Zhong, X. Hu, Y. Xiao. A novel pH-responsive hydrogel based on natural polysaccharides for controlled release of protein drugs. RSC Adv., 5 (2015), 3157-3167.

[44] S. S. Stalling, S. O. Akintoye, S. B. Nicoll. Development of photocrosslinked methylcellulose hydrogels for soft tissue reconstruction. Acta Biomater., 5 (2009), 1911-1918.

[45] P. Mohammadzadeh Pakdel, S. J. Peighambardoust, A review on acrylic-based hydrogels and their applications in wastewater treatment. J. Environ. Manage., 217 (2018), 123–143.

[46] M. R. Singh, S. Patel, D. Singh. Natural polymer-based hydrogels as scaffolds for tissue engineering. In Nanobiomaterials in soft tissue engineering, William Andrew Publishing, (2016), 231-260.

[47] A. T. Paulino, L. A. Belfiore, L. T. Kubota, E. C. Muniz, E. B. Tambourgi, Efficiency of hydrogels based on natural polysaccharides in the removal of Cd^{2+} ions from aqueous solutions. Chem. Eng. Technol., 168 (2011), 68-76.

[48] A. T. Paulino, M. R. Guilherme, E. A. de Almeida, A. G. Pereira, E. C. Muniz, E. B. Tambourgi, One-pot synthesis of a chitosan-based hydrogel as a potential device for magnetic biomaterial. J. Magn. Magn. Mater., 321 (2009), 2636-2642.

[49] R. Cruz-Acuna, A. J. García. Synthetic hydrogels mimicking basement membrane matrices to promote cell-matrix interactions. Matrix Biol., 57 (2017), 324-333.

[50] Y. Berkovitch, D. Seliktar, Semi-synthetic hydrogel composition and stiffness regulate neuronal morphogenesis. Int. J. Pharm. 523 (2017), 545-555.

[51] R. da Silva Fernandes, F. N. Tanaka, A. M. Angelotti, C. R. F. Júnior, U. G. Yonezawa, A. Watanuki Filho, M. R. de Moura, F. A. Aouada, Properties, synthesis, characterization and application of hydrogel and magnetic hydrogels: A concise review. Advances in Nano-Fertilizers and Nano-Pesticides in Agriculture, Elsevier, 1 (2021), 437-457.

[52] L. L. Palmese, R. K. Thapa, M. O. Sullivan, K. L. Kiick, Hybrid hydrogels for biomedical applications. Curr. Opin. Chem. Eng., 24 (2019), 143-157.

[53] M. J. Caulfield, G. G. Qiao, D. H. Solomon, D. H. Some aspects of the properties and degradation of polyacrylamides. Chem. Rev., 102 (2002), 3067-3084.

[54] C. Yang, T. Yin, Z. Suo, Polyacrylamide hydrogels. I. Network imperfection. J. Mech. Phys. Solids, 131 (2019), 43-55.

[55] C. E. Kandow, P. C. Georges, P. A. Janmey, K. A. Beningo, K. A. Polyacrylamide hydrogels for cell mechanics: steps toward optimization and alternative uses. Methods Cell Biol., 83 (2007), 29-46.

[56] I. Cicha, R. Detsch, R. Singh, S. Reakasame, C. Alexiou, A. R. Boccaccini, Biofabrication of vessel grafts based on natural hydrogels. Curr. Opin. Biomed. Eng. 2 (2017), 83-89.

[57] R. Jin, L. M. Teixeira, A. Krouwels, P. J. Dijkstra, C. A. Van Blitterswijk, M. Karperien, J. Feijen, Synthesis and characterization of hyaluronic acid–poly (ethylene glycol) hydrogels via Michael addition: An injectable biomaterial for cartilage repair. Acta Biomater., 6 (2010), 1968-1977.

[58] B. K. Bozoğlan, O. Duman, S. Tunç, Preparation and characterization of thermosensitive chitosan/carboxymethylcellulose/scleroglucan nanocomposite hydrogels. Int. J. Biol. Macromol., 162 (2020), 781-797.

[59] A. M. Youssef, S. El-Sayed, M. Samah. Bionanocomposites materials for food packaging applications: Concepts and future outlook. Carboh. Polym., 193 (2018), 19-27.

[60] S. Abdurrahmanoglu, V. Can, O. Okay, Design of high-toughness polyacrylamide hydrogels by hydrophobic modification. Polym. Oxford, 50 (2009), 5449-5455.

[61] S. Javanbakht, A. Shaabani, Carboxymethyl cellulose-based oral delivery systems. Int. J. Biol. Macromol, 133 (2019), 21-29.

[62] F. A. Aouada, Síntese e caracterização de hidrogéis de poliacrilamida e metilcelulose para liberação controlada de pesticidas. Doctoral thesis. Federal University of São Carlos (UFSCar), São Carlos, 2009.

[63] B. Mandal, S. K. Ray, Removal of safranine T and brilliant cresyl blue dyes from water by carboxy methyl cellulose incorporated acrylic hydrogels: Isotherms, kinetics and thermodynamic study. J. Taiwan Inst. Chem. Eng., 60 (2016), 313–327.

[64] M. Irani, H. Ismail, Z. Ahmad, Preparation and properties of linear low-density polyethylene-g-poly (acrylic acid)/organo-montmorillonite superabsorbent hydrogel composites. Polym. Test. 32 (2013), 502-512.

[65] S. Tunç, O. Duman, Preparation and characterization of biodegradable methyl cellulose/montmorillonite nanocomposite films. Appl. Clay Sci., 48 (2010), 414–424.

[66] P. H. Camani, J. P. M. Toguchi, A. P. S. Fiori, D. dos Santos Rosa, Impact of unmodified (PGV) and modified (Cloisite20A) nanoclays into biodegradability and other properties of (bio) nanocomposites. Appl. Clay Sci., 186 (2020), 105453.

[67] A. Cojocariu, L. Profire, M. Aflori, C. Vasile, In vitro drug release from chitosan/Cloisite 15A hydrogels. Appl. Clay Sci., 57 (2012), 1–9.

[68] S. Mallakpour, M. Dinari, Preparation and characterization of new organoclays using natural amino acids and Cloisite Na^+. Appl. Clay Sci., 51 (2011), 353-359.

[69] I. Hackman, L. Hollaway, Epoxy-layered silicate nanocomposites in civil engineering. Compos. A., 37 (2016), 1161–1170.

[70] X. Bao, F. Zhang, Q. Liu, Q. Sulfonated poly (2, 5-benzimidazole) (ABPBI)/MMT/ionic liquids composite membranes for high temperature PEM applications. Int. J. Hydrog. Energy, 40 (2015), 16767-16774.

[71] D. S. Dlamini, J. Li, B. B. Mamba, Critical review of montmorillonite/polymer mixed-matrix filtration membranes: Possibilities and challenges. Appl. Clay Sci., 168 (2019), 21-30.

[72] C. Wolf, H. Angellier-Coussy, N. Gontard, F. Doghieri, V. Guillard, How the shape of fillers affects the barrier properties of polymer/non-porous particles nanocomposites: A review. J. Membr. Sci., 556 (2018), 393-418.

[73] T. B. Sharmila, E. P. Ayswarya, B. T. Abraham, P. S. Begum, E. T. Thachil, Fabrication of partially exfoliated and disordered intercalated cloisite epoxy nanocomposites via in situ polymerization: Mechanical, dynamic mechanical, thermal and barrier properties. Appl. Clay Sci., 102 (2014), 220-230.

[74] A. R. Ramadan, A. M. Esawi, A. A. Gawad, Effect of ball milling on the structure of Na+-montmorillonite and organo-montmorillonite (Cloisite 30B). Appl. Clay Sci., 47 (2010), 196-202.

[75] C. K. Hong, M. J. Kim, S. H. Oh, Y. S. Lee, C. Nah, C., Effects of polypropylene-g-(maleic anhydride/styrene) compatibilizer on mechanical and rheological properties of polypropylene/clay nanocomposites. J. Ind. Eng. Chem., 14 (2008), 236-242.

[76] F. Bensadoun, F., N. Kchit, C. Billotte, F. Trochu, E. Ruiz, A comparative study of dispersion techniques for nanocomposite made with nanoclays and an unsaturated polyester resin. J. Nanomater., 2011 (2011), 1-13.

[77] D. W. S. Nascimento, M. R. de Moura, L. H. C. Mattoso, F. A. Aouada, Hybrid Biodegradable Hydrogels Obtained from Nanoclay and Carboxymethylcellulose Polysaccharide: Hydrophilic, Kinetic, Spectroscopic and Morphological Properties. J. Nanosci. Nanotechnol., 17 (2017), 821–827.

[78] M. G. Hernández, J. J. Anaya, M. A. G. Izquierdo, L. G. Ullate, Application of micromechanics to the characterization of mortar by ultrasound. Ultrasonics, 40 (2012), 217-221.

[79] Q. Chen, W. Y. Wen, F. X. Qiu, J. C. Xu, H. Q. Yu, M. L. Chen, D. Y. Yang, Preparation and application of modified carboxymethyl cellulose Si/polyacrylate protective coating material for paper relics. Chem. Pap., 70 (2016), 946-959.

[80] M. I. Syakir, N. A. Nurin, N. Zafirah, M.A. Kassim, H. A. Khalil, Nanoclay reinforced on biodegradable polymer composites: Potential as a soil stabilizer. In Nanoclay Reinforced Polymer Composites Springer, Singapore, 1 (2016), 329-356.

[81] P. S. Oliveira, M. L. P. Antunes, N. C. da Cruz, E. C. Rangel, A. R. G. de Azevedo, S. F. Durrant, Use of waste collected from wind turbine blade production as an eco-friendly ingredient in mortars for civil construction. J. Clean. Prod., 274 (2020).

[82] ([1] M. Liu, Y. Hu, Z. Lai, T. Yan, X. He, J. Wu, Z. Lu, S. Lv, Influence of various bentonites on the mechanical properties and impermeability of cement mortars. Constr. Build. Mater. 241, 12 (2020), 118015

[83] H. A. Jaber, R. S. Mahdi, A. K. Hassan, Influence of eggshell powder on the Portland cement mortar properties. Mater. Today: Proceedings 20, 4 (2020), 391.

[84] R. Bagherzadeh, H. R. Pakravan, A. H. Sadeghi, M. Latifi, A. A. Merati, An investigation on adding polypropylene fibers to reinforce lightweight cement composites (LWC). J. Eng. Fibers Fabr. 7, 4 (2012), 1.

[85] V. A. S. Siqueri, A. Watanuki Filho, M. R. de Moura, F.A. Aouada, Effect of Hydrogel Nanocomposites on the Fresh and Hardened Properties of Cementitious Pastes Macromol. Symp. 394 (2020), 2000047.

[86] A. Bortolin, F. A. Aouada, L. H. Mattoso, C. Ribeiro, Nanocomposite PAAm/methyl cellulose/montmorillonite hydrogel: evidence of synergistic effects for the slow release of fertilizers, J. Agric. Food Chem., 61, 31 (2013), 7431-7439.

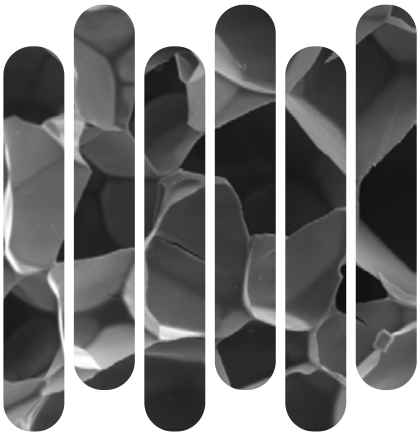
[87] Q. Zhao, J. Sun, Y. Lin, Q. Zhou, Study of the properties of hydrolyzed polyacrylamide hydrogels with various pore structures and rapid pH-sensitivities. React. Funct. Polym., 70 (2010), 602-609.

[88] M. I. Syakir, N. A. Nurin, N. Zafirah, M. A. Kassim, H. A. Khalil, Nanoclay reinforced on biodegradable polymer composites: Potential as a soil stabilizer. In Nanoclay Reinforced Polymer Composites, 329-356, Springer, Singapore, 2016.

[89] J. R. Tenório Filho, E. Mannekens, K. Van Tittelboom, D. Snoeck, N. de Belie, Assessment of the potential of superabsorbent polymers as internal curing agents in concrete by means of optical fiber sensors. Constr. Build. Mater. 238, 9 (2020) 1-8.

[90] L. Dudziak, V. Mechtcherine, V. Enhancing early-age resistance to cracking in high-strength cement-based materials by means of internal curing using super absorbent polymers. In: RILEM Proc. PRO. 2010. p. 129-139.

[91] V. Mechtcherine, Use of superabsorbent polymers (SAP) as concrete additive, RILEM Technical Letters, 10 (2016), 81-87.



CHAPTER 7

FINAL CONSIDERATIONS

“Final considerations, future perspectives, impacts and economic, social relevance”

7.1 FINAL CONSIDERATIONS

Hybrid hydrogel nanocomposites based on polyacrylamide, carboxymethylcellulose, and different Cloisite Na^+ concentrations (0%, 10%, and 20% wt/ wt of acrylamide+CMC) were successfully reproduced in their synthesis.

From FTIR and SEM techniques, it was possible to observe that the nanoclay was incorporated into the polymeric matrix and to verify some modifications in the hydrogel microstructure when swollen solution from the filtrate of the water+cement mixture. Some hydration products resulting from cement hydration were found impregnated on the hydrogel surfaces. The presence of groups of CO_3^{2-} confirmed them and SO_4^{2-} related to carbonatation and ettringite formation. XRD patterns also indicated the presence of these products in hydrogels swollen in solution from the filtrate of the water+cement mixture

Notably, XRD patterns indicated that the amorphous character of the hydrogel in the nanocomposites was discrete. In addition, the basal spacing of the nanoclay peak in the polymeric matrices was not observed, indicating that its platelets are probably exfoliated in the hydrogel chains when these hydrogels are swelled in a filtrated solution of water+Portland mixture. That confirms a satisfactory interaction between organic and inorganic compounds during the synthesis process.

The results also showed that the presence of Cloisite Na^+ interferes directly with the absorption mechanism in both swelling media. Thus, comparing the hydrogels swollen in distilled water, the nanocomposites, when placed in water and cement solution, presented an increase of 22.02, 10.03, and 20.46% in the degree of swelling of the hydrogel with 0, 10, and 20% Cloisite Na^+ concentrations respectively. This improvement can be related to the solvation process where some cement solution ions can associate with water molecules provoking an expansion of the hydrogels chain.

The physicochemical characterization of the hydrogels contributed to the development of the dosages used in this study. From the understanding of the swelling degree, it was possible to optimize the amount of water to maintain the w/c ratio constant. Moreover, the release kinetics also contributed to understanding their effect on the physical and mechanical properties of the mortars studied. For instance, the increase in the concentration of nanoclay into hydrogel caused greater water retention by the polymer, reflecting significant reductions in exudation and slump flow, corroborating the results of increased water retention of mortars in the fresh state.

Although these changes directly affect the workability of mortars, which could be solved with plasticizer admixtures, the water retention and release of water somewhat controlled by the polymer is satisfactory for maintaining the internal humidity of the cement matrix. This is very interesting for plastic shrinkage reduction, reduction of voids, and improvements in mechanical properties at later ages. In this sense, it was observed that the mortar produced with the highest nanoclay content (AHN20) was the one that presented the best performance concerning the others tested. These same mortars also showed mechanical strengths statistically similar to the control (ACTR), even under wet curing conditions that possibly kept the hydrogels swollen until the test was performed. This is a positive indication that the concentration of nanoclay in the polymeric matrix acts as a reinforcing agent, minimizing the effects of strength loss since presoaked hydrogels are low-strength inclusions in the mortar mixture.

The amount and percentage of voids in the AHN20 mortar were also statistically similar to the control, reflecting improved or similar mechanical properties to the reference. It can also verify similar behavior in the mass loss and plastic shrinkage properties. The greater water retention by the hydrogel represents a lower shrinkage by the mortar, corroborating with water retention and exudation results. This is a good indication that the nanoclay concentration indeed contributes to a more controlled release of water by the hydrogel.

In summary, from the results, it was possible to conclude that hybrid nanocomposite hydrogels have great applicability in the civil industry, especially as internal curing agents. This may bring benefits related to more effective curing procedures, improvements in cement hydration processes, and consequently increasing the performance and durability of these materials.

7.2 FUTURE PERSPECTIVES

To further contribute to the understanding of the study, the following future perspectives are presented:

- ✓ To synthesize, characterization, and application of hybrid nanocomposite hydrogels with natural clays. In addition, to use other reinforcement elements (ashes, fibers) to synthesize hydrogels and evaluate their effects on their hydrophilic properties.

- ✓ To evaluate the absorption and release kinetics of the hydrogels when applied in dry and swollen states into cementitious materials. In addition to understanding the internal hydration mechanisms carried out.
- ✓ To analyze the microstructure of cementitious materials using other techniques such as microtomography, permeability, porosity, among others.
- ✓ To evaluate the contribution of these hydrogels in the freeze-thaw properties
- ✓ To verify aspects of degradation and cycles of absorption and release over time within cementitious matrices.

7.3 IMPACTS AND ECONOMIC, SOCIAL RELEVANCE

This study showed that the hybrid nanocomposite hydrogel in construction could contribute considerably to the economic aspects. This type-material can reduce water consumption during cementitious matrices because the traditional curing process requires a large amount of water during the hardening stage. Another factor is the characteristics of the materials produced with these nanocomposites. The constructions can have improved durability and performance, extending their useful life since pathologies related to shrinkage can be minimized with their application.

The environmental relevance is based on the use of more biodegradable raw materials in the production of hydrogels, such as polysaccharides in their matrix. In this sense, we also highlight reducing water waste during the curing process since a small amount of polymer applied can ensure the necessary moisture to cure the cementitious material internally. Another aspect is the durability that also reflects on the environmental aspect in better performance of buildings because by extending its life, there is a lower generation of construction waste.

The social relevance is in disseminating and popularizing scientific studies since the application of new materials such as hydrogels in the construction industry. Additionally, improving traditional procedures by facilitating their execution can lead to the dissemination of new concepts to society, highlighting the importance of research and science to improve existing procedures. Therefore, the material developed and applied in this work has notable environmental, social, and economic relevance as a consequence.

ACKNOWLEDGMENTS

"This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001".