UNIVERSIDADE FEDERAL DE LAVRAS

**DANILLO WISKY SILVA**

# INFLUENCE OF DIFFERENT ADDITIVES ON PROPERTIES OF CEMENT BASED COMPOSITES REINFORCED WITH EUCALYPTUS KRAFT PULP

**LAVRAS - MG**
**2018**

**DANILLO WISKY SILVA**

# INFLUENCE OF DIFFERENT ADDITIVES ON PROPERTIES OF CEMENT BASED COMPOSITES REINFORCED WITH EUCALYPTUS KRAFT PULP

Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Engenharia de Biomateriais, área de concentração em Compósitos e Nanocompósitos Lignocelulósicos para a obtenção do título de Doutor.

Prof. Dr. Lourival Marin Mendes (UFLA) – Brasil
Orientador
Prof$^{a}$. Dra. Camila Soares Fonseca (UFLA) – Brasil
Coorientadora
Prof. Dr. Gustavo Henrique Denzin Tonoli (UFLA) – Brasil
Coorientador

**LAVRAS - MG**
**2018**

**Ficha catalográfica elaborada pelo Sistema de Geração de Ficha Catalográfica da Biblioteca Universitária da UFLA, com dados informados pelo(a) próprio(a) autor(a).**

Silva, Danillo Wisky.
Influence of different additives on properties of cement based composites reinforced with eucalyptus Kraft pulp / Danillo Wisky Silva. - 2018.
76 p. : il.

Orientador(a): Lourival Marin Mendes.
Coorientador(a): Camila Soares Fonseca, Gustavo Henrique Denzin Tonoli.
Tese (doutorado) - Universidade Federal de Lavras, 2018.
Bibliografia.

1. Fibrocimento. 2. Incorporadores de ar. 3. Processo de extrusão. I. Mendes, Lourival Marin. II. Fonseca, Camila Soares. III. Tonoli, Gustavo Henrique Denzin. IV. Título.

**DANILLO WISKY SILVA**

# INFLUENCE OF DIFFERENT ADDITIVES ON PROPERTIES OF CEMENT BASED COMPOSITES REINFORCED WITH EUCALYPTUS KRAFT PULP

# INFLUÊNCIA DE DIFERENTES ADITIVOS NAS PROPRIEDADES DE COMPÓSITOS A BASE DE CIMENTO REFORÇADOS COM POLPA KRAFT DE EUCALIPTO

Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Engenharia de Biomateriais, área de concentração em Compósitos e Nanocompósitos Lignocelulósicos para a obtenção do título de Doutor.

APROVADA em 18 de junho de 2018.

Dr. Lourival Marin Mendes UFLA

Dr. David Cardoso Dourado UFSSP

Dr. Saulo Rocha Ferreira UFLA

Dr. Rafael Farinassi Mendes UFLA

Dr. Giovanni Francisco Rabelo UFLA

Prof.Dr. Lourival Marin Mendes
Orientador

**LAVRAS - MG**
**2018**

# AGRADECIMENTOS

A Deus que me presenteou com a dádiva da vida e nunca deixou de guiar meus passos.

Aos meus pais José Aparecido e Rosemeire Wisky, que sempre me apoiaram.

A minha esposa Marina Resende e o meu filho Tomás Resende Wisky, que me transmitem forças para continuar em frente.

Ao meu irmão Gabriel Wisky que sempre consegue me transmitir paz e alegria.

À Universidade Federal de Lavras, ao Departamento de Ciências Florestais e ao Programa de Pós-graduação em Engenharia de Biomateriais pelo apoio técnico.

Ao professor Lourival pelo acolhimento, conhecimento, orientação e amizade.

Aos professores Rafael e Gustavo, por todo o ensinamento, paciência, confiança, orientação e amizade.

À CAPES pela concessão da bolsa de doutorado. A FAPEMIG e ao CNPq.

Aos amigos da UEPAM por todo o aprendizado, parceria e pelos momentos de descontração. Em especial ao Alan, Tony e Adriele.

Aos eternos brejeiros, amigos para a vida toda, pelas histórias vivenciadas, pelos risos compartilhados e os apertos superados sempre como uma família. Em especial ao Douglas, Willian, Tales e Tadeu.

As inúmeras amizades, aos colegas de turma e aos professores.

A sociedade brasileira que financiou todo este trabalho.

# RESUMO

O processo de extrusão vem ganhando destaque na produção de fibrocimentos. Esse processo apresenta várias vantagens na linha de produção em comparação ao processo convencional, como: orientação das fibras, menor relação água/cimento, menor custo de implantação e bom desempenho mecânico dos compósitos. No entanto, devido à compactação que ocorre no decorrer do processo, os compósitos gerados são mais densos, quando comparados aos compósitos produzidos por outros processos. Os objetivos deste estudo foram produzir, caracterizar e avaliar o comportamento de compósitos cimentícios extrudados com diferentes concentrações de polímero superabsorvente hidratado (SAP) e incorporadores de ar comerciais. Os compósitos cimentícios foram produzidos com cimento Portland CPV-ARI, calcário, SAP, hidroxipropilmetilcelulose (HPMC) e poliéter carboxílico (ADVA 175). Foram produzidos compósitos cimentícios com diferentes concentrações de SAP (0,5; 1,0; 1,5; e 2,0%) e foram avaliados após 28 dias de cura e após 30 ciclos de envelhecimento acelerado. Para a produção dos fibrocimentos foram utilizados a mesma matriz cimentícia, SAP, incorporador de ar Darafill 300 EXP, incorporador de ar Drycast, polpa Kraft marrom de *Eucalyptus* spp., HPMC e ADVA 175. Os fibrocimentos com diferentes concentrações de SAP (0,3; 0,5 e 0,7%), de Darafill (0,6; 0,8 e 1,2%) e de Drycast (0,6 e 1,2%) foram avaliados após 28 dias de cura. O SAP foi eficiente quanto a incorporação de ar nos compósitos cimentícios sem reforço e nos fibrocimentos, no entanto, houve formação de vazios milimétricos, diminuindo substancialmente o desempenho mecânico dos materiais. Após o envelhecimento acelerado todos os compósitos sem reforço apresentaram redução equivalente no desempenho mecânico. Os fibrocimentos, apesar da degradação das fibras, apresentaram-se mais resistentes aos ciclos de envelhecimento. Os surfactantes não incorporaram ar nos fibrocimentos, como era esperado, no entanto, devido ao aumento da molhabilidade, houve uma hidratação efetiva dos grãos anidros de cimento, que acarretou em maior desempenho mecânico, maior densidade, menor porosidade e menor número de vazios no interior da matriz cimentícia. No geral, os fibrocimentos com SAP são menos densos e apresentaram menor desempenho mecânico em comparação com os fibrocimentos controle, o que restringe sua aplicação a materiais não estruturais. Já o uso de surfactantes, apesar de não incorporar ar nos fibrocimentos, pode ser interessante, devido ao acréscimo no desempenho mecânico em fibrocimentos extrudados.

**Palavras-chave:** Fibrocimento, processo de extrusão, polímero superabsorvente, surfactantes, envelhecimento acelerado.

# ABSTRACT

The extrusion process has been gaining prominence in the production of fiber cement. This process presents several advantages in the production line compared to the conventional process, such as: fiber orientation, lower water / cement ratio, lower implantation cost and good mechanical performance of the composites. However, due to the compaction that occurs during the process, the composites generated are denser when compared to the composites produced by other processes. The objectives of this study were to produce, characterize and evaluate the behavior of extruded cementitious composites with different concentrations of hydrated superabsorbent polymer (SAP) and commercial air-entraining. Cement composites were produced with Portland cement CPV-ARI, limestone, SAP, hydroxypropyl methylcellulose (HPMC) and polyether carboxylic acid (ADVA 175). Cement composites with different SAP concentrations (0.5, 1.0, 1.5, and 2.0%) were produced and evaluated after 28 days of curing and after 30 cycles of accelerated aging. The same cementitious matrix SAP, Darafill 300 EXP air incorporator, Drycast air incorporator, brown Kraft pulp of Eucalyptus spp., HPMC and ADVA 175 were used for the production of the fiber cement. The fiber cements with different concentrations of SAP (0.3, 0.5 and 0.7%), Darafill (0.6, 0.8 and 1.2%) and Drycast (0.6 and 1.2%) were evaluated after 28 days of cure. SAP was efficient in the incorporation of air in cementitious composites without reinforcement and in fiber cement, however, there was formation of millimetric voids, substantially reducing the mechanical performance of the materials. After accelerated aging, all non-reinforced composites showed equivalent reduction in mechanical performance. The fiber cement, despite the degradation of the fibers, were more resistant to the aging cycles. The surfactants did not incorporate air in the cements as expected, however, due to the increased wettability, there was an effective hydration of the dry cement grains, which resulted in higher mechanical performance, higher density, lower porosity and lower voids in the interior of the cementitious matrix. In general, fiber cements with SAP are less dense and presented lower mechanical performance in comparison with the control fiber cement, which restricts their application to non-structural materials. However, the use of surfactants, although it does not incorporate air in the cements, may be interesting, due to the increase in the mechanical performance in extruded fiber cement.

**Keywords:** Fiber cement, extrusion process, SAP, surfactants, accelerated aging.

# SUMÁRIO

# PRIMEIRA PARTE

## 1 INTRODUÇÃO

### 1.1 Introdução geral

Nos últimos 10 anos, inúmeras pesquisas têm avaliado o potencial uso das fibras vegetais como reforço em compósitos cimentícios, em substituição ao amianto e as fibras sintéticas, principalmente por serem: renováveis, atóxicas e de grande interesse econômico (TONOLI, 2010; TONOLI et al., 2010; TONOLI et al., 2009; BELAADI et al., 2013; SAWSEN et al., 2015; FONSECA et al., 2016; SILVA et al., 2016). Outras pesquisas buscam novos processos de produção que sejam alternativos ao Hatschek, como o de extrusão, que apresenta menor custo de implantação, menor relação água/cimento, propriedades físico-mecânicas semelhantes, produção de compósitos com reforço fibroso orientado, possibilidade de produtos nas mais variadas formas e tamanhos, e o potencial uso de resíduos lignocelulósicos regionais como reforço na matriz cimentícia (FONSECA et al., 2016; SILVA et al., 2016; SANTOS et al., 2015; TONOLI et al., 2013; TONOLI et al., 2012a; TONOLI et al., 2012b).

No entanto, também foi observado nesses estudos que devido à maior compactação desse processo de produção, o produto final fica com densidade superior aos produzidos por outros métodos utilizados para fibrocimentos (sucção, Hatschek, etc.), o que pode implicar em maiores gastos com estrutura, por exemplo, nos telhados. O uso de incorporadores de ar comerciais se apresenta como uma opção para diminuir a densidade destes compósitos, entretanto, os incorporadores de ar atuam formando espumas e bolhas de ar na pasta cimentícia, e estas bolhas de ar provavelmente não resistiriam à compactação exercida pela boquilha da extrusora.

Alguns estudos apontam que o uso de polímeros superabsorventes (SAP) em concreto auxilia na redução de fissuras causadas por retração na fase de cura e secagem, e são utilizados no processo de “cura interna” onde liberam gradativamente água no interior da matriz cimentícia (JUSTS et al., 2015). Estes SAPs também são capazes de promover a “auto-selagem” de fissuras no concreto, evitando a passagem de água através das fissuras (LEE; WONG; BUENFELD, 2016; LIU et al., 2016). No entanto, o uso dos SAPs na matriz cimentícia provoca aumento na porosidade, podendo diminuir a resistência mecânica e a densidade aparente do concreto (WANG et al., 2013).

Devido aos fibrocimentos extrudados serem destinados para fins de vedação e cobertura na construção civil, os SAPs podem ser uma alternativa na busca de incorporação de ar na matriz cimentícia e, por conseguinte, na diminuição da densidade dos compósitos. Nesse contexto, os objetivos deste estudo foram produzir, caracterizar e avaliar o comportamento de compósitos cimentícios extrudados com diferentes concentrações de SAP e incorporadores de ar comerciais.

### 1.2 Objetivo e estrutura da tese

Os objetivos deste estudo foram produzir, caracterizar e avaliar o comportamento de compósitos cimentícios extrudados com diferentes concentrações de SAP e incorporadores de ar comerciais.

No manuscrito 1, investigou-se a viabilidade da inclusão de diferentes concentrações de SAP na produção de compósitos cimentícios por extrusão. No manuscrito 2, primeiramente, investigou-se os efeitos da inclusão de SAP na matriz cimentícia. Posteriormente, foi realizado o envelhecimento acelerado desses compósitos, e finalmente investigou-se o comportamento dos compósitos com adição de SAP após os 30 ciclos de envelhecimento acelerado. Além disso, no manuscrito 3, investigou-se os efeitos do uso de surfactantes comerciais e de SAP, em diferentes concentrações, nas propriedades microestruturais e mecânicas de fibrocimentos extrudados reforçados com polpa Kraft marrom de eucalipto.

## 2 REFERENCIAL TEÓRICO

### 2.1 O processo de extrusão na produção de fibrocimentos

Industrialmente, a extrusão é largamente utilizada na conformação de materiais metálicos, poliméricos e argilas. Para esses tipos de materiais, o processo contínuo confere altas taxas de produtividade e ampla variedade geométrica nos produtos finais, porém na indústria cimentícia, o interesse e as pesquisas sobre o processo são recentes (ALFANI; GUERRINI, 2005).

A fabricação de produtos de fibrocimento em escala industrial tem sido realizada principalmente pelo processo Hatschek. Entretanto, diversos estudos têm apresentado o processo de extrusão como alternativa econômica para produção de elementos construtivos com características mecânicas e físicas semelhantes ou ainda melhores que os oriundos do processo Hatschek (SHAO et al., 1995; SHAO et al., 2000; SHAO; SHAH, 1997; SHRINIVASAN; DEFORD; SHAH, 1999; QIAN et al., 2003; LI et al., 2001; TAKASHIMA et al., 2003).

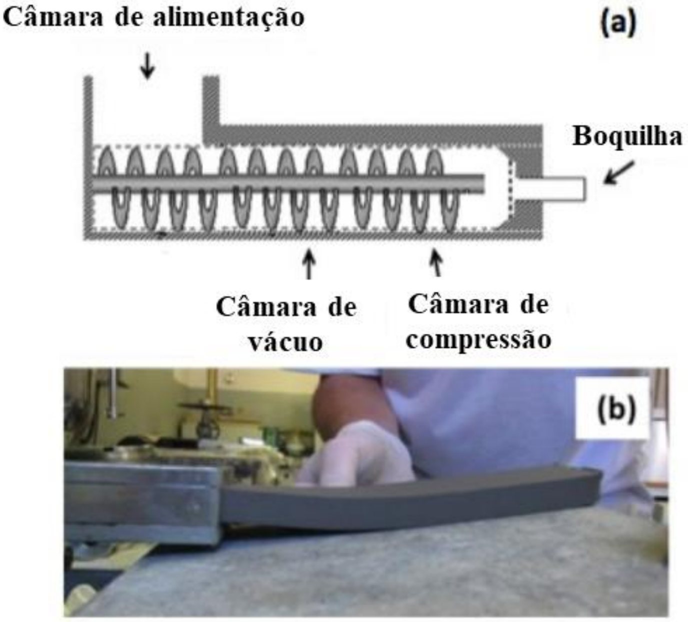
A patente de Shah, Shão e Marikunte (1999) demonstra o potencial do processo de extrusão para produção de compósitos de fibrocimento mais resistentes. Outra patente publicada descreve um novo método e equipamento para extrusão de fibrocimentos com polpas celulósicas (CHEN et al., 2009). Estas patentes apresentam algumas vantagens do processo de extrusão em relação aos processos convencionais de produção do fibrocimento. Entretanto, as principais informações sobre as variáveis do processo de extrusão e das matérias-primas empregadas encontram-se protegidas por estas patentes. Adicionalmente, o aprimoramento e a adequação destas tecnologias ainda requerem experimentações consistentes devido ao grande número de variáveis envolvidas e dos aspectos relacionados ao aumento da densidade do produto final quando comparados a outros processos de produção de fibrocimento.

De acordo com Horst (2002), as extrusoras utilizadas na indústria de cerâmica são adaptáveis para o processo de extrusão de materiais cimentícios, por conseguinte assume-se que os valores de investimento para a implementação de uma linha de produção de fibrocimento por extrusão sejam valores próximos ao de uma linha de materiais cerâmicos e com capacidade de produção instalada semelhante. Portanto, assume-se um menor custo de investimento inicial quando comparado ao processo Hatschek, possibilitando a produção descentralizada e longínqua dos grandes centros. Além disso, o processo de extrusão possibilita linhas de produção em fábricas de baixa capacidade instalada, com o objetivo de atender aos mercados regionais (TEIXEIRA, 2010).

Como resultado, a barreira de altos investimentos para a implementação de indústrias de fibrocimento é quebrada, o que permite a formação de novos fornecedores no mercado. Por conseguinte, tal panorama beneficia os consumidores devido a uma competição mais acirrada, com melhores e mais diversificados produtos. Adicionalmente, tem a possibilidade de se utilizar materiais de reforço alternativos, tais como, os resíduos lignocelulósicos locais. O que vêm incentivando o desenvolvimento de inúmeras pesquisas quanto à capacidade de reforço e a interação desses materiais lignocelulósicos residuais com a matriz de cimento (TONOLI et al., 2012a; TONOLI et al., 2012b; TONOLI et al., 2013; SANTOS et al., 2015; SAWSEN et al., 2015; FONSECA et al., 2016; SILVA et al., 2016).

Portanto, observa-se que a implantação do processo de extrusão de compósitos cimentícios em países em desenvolvimento, tal como o Brasil, pode gerar benefícios sociais, econômicos e ambientais. Entretanto, devido à compactação do material ao passar pela boquilha da extrusora (ver Figura 1) ocorre um ganho próximo de 40% na densidade aparente dos compósitos. A fim de comparação, fibrocimentos produzidos experimentalmente pelo processo Hatschek apresentaram densidade aparente de aproximadamente 1,30 $g.cm^{-3}$ (FARRAPO, 2015), enquanto que fibrocimentos produzidos por extrusão apresentaram densidade aparente de aproximadamente 1,80 $g.cm^{-3}$ (SILVA, 2015; SILVA et al., 2016).

Figura 1 - (a) Detalhes do mecanismo de operação do processo de extrusão; (b) produção do compósito extrudado em placa de metal.



Fonte: (a) Santos; Tonoli; Savastano Jr. (2011); (b) Soto et a. (2007).

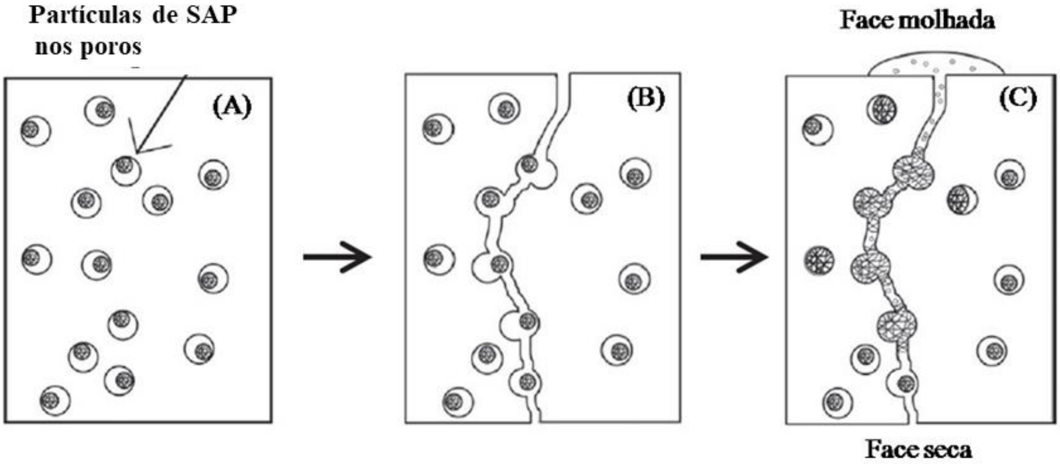
## 2.2 Incorporadores de ar na matriz cimentícia

No caso específico das matrizes cimentícias, a inclusão de incorporadores de ar tem sido estudada, para reduzir a densidade do produto final, sem prejudicar demasiadamente as propriedades mecânicas dos compósitos (WANG et al., 2013; LEE; WONG; BUENFELD, 2016; LIU et al., 2016). A descoberta da utilização dos incorporadores de ar, segundo Cunha e Neuman (1979, apud CALHAU, 2000) foi casualmente nos Estados Unidos quando, a partir de 1933, foram utilizados os primeiros aditivos incorporadores de ar que conferiam ao concreto e argamassa maior durabilidade à ação destrutiva do congelamento/degelo, devido à presença na massa de minúsculas bolhas de ar que serviam como ponto de descompressão para a água capilar do ciclo congelamento/degelo. Quando o ar é incorporado intencionalmente nessas composições, as bolhas são geradas na fase contínua (pasta), e seu volume e estabilidade dependem de diversos fatores, como teor de água, tipo e característica do ligante, temperatura, tipo e teor do aditivo, etc. (SALAGER, 2002; ROMANO et al., 2009; ROMANO; PILEGGI, 2012).

Existem basicamente três maneiras de se produzir matrizes de cimento leve, sendo estes: (1) o uso de agregados leves (os vazios de ar são principalmente nos agregados), (2) cimento celular e espuma de cimento (vazios de ar estão na pasta de cimento), e (3) sem o uso de agregados finos (os vazios de ar estão entre as partículas do agregado mais grosseiro) (WANG et al., 2013). O primeiro método de produção utiliza a exemplo: argila expandida, xisto expandido, agregados de cinzas volantes sinterizadas entre outros (KOCKAL; OZTURAN, 2011; HARUN, 2009), no segundo método são normalmente utilizados os plastificantes e superplastificantes, com intuito de gerar bolhas de ar (espuma) na pasta cimentícia, enquanto que no terceiro método trabalha-se com as granulometrias dos agregados.

Devido à extrusora compactar a pasta cimentícia durante o processo de produção, o método mais adequado seria o uso de agregados leves, que apesar de porosos resistiriam à pressão exercida na passagem da pasta pela boquilha da extrusora, diminuindo a densidade dos compósitos. No entanto, recentemente, inúmeros estudos vêm trabalhando com polímeros superabsorventes (SAPs) adicionados na matriz cimentícia, visando “auto-selar” as microfissuras (Figura 2) que podem ocorrer nos compósitos cimentícios (LEE; WONG; BUENFELD, 2016; LIU et al., 2016), pela aplicação de carga, gelo/degelo, expansão e contração das fibras de reforço entre outras causas.

Figura 2 – (a) O SAP é adicionado à matriz cimentícia durante a mistura. O inchaço inicial é confinado. À medida que o concreto endurece, o SAP encolhe e fica dormente na microestrutura; (b) as microfissuras se propagam através dos vazios, expondo o SAP; e (c) a entrada de água faz com que o SAP se hidrate, expandindo para dentro da fenda que por sua vez restringe o fluxo.



Fonte: LEE; WONG; BUENFELD (2010).

Normalmente, esses polímeros superabsorventes (poliacrilato, poliacrilamida, acrilato de potássio, entre outros) são de baixa densidade e quando hidratados assumem grande volume (até 3000 vezes maior), possibilitando o uso destes polímeros como incorporadores de ar, desde que sejam introduzidos na forma hidratada.

Outro aspecto bastante elucidado na literatura é com relação ao efeito da quantidade de ar, da distribuição de tamanho dos vazios, do espaçamento (dispersão) e da forma dos vazios de ar sobre as propriedades mecânicas, a estabilidade do volume e a durabilidade do compósito cimentício endurecido (VERBECK, 1966; HOVER, 1993). Estudos apontam que com acréscimo de 1% em espaços vazios se tem uma perda de 4% na resistência à compressão dos compósitos cimentícios (CHOI; YEON; YUM, 2016; MEHTA; MONTEIRO, 2006). Outros estudos mostraram que os tamanhos dos poros de materiais à base de cimento afetam as mudanças de volume induzidas pela umidade, como a retração e o inchaço de secagem, porque o líquido mantido em poros é submetido a uma forte pressão de fluido de poro (ou estresse capilar) aplicado no menisco da interface líquido-vapor, e essa pressão aumenta à medida que o raio do poro diminui (GRASLEY; LANGE, 2007; YEON; CHOI; WON, 2009).

Um ganho na durabilidade dos compósitos também pode estar relacionado ao número, espaçamento e distribuição de pequenos poros dentro da matriz, esses poros podem agir como válvula de escape aliviando a pressão hidrostática interna da matriz, evitando a formação de microfissuras (HOVER, 1993; KOSMATKA; PANARESE, 1994).

## 2.3 Adição de polímeros superabsorventes em matrizes cimentícias

Os SAPs surgiram no mercado em 1978, como componentes de absorventes higiênicos femininos no Japão. A partir de 1980 alguns países Europeus passaram a produzir e adicionar estes SAPs em fraldas descartáveis. No ano de 2005, aproximadamente 85% da produção mundial de SAPs ainda eram utilizados em artigos de higiene pessoal (KOVLER; JENSEN, 2005). Todavia, os SAPs também são utilizados em próteses, hidroponia, combate a incêndios, combate a lixiviação do solo e a erosão de encostas, plantio de mudas, cura interna de compósitos cimentícios, concretos auto-seláveis, entre outros (RILEM, 2004; TRAMFLOC, 2007, JUSTS et al., 2015; LIU et al., 2016).

Estes polímeros comerciais têm como precursor básico o ácido acrílico, sendo os SAPs compostos por poliacrilatos interligados por ligações covalentes cruzadas, ou poliacrilatos/poliacrilamidas copolimerizados. Devido a sua natureza iônica e sua estrutura de ligações cruzadas, consegue absorver centenas de vezes seu peso em água sem se dissolverem (TRAMFLOC, 2007).

Para as matrizes cimentícias, a água absorvida pelo SAP pode ser considerada quimicamente toda disponível para reagir com o cimento. Algumas propriedades como a forma, capacidade de absorção de água, resistência e módulo de deformação do gel inchado são importantes e influenciam nas propriedades da matriz cimentícia (KOVLER; JENSEN, 2005). As dimensões mais utilizadas dos SAPs em estado seco nas matrizes cimentícias estão entre 100 a 250 µm, e apresentam eficiência otimizada no combate à retração do compósito (LURA; DURAND; JENSEN, 2006).

Normalmente, com a adição de SAPs na matriz cimentícia tem-se um ganho na porosidade que, por conseguinte, acarretaria em perda da resistência, diminuição da durabilidade e da densidade nos compósitos. Entretanto, ocorre uma modificação no formato e distribuição dos espaços vazios, que sem SAP são irregulares e parcialmente interconectados, e passam a ser esféricos, não conectados e de forma definida. Assim, podendo ocorrer um ganho na durabilidade, diminuição da densidade e perda na resistência, uma vez que os sólidos de gel são menos resistentes que o cimento anidro (LURA; DURAND; JENSEN, 2006).

Dentre as possibilidades de incorporadores de ar no cimento, os SAPs apresentam propriedades que vão além de diminuir a densidade dos compósitos, como por exemplo: ganho em durabilidade, diminuição da retração, auto-selagem que impede a infiltração de água, entre outras (LEE; WONG; BUENFELD, 2016; LIU et al., 2016). O que, por sua vez, pode auxiliar na adequação do processo de extrusão para produção de telhas onduladas de fibrocimentos livres de amianto.

## 2.4 Durabilidade do fibrocimento livre de amianto

O efeito dos SAPs na diminuição da retração, bem como, na produção de poros esféricos com distribuição uniforme na matriz cimentícia podem influenciar na durabilidade dos compósitos cimentícios (LEE; WONG; BUENFELD, 2016; LIU et al., 2016), entretanto, quando se trata de fibrocimentos reforçados com fibras vegetais a perda em durabilidade vem pela degradação das fibras em meio alcalino (SANTOS et al., 2014).

Apesar das pesquisas apontarem o potencial uso de fibras vegetais como reforço em compósitos cimentícios, existe algumas ressalvas quanto à baixa durabilidade dos compósitos e os mecanismos de degradação dessas fibras na matriz cimentícia. Muitas tentativas de produção de argamassas ou pastas de cimento *Portland* comum reforçadas com fibras vegetais não obtiveram êxito devido aos compósitos apresentarem vida útil entre 2 a 4 anos (AGOPYAN, 1991).

Uma das principais causas dessa rápida degradação é a elevada alcalinidade (pH próximo de 13) da água presente nos poros da matriz de cimento *Portland*, os álcalis agem principalmente nas regiões amorfas das fibras, degradando primeiramente as hemiceluloses e a lignina (GRAM, 1983; TOLÊDO FILHO et al., 2000). Outro mecanismo de degradação importante é a chamada mineralização das fibras, que consiste no acumulo dos álcalis da hidratação do cimento no interior da célula (lúmen), acarretando na diminuição da flexibilidade, bem como, em um comportamento frágil e quebradiço das fibras, diminuindo assim a tenacidade do compósito (MOHR; NANKO; KURTIS, 2005; TOLÊDO FILHO et al., 2000).

A baixa estabilidade dimensional normalmente característica das fibras lignocelulósicas também prejudica a durabilidade dos compósitos, devido ao efeito de expansão e contração das fibras, que com o tempo vai quebrando as ligações na interface fibra/matriz, formando espaços vazios, o que pode acarretar em uma diminuição significativa das propriedades mecânicas dos compósitos (SAWSEN et al., 2015).

Quanto ao efeito dos componentes químicos das fibras lignocelulósicas na matriz cimentícia, algumas pesquisas revelam que a lignina presente nas fibras é facilmente degradada pelos álcalis presentes na água do cimento, enfraquecendo as ligações entre fibra/matriz, corroborando com a diminuição da vida útil dos compósitos (AGOPYAN et. al., 2005; BENTUR; AKERS, 1989). Porém outras pesquisas apontam que a lignina aumenta a estabilidade dimensional e diminui o caráter higroscópico das fibras, acarretando em melhora da interface fibra/matriz e diminuição do mecanismo de mineralização das fibras (MORH; BIERNACKI; KURTIS, 2006; NANKO; ASANO; OHSAWA, 1991). Já os extrativos presentes nos materiais lignocelulósicos podem interferir no tempo de pega e hidratação do cimento, prejudicando a resistência mecânica dos compósitos, ou mesmo, inviabilizando o uso das fibras *in natura* (SELLAMI; MERZOUD; AMZIANE, 2013; CHAFEI et al., 2014). As hemiceluloses são responsáveis por boa parte da higroscopicidade das fibras, agindo como um facilitador do processo de mineralização das fibras, além de ser facilmente degradada pelos álcalis presentes na água do cimento, prejudicando a interface fibra/matriz (CHAFEI et al., 2012; CHAFEI et al., 2014).

O fato dos SAPs serem mais hidrofílicos que as fibras vegetais podem influenciar na dinâmica de degradação/mineração das fibras, uma vez que o polímero tende a absorver a água livre da matriz cimentícia. Portanto, estudos que visem avaliar a durabilidade dos compósitos com adição de SAPs são interessantes no intuito de identificar novos mecanismos de degradação.

# 3 CONCLUSÃO

A inclusão de polímeros superabsorventes não prejudicou a moldagem dos compósitos cimentícios pelo processo de extrusão, no entanto, houve uma expansão dos compósitos que continham mais que 1% de SAP. Devido ao método físico de incorporação de ar, o uso de SAP na matriz formou vazios que prejudicaram a resistência mecânica dos compósitos. Entretanto, ocorreu uma diminuição da densidade aparente e um aumento da porosidade, provando a eficiência desses materiais como incorporadores de ar. Com o uso de até 0.5% de SAP em compósitos extrudados é possível a incorporação de ar, redução da densidade (~10%) sem causar prejuízos substanciais na resistência mecânica dos compósitos cimentícios.

Os compósitos cimentícios extrudados que continham SAP apresentaram degradação semelhante aos compósitos sem SAP, quando submetidos a 30 ciclos de envelhecimento acelerado com irradiação UV-B, spray de água e condensação a vapor. Em contrapartida, os fibrocimentos obtiveram maior resistência aos ciclos de envelhecimento, mesmo com a degradação das fibras celulósicas no interior da matriz.

Os surfactantes comerciais (incorporadores de ar) não apresentaram eficiência na incorporação de ar nos fibrocimentos extrudados, como sugeria a hipótese, as forças exercidas na moldagem por extrusão impediram a formação de bolhas de ar no interior da matriz. Entretanto, devido as características de aumento da molhabilidade, ocorreu uma hidratação efetiva das fases do cimento e uma diminuição do número de vazios, que acarretou em uma densificação e consequente ganho em desempenho mecânico. Essa diminuição da permeabilidade pode aumentar a durabilidade das fibras no interior da matriz. Já com o uso de SAP nos fibrocimentos extrudados, ocorreu um aumento na formação de vazios, que prejudicou o desempenho mecânico. Nos fibrocimentos com 0,7% de SAP não foi observada a camada compacta na superfície dos fibrocimentos, devido à expansão dos corpos de prova após a moldagem. Estes fibrocimentos provaram ser mais susceptíveis a carbonatação natural que os demais tratamentos.

No geral, a aplicação do SAP em estudo para a produção de fibrocimentos extrudados tem restrições, deve-se considerar usos que exijam baixo desempenho mecânico. Já o uso de surfactantes, apesar de não incorporar ar nos fibrocimentos pode ser interessante, devido ao acréscimo no desempenho mecânico em fibrocimentos extrudados.

# REFERÊNCIAS

AGOPYAN, V. **Materiais reforçados com fibras para construção civil nos países em desenvolvimento: uso de fibras vegetais**. 1991. 204 f. Tese (Livre-Docência) – Escola Politécnica, Universidade de São Paulo, São Paulo, 1991.

AGOPYAN, V.; SAVASTANO JUNIOR, H.; JOHN, V. M.; CINCOTTO, M. A. Developments on vegetable fibre-cement based materials in São Paulo, Brazil: an overview. **Cement and Concrete Composites**, Barking, v. 27, p. 527-536, 2005.

ALFANI, R.; GUERRINI, G. L. Rheological test methods for the characterization of extrudable cement-based materials – A review. **Materials and Structures**, Bergamo, v. 38, n. 2, p. 239-247, 2005.

BELAADI, A. et al. Tensile static and fatigue behavior of sisal fibres. **Materials & Design,** Surrey, v. 46, p. 76-83, 2013.

BENTUR, A.; AKERS, S. A. S. The microstructure and ageing of cellulose fibre reinforced cement composites cured in a normal environment. **The International Journal Cement Composites Lightweight Concrete**, Oxford, v. 11, n. 2, p. 99-109, 1989.

CALHAU, E. L. **Argamassa de revestimento com aditivo incorporador de ar: propriedades e recomendações.** 2000. 148p. (Dissertação de mestrado). Universidade Federal do Espírito Santo, Vitória-ES, 2000.

CHAFEI, S. et al. Influence du traitement des fibres de lin sur la rhéologie et les erformances d’un mortier-analyse de la durabilité. **In:** Proceedings of the French International Symposium. Toulouse, France: NoMaD; 2012.

CHAFEI, S. et al. Optimizing the formulation of flax fiber-reinforced cement composites. **Constr Build Mater**, Guildford, v.54, pag. 59-64, 2014.

CHEN, H; BURWOOD, R. J.; MAXWELL, I. A.; GORINGE, N.S. Method and apparatus for extruding cementitious articles. **United States Patent Application Publication,** US 2009/0218720 A1. 2009.

CHOI, P.; YEON, J. H.; YUN, K. Air-void structure, strength, and permeability of wet-mix shotcrete before and after shotcreting operation: The influences of silica fume and air-entraining agent. **Cement and Concrete Composites**, v. 70, p. 69-77, 2016.

FARRAPO, C. L. **Durabilidade de fibrocimentos reforçados com polpa de sisal após 10 anos de envelhecimento natural.** 2015. 87 p. Dissertação (Mestrado em Engenharia de Biomateriais) – Universidade Federal de Lavras, Departamento de Ciências Florestais, Lavras-MG, 2015.

FONSECA, C. S.; SILVA, T. F. D. A.; SILVA, M. T.; OLIVEIRA, I. R. C.; MENDES, R. F.;

HEIN, P. R. G.; MENDES, L. M.; TONOLI, G. H. D. Micro/nanofibrilas celulósicas de Eucalyptus em fibrocimento extrudados. **Cerne**, Lavras, v. 22, n. 1, p. 59-68, 2016.

GRAM, H. E. Durability of natural fiber in concrete. Research Report, Swedish Cement and **Concrete Research Institute**, Stockholm, Sweden, 1983.

GRASLEY, Z.C.; LANGE, D.A.. Thermal dilation and internal relative humidity of hardened cement paste. **Materials and Structure.**, Bergamo, v. 40, p. 311-317, 2007.

HARUN, T.. Fuzzy logic model for prediction of mechanical properties of lightweight concrete exposed to high temperature. **Materials & Design,** Birmingham, v. 30, n. 6, p. 2205-2210, 2009.

HORST, G. G. Extrusion of FRC products: technology and practical aspects. In: INTERNATIONAL CONFERENCE INORGANIC-BONDED WOOD AND FIBER COMPOSITE MATERIALS, 8., 2002, Sun Valley. **Proceedings...** Sun Valley: [s. n.], p. 36-46, 2002.

HOVER, K.C.. Why is there air in concrete? **Concr. Constr**., v. 38, n. 1, p. 11-15, 1993.

JUSTS, J.; WYRZYKOWSKI, M.; BAJARE, D.; LURA, P. Internal curing by superabsorbent polymers in ultra-high performance concrete. **Cement and concrete Research**, Elmsford, v. 76, p. 82-90, 2015.

KOCKAL, N. U.; OZTURAN, T.. Strength and elastic properties of structural lightweight concretes. **Materials & Design**, Birmingham, v. 32, n. 4, p. 2396-2409, 2011.

KOSMATKA, S.H.; PANARESE, W.C.. **Design and Control of Concrete Mixtures**. Thirteenth **ed.**, Portland Cement Association, Skokie, USA, 1994.

KOVLER, K.; JENSEN, O. M. Novel techniques for concrete curing. **Concrete International**, Detroit, v. 27, n. 9, p. 39-42, 2005.

LEE, H. X. D.; WONG, H. S.; BUENFELD, N. R. Self-sealing of cracks in concrete using superabsorbent polymers. **Cement and Concrete Research**, Elmsford, v. 79, p. 194-208, 2016.

LEE, H. X. D.; WONG, H. S.; BUENFELD, N. R.. The potential of superabsorbent polymer for self-sealing cracks in concrete. **Adv. Appl. Ceram**., v. 5, p. 296-302, 2010.

LI, Z.; MU, B.; CHUI, S. N. C. Static and dynamic behavior of extruded sheets with short fibers. **Journal of Materials in Civil Engineering**, Reston, July/August, p.248-254, 2001.

LIU, H.; BU, Y.; SANJAYAN, J. G.; NAZARI, A.; SHEN, Z. The application of coated superabsorbent polymer in well cement for plugging the microcrack. **Construction and Building Materials**, Guildford, v. 104, p. 72-84, 2016.

LURA, P.; DURAND, F., JENSEN, O. M.. Autogenous strain of cement pastes with superabsorbent polymers. **In:** “International RILEM Conference on Volume Changes of Hardening Concrete: Testing and Mitigation”, Lyngby, 2006, RILEM Proceedings, PRO 52, O. M. Jensen, P. Lura, K. Kovler, p. 57-65, 2006.

MEHTA, P.K.; MONTEIRO, P.J.M.. **Concrete: Microstructure, Properties, and Materials**. Third ed., McGraw-Hill, New York, 2006.

MOHR, B. J.; BIERNACKI, J. J.; KURTIS, K. E. Microstructural and chemical effects of wet/dry cycling on pulp fiber–cement composites. **Cement and Concrete Research**, Elmsford, v. 36, n. 7, p. 1240-1251, 2006.

MOHR, B. J.; NANKO, H.; KURTIS, K. E. Durability of kraft pulp fiber-cement composites to wet/dry cycling. **Cement and Concrete Composites**, Barking, v.27, n.4, pag. 435-448, 2005.

NANKO, H.; ASANO, S.; OHSAWA, J. Shrinkage behavior of pulp fibers during drying. **In:** TAPPI INTERNATIONAL PAPER PHYSICS CONFERENCE, 1991, Kona. Proceedings… Kona: 1991, p. 365-374.

QIAN, X.; ZHOU, X.; MU, B.; LI, Z. Fiber alingment and property direction dependency of FRC extrudate. **Cement and Concrete Research**, Elmsford, v. 33, p.1575-1581, 2003.

RILEM Technical Committee “Internal Curing of Concrete”, **TC 196 – ICC**. Document ICC-N18, Draft of chapter 4: Materials and methods for internal curing. Trabalho não publicado, 2004.

ROMANO, R. C. O. et al. Impacto do Tipo de Misturador e do Tempo de Mistura nas Propriedades de Argamassas Industrializadas. **Ambiente Construído**, Porto Alegre, v. 9, n. 4, p. 109-118, 2009.

ROMANO, R. C. O.; PILEGGI, R. G. Temperature's Role in the Rheological Behavior of Cementitious Pastes Prepared With Air-Entraining Admixtures. **Applied Rheology**, v. 22, 2012.

SALAGER, J. L. SURFACTANTS Types and Uses. 2002 link< http://nanoparticles.org/pdf/Salager-E300A.pdf>. Acesso em agosto de 2017.

SANTOS, S. F. et al. Effect of colloidal sílica on the mechanical properties of fiber-cement reinforced with cellulosic fibers. **Journal of Materials Science**, New York, v. 49, n. 21, p 7497-7506, 2014.

SANTOS, S. F. et. al. Supercritical carbonation treatment on extruded fibre-cement reinforced with vegetable fibres. **Cement and Concrete Research,** Elmsford, v. 56, p. 84-94, Feb. 2015.

SANTOS, S. F.; TONOLI, G. H. D.; SAVASTANO Jr., H. Materias-primas e procesos de fabricación para fibrocemento. **In:** Universidad Politécnica de Valencia, editor. Aprovechamiento de residuos agro-industriales como fuente sostenible de materiales de construcción. España: p. 327-343, 2011.

SAWSEN, C. et al. Effect of flax fibers treatments on the rheological and the mechanical behavior of a cement composite. **Construction and Building Materials,** Guildford, v. 79, p. 229-235, 2015.

SELLAMI, A.; MERZOUD, M.; AMZIANE, S. Improvement of mechanical properties of green concrete by treatment of the vegetals fibers. **Construction and Building Materials**, Guildford, v.47, n.11, pag. 17- 24, 2013.

SHAH, S.; SHAO, Y.; MARIKUNTE, S. Method of making extruded fiber reinforced cement matrix composites. **United States Patent,** n. 5,891,374; 1999.

SHAO, Y. et al. Wood fibre-cement composites by extrusion. **Canadian Journal of Civil Engineering**, Ottawa, v. 27, n. 3, p. 543-552, 2000.

SHAO, Y.; MARIKUNTE, S.; SHAH, S. P. Extruded fiber-reinforced composites. **Concrete International**, Detroit, v. 17, n. 4, p. 48-52, 1995.

SHAO, Y.; SHAH, S. Mechanical properties of PVA fiber reinforced cement composites fabricated by extrusion processing. **ACI Material Journal**, Michigan, v. 94, p.555-564. 1997.

SHRINIVASAN, R.; DEFORD, D.; SHAH, P. S. The use of extrusion rheometry in the development of extrudate fiber-reinforced cement composites. **Concrete Science and Engineering**, v. 1, p. 26-36, 1999.

SILVA, D. W.; MENDES, R. F.; FREIRE, C. S.; VILELA, B. L.; TONOLI, G. H. D.; TEIXEIRA, R. S.; SANTOS, S. F.; SAVASTANO JR., H. Cementitious composites reinforced with kraft pulping waste. **Key Engineering Materials**, v. 668, p. 390-398, 2016.

SILVA, D. W. **Propriedades físico-mecânicas de fibrocimentos reforçados com fibras de eucalipto tratadas térmicamente.** 2015. 66 p. Dissertação (Mestrado em Engenharia de Biomateriais) – Universidade Federal de Lavras, Departamento de Ciências Florestais, Lavras- MG, 2015.

SOTO, Y. J. M.; TONOLI, G. H. D.; TEIXEIRA, R.S.; SANTOS, S. F.; SAVASTANO JR, H. Prospective study on vegetable wastes as reinforcement in extruded fibre-cement. International Conference on Non-Conventional Materials and Technologies: Ecological Materials and technologies for Sustainable Constructions, 2007, Maceió. **Anais do Brasil-NOCMAT**. (Abmtenc) Maceió, 2007.

TAKASHIMA, H. et al. A design approach for the mechanical properties of polypropylene discontinuous fibre reinforced cementitious composites by extrusion molding. **Engineering Fracture Mechanics**, Ithaca, v. 70, n. 7/8, p. 853-870, 2003.

TEIXEIRA R. S.; TONOLI, G. H. D.; SANTOS, S. F.; FIORELLI, J.; SAVASTANO JUNIOR, H.; LAHR, F. A. R. Extruded cement based composites reinforced with sugar cane bagasse fibres. **Key Engineering Materials**, v. 517, p. 450-457, 2012.

TEIXEIRA, R. S. **Utilização de resíduos sucro-alcooleiros na fabricação de fibrocimento pelo processo de extrusão**. 2010. 135 p. Dissertação (Mestrado em Engenharia de Materiais) – Escola de Engenharia de São Carlos, Instituto de Física de São Carlos, Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, 2010.

TOLÊDO FILHO, R. D.; SCRIVENER, K.; ENGLAND, G. L.; GHAVAMI, K. Durability of alkali-sensitive sisal and coconut fibres in cement mortar composites. **Cement and Concrete Composites**, Barking, v.22, n.2, pag. 127-143, 2000.

TONOLI, G. H. D. et al. Cellulose modified fibres in cement based composites. **Composites Part A: Applied Science and Manufacturing**, Kidlinton, v. 40, n. 12, p. 2046-2053, 2009.

TONOLI, G. H. D. et al. Impact of bleaching pine fibre on the fibre/cement interface. **Journal of Materials Science,** Norwell, v. 47, p. 4167-4177, 2012a.

TONOLI, G. H. D. et al. Processing and dimensional changes of cement based composites reinforced with surface-treated cellulose fibres. **Cement Concrete and Composites**, Barking, v. 37, p. 68–75, 2013.

TONOLI, G. H. D. **Fibras curtas de Eucalipto para novas tecnologias em fibrocimento**. 2009. 148 p. Tese (Doutorado em Ciência e Engenharia dos Materiais) – Escola de Engenharia de São Carlos, Instituto de Física de São Carlos, Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, 2010.

TONOLI, G. H. D.; SAVASTANO JR., H.; FUENTE, E.; NEGRO, C.; BLANCO, A.; ROCCO LAHR, F. A. Eucalyptus pulp fibres as alternative reinforcement to engineered cement-based composites. **Ind Crops Prod**, Berlin, v. 31, n. 2, p. 225-232, 2010.

TONOLI, G. H. D.; TEIXEIRA, E. M.; CORREA, A. C.; MARCONCINI, J. M.; CAIXETA, L. A.; PEREIRA-DA-SILVA, M. A.; MATTOSO, L. H. C. Cellulose micro/nanofibres from Eucalyptus kraft pulp: preparation and properties. **Carbohydrate Polymers**, Worcester, v. 89, p. 80-88, 2012b.

TRAMFLOC, Inc. Super Absorbent Polymers for Water Retention and Erosion Control. 2007. Disponível em: <http://www.tramfloc.com/tf62.html>. Página visualizada em março de 2018.

VERBECK, G.. Pore Structure, in: Significance of Tests and Properties of Concrete and Concrete Aggregates. **American Society of Testing and Materials,** West Conshohocken, p. 262-274, 1966.

WANG, J. Y.; CHIA, K. S.; LIEW, J. Y. R.; ZHANG, M. H. Flexural performance of fiber-reinforced ultra lightweight cement composites with low fiber content. **Cement and Concrete Composites**, Barking, v. 43, p. 30-47, 2013.

YEON, J.H.; CHOI, S.; WON, M. C.. Effect of relative humidity on coefficient of thermal expansion of hardened cement paste and concrete. **Transp. Res. Rec.,** v. 2113, p. 83-91, 2009.

# SEGUNDA PARTE – MANUSCRITOS

## MANUSCRITO 1 - APPLICATION OF SUPERABSORBENT POLYMER IN THE PRODUCTION OF CEMENT COMPOSITES BY EXTRUSION

Manuscript to be submitted to Minerals Engineering (2018). Can be modified according the suggestions of the reviewers.

Danillo Wisky Silva [a*], Alan Pereira Vilela [a], Camila Soares Fonseca [b], Saulo Rocha Ferreira [b], Maria Alice Martins [c], Juliano Elvis Oliveira [b], Gustavo Henrique Denzin Tonoli [a], Lourival Marin Mendes [a]

[a] Federal University of Lavras, Department of Forestry Sciences, Campus Universitário, Caixa postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil. *danilowisky@hotmail.com (corresponding author)

[b] Federal University of Lavras, Department of Engineered, Campus Universitário, Caixa postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil.

[c] LNNA, Brazilian Agricultural Research Corporation (EMBRAPA Instrumentação), Rua XV de Novembro, 1452, caixa postal 741, CEP 13565-970, São Carlos, São Paulo, Brazil.

## Abstract

The objective of this research was to develop and evaluate cementitious composites with the addition of superabsorbent polymer (SAP) by the extrusion method, aiming at the production of lightweight cement composites. A simple cement matrix was used (70% of cement and 30% of limestone filler). In the composites, 0.0 to 2.0% of SAP was added per mass of cement. The different percentages of SAP evaluated did not interfere in the extrusion process, however, an expansion of the composites with 1.0, 1.5 and 2.0% SAP occurred when passing through the extruder nozzle. The composites were tested after 28 days of curing in a wet room (99% RH). The physical properties were evaluated by the absorption capacity and porosity. The mechanical properties were evaluated for modulus of rupture (MOR), modulus of elasticity (MOE), limit of proportionality (LOP) and toughness (TO), both by resistance to static bending. The results indicate a gradual increase in water absorption and apparent porosity with increasing SAP. On the other hand, a decrease of the density of the composites was observed. Composites with 1.0, 1.5 and 2.0% SAP showed a substantial decrease in mechanical performance. In general, the addition of 0.5% SAP decreased the density by about 10%, without compromising the mechanical performance of the cementitious composites.

**Keywords:** Cement matrix, bulk density, mechanical properties, air-entraining, extrusion process.

## Introduction

Studies demonstrate that the use of SAPs in the concrete are capable of promoting the self-sealing of possible cracks due to their capacity of water absorption and expansion, obstructing the region of the crack. In this process of expansion / retraction of the polymer in the concrete cracks, cement hydration products are deposited in the region, which gradually obstructs the region permanently (LEE; WONG; BUENFELD, 2016; LIU et al., 2016). However, the use of SAPs in mortars and concretes increases porosity, and consequently there is loss in mechanical strength and apparent density of materials (WANG et al., 2013). Studies show that the 1% increase in void spaces leads to loss of up to 4% in the compressive strength of cementitious composites (MEHTA; MONTEIRO, 2006; CHOI; YEON; YUM, 2016).

Acrylic acid is the basic precursor of superabsorbent polymers (SAP), which are composed of polyacrylates interconnected by cross-linked covalent bonds, or copolymerized polyacrylates / polyacrylamides. SAPs are insoluble in water, but because of their ionic nature and cross-linking structure they can absorb hundreds of times their mass in water (TRAMFLOC, 2007). Numerous researches have evaluated the effect of SAPs on mixing with mortars and concretes. The interest arises from the water absorption capacity of the SAPs, since all absorbed water will be chemically available to react with the cement (KOVLER et al., 2005). In this work, the process of "internal cure" is made possible by the gradual release of water from the hydrated SAPs into the cement matrix (JUSTS et al., 2015). The results are promising, avoiding the initial retraction of the cement due to curing and drying (LURAS et al., 2006; JUSTS et al., 2015), the studies also show that these polymers produce uniform and unconnected spherical pores, decreasing the expansion/retraction of the matrix, for example in case of freezing / thawing, increasing the durability of the composites (LURAS et al., 2006).

The characteristics of SAPs in mortars and concretes may also be of interest for the production of corrugated tiles by extrusion. The addition of SAPs to cementitious composites produced by extrusion can aid in decreasing the density of these materials. Since the density of the extruded cementitious composites compared to conventional fiber cement production methods (suction, Hatscheck, etc.) are 40% higher (FARRAPO, 2015; SILVA, 2015; SILVA et al., 2016). The gain in density provided by the extrusion process would require in the case of corrugated tiles an additional cost related to the reinforcement of the roof fastening structure. The extrusion process involves the formation of cohesive fiber-cement composites by forcing it through the die that can be adjusted to various shape configurations (TEIXEIRA et al., 2012). This process is continuous, requires lower cost of investment in relation to well established methods (such as Hatschek method) and presents great potential for low cost commercial applications. The advantage of extrusion is that it is an economical mass-production method capable of producing not only flat shapes, but also structural and hollow shapes. This process allows the use of a variety of waste materials that can be successfully incorporated into the matrix, including the use of lignocellulosic fibers as reinforcement in fiber-cement composites (SANTOS et al., 2011). In this context, the objective of this research was to develop and evaluate cementitious composites with the addition of superabsorbent polymer (SAP) by the extrusion method, aiming at the production of lightweight cement composites.

## Materials and methods

### *Materials*

A matrix with mix design of 1:0.5:0.3 (binder: filler: water/binder) by weight was used. The binder used was Brazilian ordinary Portland cement CPV ARI (based on NBR 5733 - ABNT, 1983), with granulated blast furnace slag (based on ASTM C150/C150 M − 12, Type IV, 2011) and filler was calcium carbonate (limestone). To assist in the extrusion process, two rheological modifiers, hydroxypropyl-methylcellulose (HPMC) and polyether carboxylic acid (ADVA 175) supplied by the multinational company Grace Construction Products-BR.

The polymer to be used in the cementitious matrix has in its basic composition polyacrylamide and potassium acrylate, with an absorption capacity of 350 to 500 times its weight in water and can increase its volume by up to 100 times; this polymer was supplied by the company Hydroplan EB (see Table 1). It is expected that this polymer presents air incorporation characteristics, seeking to reduce the apparent density of the cementitious composites.

Table 1 - SAP physical characteristics.

| | |
|---|---|
| Appearance | White powder |
| Particle Size | < 1 mm |
| Ionic characteristics | Anionic |
| Active ingredient (% solid content) | 100 |
| Solubility | Insoluble in water |
| Theoretical absorption (g for 1g) | 500 |
| Practical Absorption (g to 1g) | 350 |
| Specific weight (in g / cm$^3$) | 1.0 |
| Absorption time to 60% equilibrium (in minutes) | 30 |

*Extrusion of the cement-based composites*

Before the production process of the composites, the SAP will be hydrated in deionized water; the amount of water to be used will be 0.40 in relation to the mass of the cement. The hydration process consists in adding the SAP in water, where it will remain for 6 hours to guarantee the total hydration of the polymer.

The cementitious matrix consisted of cement CPV ARI (based on NBR 5733 - ABNT, 1983), corresponding to ASTM-C150, Type I (ASTM, 2011) and filler limestone. The main chemical and physical characteristics of these cement and filler limestone are presented in Tonoli et al. (2012). The mixture for extrusion was prepared with the addition of 1% (by mass) of rheology modifiers: hydroxypropyl-methylcellulose (HPMC) and self-compacting additive for concrete polyether carboxylic (commercially named ADVA 175 and provided by Grace-BR). The final water:cement ratio was of around 0.40. The dry powders (cement, filler and HPMC) were mixed together in a planetary mixer for 15 minutes, and then the hydrated SAP was gradually added in order to obtain a good distribution into the mixture. The ADVA was mixed with water (ratio was around 0.1) and subsequently added to the mixture until the final stage of the mixing process, which took about 5 min. Then, the mass was introduced in the helical extruder for obtaining the extruded composites with 20 x 30 x 200 mm nominal dimensions.

The composites were produced on a laboratory scale by extrusion in a VERDES 051 model helical extruder. The mix-design formulations of the composites are described in Table 2. Seven replicates were produced for each treatment.

Table 2 – Experimental design of the extruded fiber-cement composites.

| Treatments | Cement | Limestone | SAP |
|---|---|---|---|
| | -------------------------- (% by mass) --------------------- | | |
| Control | 70.00 | 30.00 | 0.00 |
| $SAP\_{0.5}$ | 69.65 | 29.85 | 0.50 |
| $SAP\_{1.0}$ | 69.30 | 29.70 | 1.00 |
| $SAP\_{1.5}$ | 68.95 | 29.55 | 1.50 |
| $SAP\_{2.0}$ | 68.60 | 29.40 | 2.00 |

*Infrared spectroscopy (FTIR)*

The infrared spectrum analysis was conducted using the Fourier transform spectroscopy with the Digilab Excalibur FTS 3000 equipment. The infrared absorption spectrum was measured using the KBr pellet method. The influences of the SAP on cement paste can be evaluated by observing the disappearance, decay, transport, and enhancement of infrared spectrums.

*Scanning Electron Microscopy (SEM)*

The microstructural properties of cementitious composites were evaluated after 28 days of cure. The analyses were performed on the rupture surface of the plates that were tested by static bending. This observation aims to evaluate the effect of SAP on physical-mechanical properties. The composites samples were coated with golden conducting films in the vacuum coating machine using the vaporization method. The SEM (JEOL® JMS – 6510 type) was employed to observe the samples microstructures. In this experiment, the interface between the SAP and cement matrix was located under the center of the SEM so that the interfacial transition zone would be observable.

*Characterization of the composites and data analysis*

Apparent porosity (AP), bulk density (BD) and water absorption (WA) of the composites were determined following the procedures described in ASTM C 948-81 (ASTM, 1981) standard. Mechanical test was performed using the universal testing machine EMIC DL30000 equipped with a 0.5 kN load cell. Three-point bending was performed. Modulus of rupture (MOR), modulus of elasticity (MOE), limit of proportionality (LOP) and toughness (TO) be evaluated (RILEM, 1984) and are described in detail in previous works (TONOLI et al., 2010; TONOLI et al., 2011). Data analysis was performed using a randomized design. The ANOVA and regression analysis were performed at 5% of significance.

## Results and discussion

### *Visual appearance and microstructural characterization*

The use of SAP in the cementitious composites did not impede the production by extrusion. However, there was an expansion of the composites when passing through the nozzle of the extruder at percentages greater than 1% SAP (Figure 1). The cause of this expansion is linked to the release of the tension exerted by the extruder and the high expansive capacity of the SAP used.

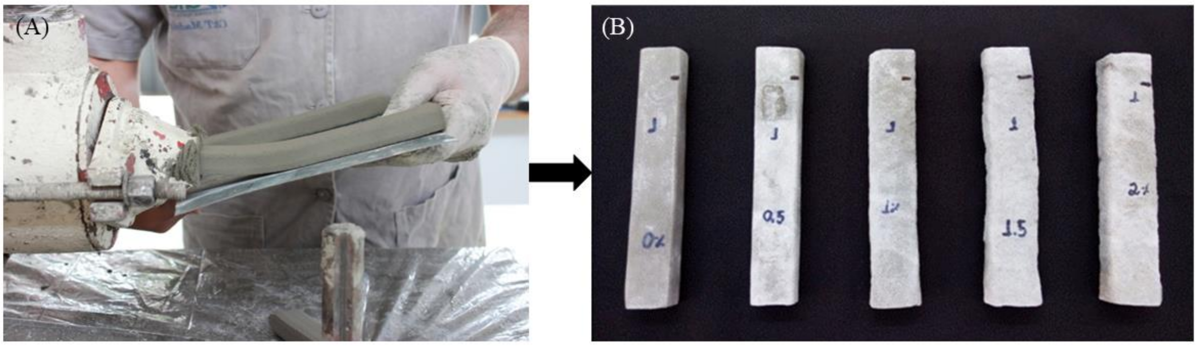


Figure 1 – (A) Extrusion process and (B) expansion / deformation of specimens with different percentages of SAP

The expansion of the composites caused by hydrated SAP agglomerations forms holes due to loss the of SAP water for cementitious matrix (see Figure 2), indicating that percentages of SAP greater than 1% are not feasible in the production of extruded cementitious composites.

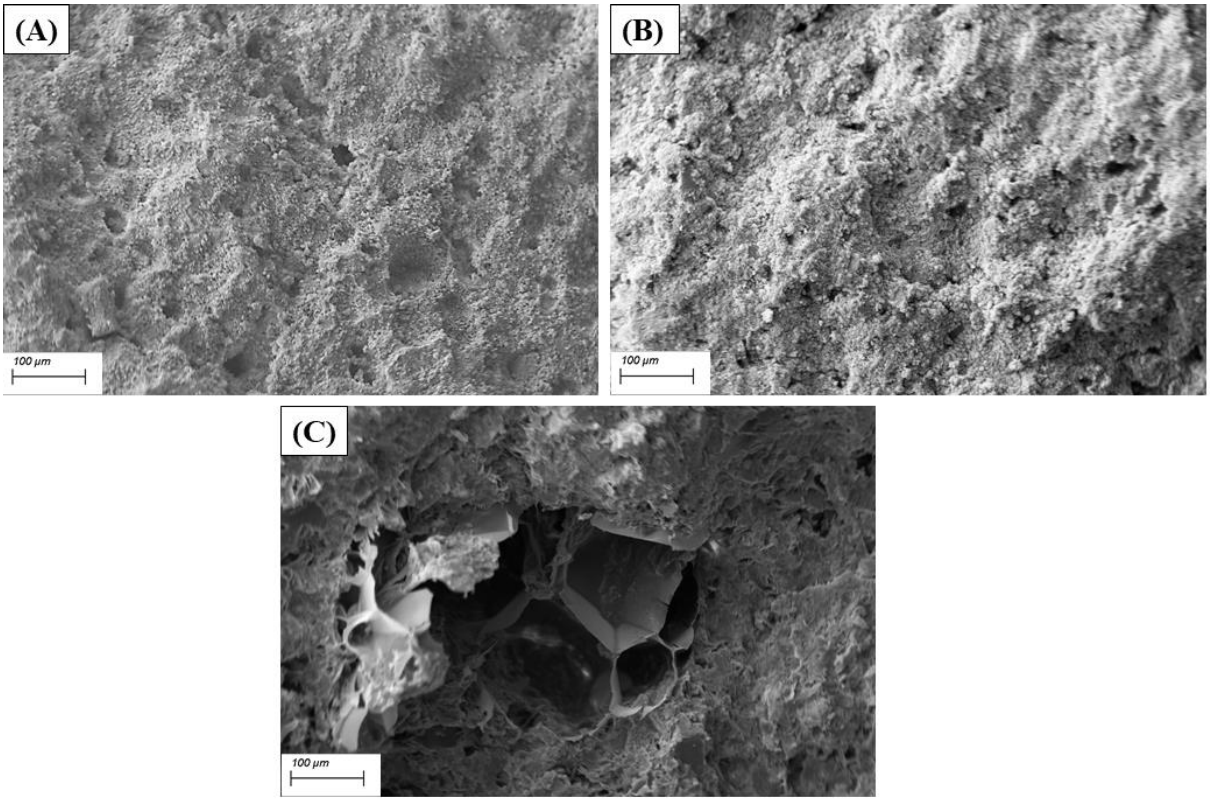


Figure 2 – Scanning electron microscopy (SEM) micrographs of the surface of fracture of test specimens: (A) 0.0% of SAP; (B) 0.5% of SAP; and (C) 2.0% of SAP

Another relevant aspect is the fact that SAP has a higher hydrophilicity than cement, causing a slow release of the water present in the polymer to the cement matrix, reducing the cement retraction and consequently, the formation of microcracks in the matrix, this low loss gradient water allows internal cure of composites (JUSTS et al., 2015).

There was no chemical interaction between SAP and the cementitious matrix (see Figure 3), however, the polymer incorporates air into the matrix through physical interactions intrinsic to the mixing process and the loss of water from the polymer to the matrix, which causes the polymer return to its solid state.

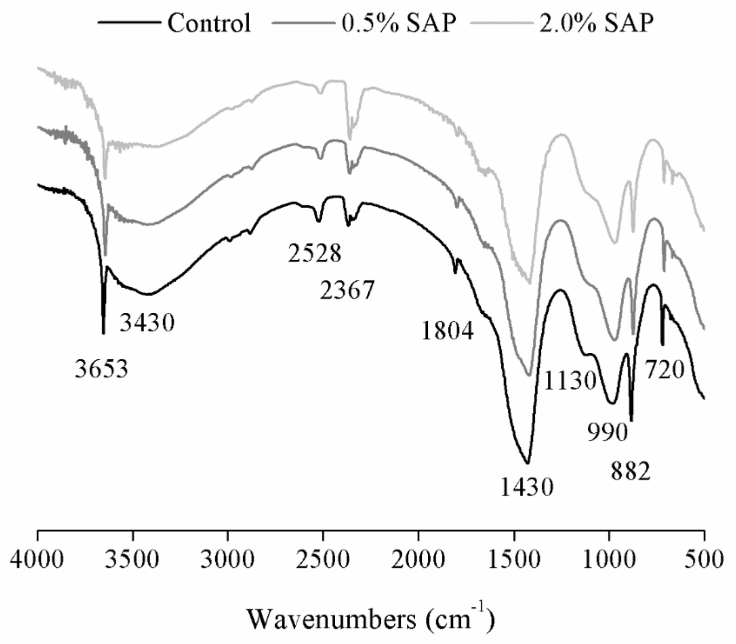


Figure 3 – Fourier transform infrared spectroscopy (FTIR) of cement composites.

FTIR spectra of the control, SAP_0.5 and SAP_2.0 confirm the presence of $CO_3^{2-}$ of calcium carbonate polymorphs (between 850-890 cm$^{-1}$ and 1400-1500 cm$^{-1}$), $SO_4^{2-}$ groups (between 900-1000 cm$^{-1}$) and $OH^-$ (between 3200-3500 cm$^{-1}$) of the ettringite and $S^-$ rich phases (Fig. 3). Only symmetric stretches can be verified proving that the SAP does not interact with the cement matrix.

### *Physical properties of the composites*

The higher the SAP content, the higher the water absorption and apparent porosity and the lower the bulk density of the cement composites (see Figure 4). It occurs because density of the SAP is significantly lower than cement matrix (WANG et al., 2013; JUSTS et al., 2015) and due also to the voids formed by the loss of water from SAP to the cementitious matrix. The voids formed by the agglomeration of the hydrated SAP (see Figure 2) may also have influenced these physical properties accentuating the difference in the composites with 1.0, 1.5 and 2.0% of SAP (see Table 3), since the expansion of these cementitious composites occurred exiting the extruder (see Figure 1).

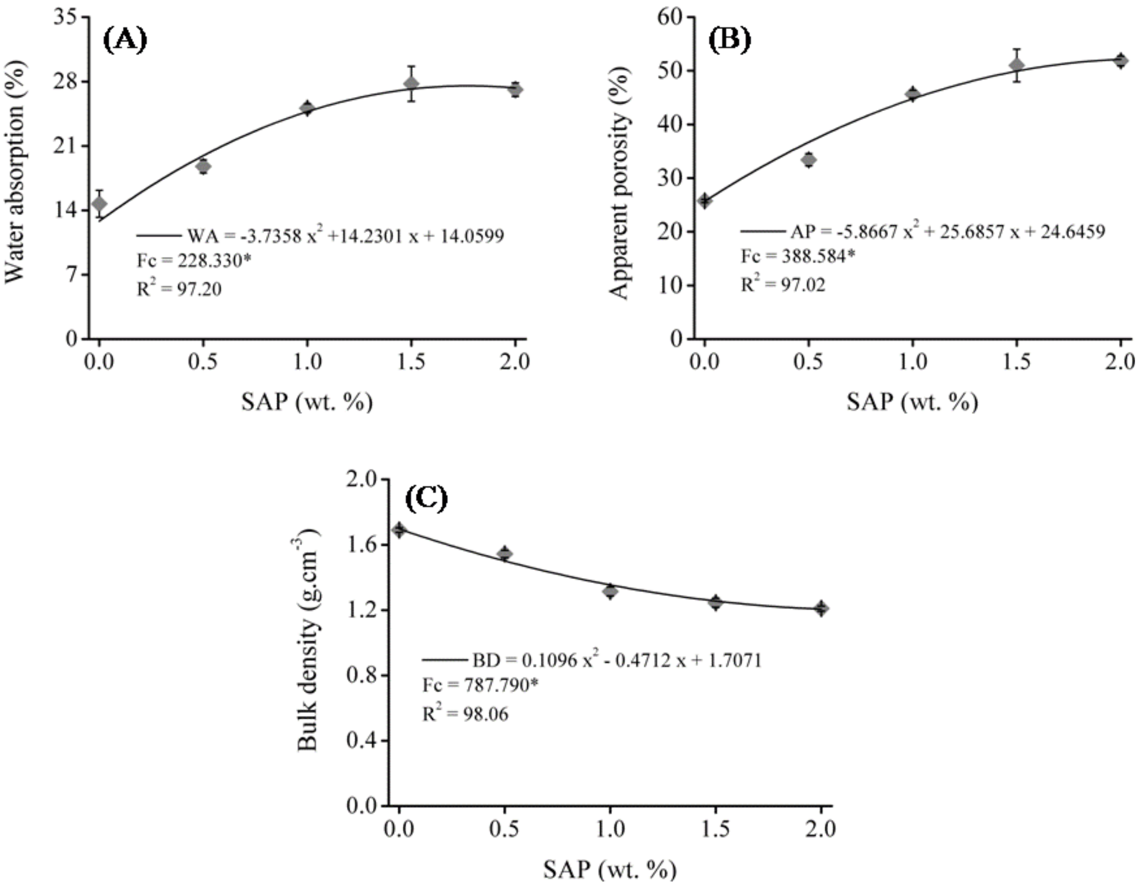


Figure 4 – Average and standard deviation values of: (a) water absorption, (b) apparent porosity, and (c) bulk density in cementitious composites with the addition of SAP. *Significant *P* value at 5% significance level

Table 3 – Percentage change in physical properties as a function of the superabsorbent polymer content increase in the composites at 28 days of cure in comparison to the control samples.

| Treatment | Water absorption | Apparent porosity | Bulk density |
|---|---|---|---|
| | ------------------------------------- | --% -- | ------------------------------- |
| Control | 0.0 | 0.0 | 0.0 |
| SAP_$_{0.5\%}$ | +27.7 | +29.8 | -8.6 |
| SAP_$_{1.0\%}$ | +70.6 | +77.3 | -22.3 |
| SAP_$_{1.5\%}$ | +88.7 | +98.0 | -26.4 |
| SAP_$_{2.0\%}$ | +84.4 | +101.3 | -28.4 |

All percentages of SAP used in the production of cementitious composites obtained water absorption values ranging from 14.7 to 27.8%, satisfying the requirements of norm NBR 12800 (ABNT, 2003) for asbestos-free fiber-cement (<37%). It can also be observed that the SAP incorporates air in the cement matrix; this characteristic is evident with the increase of the porosity and the decrease of the density.

Evaluating the physical properties, all SAP percentages evaluated were satisfactory, and the higher the percentage of SAP, the lower the density of the cementitious composites. This result is interesting, aiming at the production of corrugated tiles by extrusion. Before concluding the best percentage of SAP in order to reduce the density, it is necessary to evaluate the mechanical properties so that the composites meet both requirements.

*Mechanical properties of the composites*

Fig. 5 shows the typical static stress vs. deflection curves of the control sample and SAP content increase in cement composites after 28 days of curing.

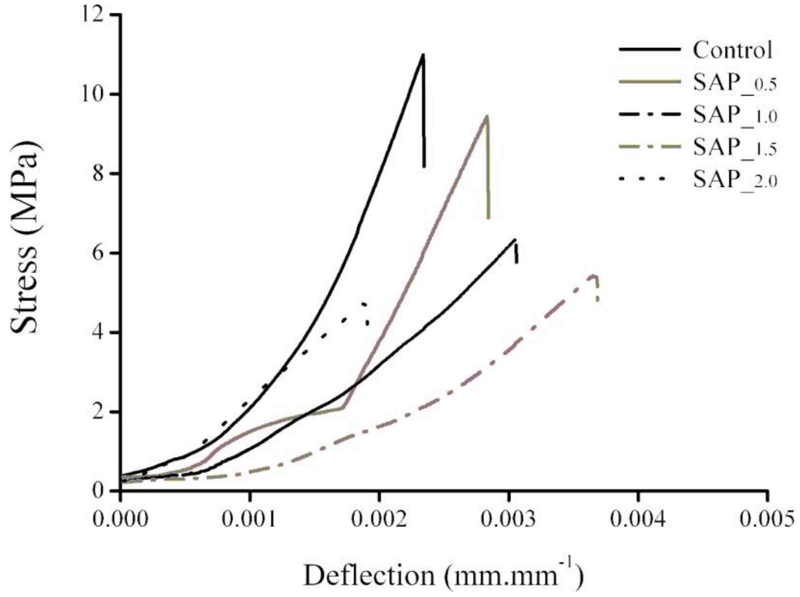


Figure 5 - Typical stress-deflection curves of the superabsorbent polymer increase content in cement composites at 28 days of cure.

In general, the addition of SAP to the cementitious composites decreased mechanical strength and did not show reinforcing characteristics (see Figure 5). This occurred due to the substantial increase of porosity in the composites with 1.0, 1.5 and 2.0% SAP (see Table 3). The agglomerations of hydrated SAP present in these percentages are also responsible for the loss in mechanical strength due to the formation of millimetric voids of than the pores (see Figure 2). Another aspect elucidated in the literature is the low mechanical resistance of the SAP particle in comparison to the cement grain which also favors the loss of mechanical resistance in the composites (LURAS et al., 2006).

The increase of the SAP content led to a significant decrease of modulus of rupture, limit of proportionality and modulus of elasticity, and did not modified of the toughness of the composites at 28 days of cure (see Figure 6 and Table 4).

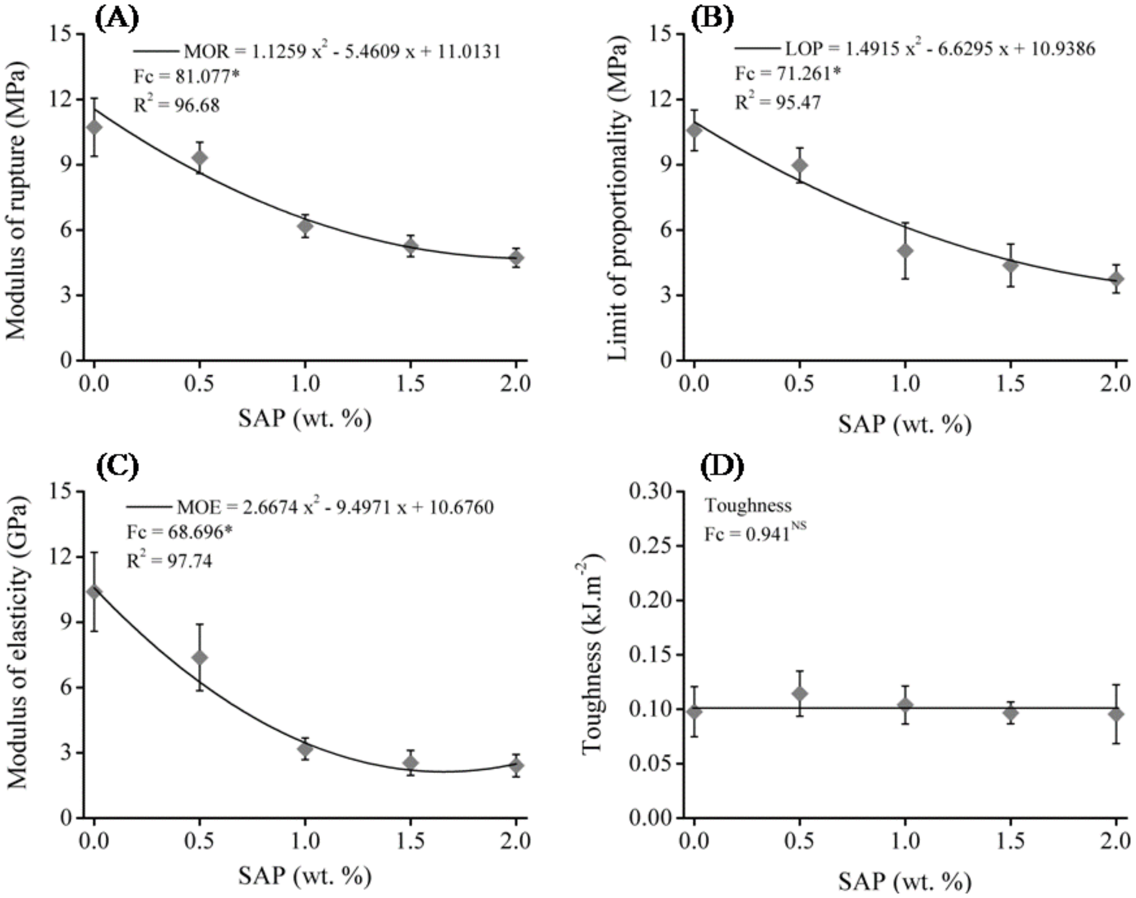


Figure 6 – Average and standard deviation values of: (A) modulus of rupture, (B) proportionality limit, (C) modulus of elasticity, and (D) toughness in cementitious composites with the addition of SAP. *Significant *P* value at 5% significance level

Table 4 - Percentage change of the mechanical properties as a function of the superabsorbent polymer content increase in the composites at 28 days of cure in comparison to the control samples.

| Composites | Modulus of rupture | Modulus of elasticity | Toughness | Proportionality limit |
|---|---|---|---|---|
| | ---------------------------------------------- | ---------------------- % | ---------------------- | ---------------------- |
| Control | 0.0 | 0.0 | 0.0 | 0.0 |
| SAP$_{\_0.5\%}$ | -13.1 | -29.1 | +16.9 | -15.2 |
| SAP$_{\_1.0\%}$ | -42.3 | -69.4 | +6.3 | -52.3 |
| SAP$_{\_1.5\%}$ | -50.9 | -75.6 | -1.1 | -58.6 |
| SAP$_{\_2.0\%}$ | -55.9 | -76.8 | -2.4 | -64.5 |

The increase of the SAP content led to a significant decrease of mechanical properties of the composites at 28 days of cure (Figure 6 and Table 4), due to the increase of porosity and formation of voids in the matrix. The composites containing 0.5% SAP lost only -13.1% of modulus of rupture and a gain of +16.9% in toughness (see Table 4), although there was no statistical difference between the treatments (see Figure 6). Only the control treatment and the composites with 0.5% of SAP (see Figure 6) were within the range of 7.0 to 13.0 MPa for rupture modulus, according to interval referring to the resistance of the asbestos free corrugated tiles according to norm NBR 15498 (ABNT, 2007).

In the literature, the decrease in the mechanical strength of the cementitious composites with the incorporation of SAPs has already been elucidated, since there is an increase in the porosity that, consequently, would decrease the mechanical strength, durability and density of the composites. However, there is a change in the format and distribution of voids, leaving them more spherical, not connected and defined (LURAS et al., 2006). That can influence in increase of the durability, decrease of the density and loss in the resistance (WANG et al., 2013). Besides these characteristics, it is possible to reduce the retraction of the composites and to create self-sealable composites, reducing the infiltration of water from one environment to another (LEE; WONG; BUENFELD, 2016; LIU et al., 2016).

## Conclusion

The use of SAP does not preclude the production of cementitious composites by the extrusion process; however, percentages greater than 1% promote an expansion of the composites after the mixture exits the extruder. It was also possible to conclude that the use of different levels of SAP in addition in the cementitious matrix influences the physical-mechanical properties of cement-based composites produced by extrusion. Water absorption and apparent porosity increased with increasing SAP content, while apparent density decreased with SAP content. The modulus of rupture and modulus of elasticity decreased with increasing SAP content, but the toughness was not altered. SAP percentages greater than or equal to 1% preclude the application of these cementitious composites in the production of corrugated tiles due to loss in mechanical strength. However, it is possible to reduce the density of cementitious composites by 10% with little damage to the mechanical resistance with the use of 0.5% SAP. New research evaluating the durability of these composites, as well as different percentages of SAP in the range of 0.0 to 1.0% is necessary for the production of new information and knowledge on the subject.

## Acknowledgements

Thanks to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Rede Brasileira de Compósitos e

Nanocompósitos Lignocelulósicos (RELIGAR), Federal University of Lavras (UFLA), and Grace Construction Products-BR for the donation of surfactants and superplasticizer used in this research.

## References

American Society for Testing and Materials – ASTM 949-81. Test method for dry and wet bulk density, water absorption, and apparent porosity of thin sections of glass-fiber reinforced concrete. West Conshohocken, 1981.

American Society for Testing and Materials - ASTM C150/C150M-11 Standard Specification for Portland Cement, 2011.

Associação Brasileira de Normas Técnicas (ABNT). NBR 12800: Telha de fibrocimento, tipo pequenas ondas. Rio de Janeiro: ABNT; 1993.

Associação Brasileira de Normas Técnicas. NBR 15498: placa plana cimentícia sem amianto – requisitos e métodos de ensaio. Rio de Janeiro, Brasil, 2007. 26 p.

Brazilian Association of Technical Standards – NBR5733. Cement Portland high early strength, specification, 1983.

Choi P, Yeon JH, Yun UNK. Air-void structure, strength, and permeability of wet-mix shotcrete before and after shotcreting operation: The influences of silica fume and air-entraining agent. Cement and Concrete Composites. 2016;70:69-77.

Farrapo CL. Durabilidade de fibrocimentos reforçados com polpa de sisal após 10 anos de envelhecimento natural. 2015. 87 p. Dissertação (Mestrado em Engenharia de Biomateriais) – Universidade Federal de Lavras, Departamento de Ciências Florestais, Lavras-MG, 2015.

Justs J, Wyrzykowski M, Bajare D, Lura P. Internal curing by superabsorbent polymers in ultra- high performance concrete. Cement and concrete Research 2015;76:82-90.

Kovler K, Jensen OM. Novel techniques for concrete curing. Concrete International 2005;27(9):39-42.

Lee HXD, Wong HS, Buenfeld NR. Self-sealing of cracks in concrete using superabsorbent polymers. Cement and Concrete Research 2016;79:194-208.

Liu H, Bu Y, Sanjayan JG, Nazari A, Shen Z. The application of coated superabsorbent polymer in well cement for plugging the microcrack. Construction and Building Materials 2016;104:72-84.

Lura P, Durand F, Jensen OM. Autogenous strain of cement pastes with superabsorbent polymers. In: “International RILEM Conference on Volume Changes of Hardening Concrete: Testing and Mitigation”, Lyngby, 2006, RILEM Proceedings, PRO 52, O. M. Jensen, P. Lura, K. Kovler (2006) 57-65.

Mehta PK, Monteiro PJM. Concrete: Microstructure, Properties, and Materials. Third ed., McGraw-Hill, New York, 2006.

Rilem Technical Committee 49 TFR. Testing methods for fibre reinforced cement-based composites. Mat Struc 1984;17:441-456.

Santos SF, Tonoli GHD, Savastano Jr. H. Materias-primas e procesos de fabricación para fibrocemento. In: Universidad Politécnica de Valencia, editor. Aprovechamiento de residuos agro-industriales como fuente sostenible de materiales de construcción. España 2011;327-43.

Silva DW, Mendes RF, Freire C, Vilela B, Tonoli GHD, Teixeira RS, Santos SF, Savastano Jr. H. Cementitious composites reinforced with Kraft pulping waste. Key Engin Mater 2016;668:390-8.

Silva DW. Propriedades físico-mecânicas de fibrocimentos reforçados com fibras de eucalipto tratadas térmicamente. 2015. 66 p. Dissertação (Mestrado em Engenharia de Biomateriais) – Universidade Federal de Lavras, Departamento de Ciências Florestais, Lavras-MG, 2015.

Teixeira RS, Tonoli GHD, Santos SF, Fiorelli J, Savastano Jr. H, Lahr RFA. Extruded cement based composites reinforced with sugar cane bagasse fibres. Key Eng Mat 2012;517:450-7.

Tonoli GHD, Belgacem MN, Bras J, Pereira-da-Silva MA, Lahr FR, Savastano Jr. H. Impact of bleaching pine fibre on the fibre/cement interface. J of Materials Science 2012;47:4167-77.

Tonoli GHD, Santos SF, Joaquim AP, Savastano Jr. H. Effect of accelerated carbonation on cementitious roofing tiles reinforced with lignocellulosic fibre. Constru Build Mater 2010;24:193-201.

Tonoli GHD, Savastano Jr. H, Santos SF, Dias CM, John VM, Larh FAR. Hybrid reinforcement of sisal and polypropylene fibres in cement-based composites. J Mat Civil Eng 2011;23:177-87.

Tramfloc. Inc. Super Absorbent Polymers for Water Retention and Erosion Control. 2007. Disponível em: <http://www.tramfloc.com/tf62.html>. Página visualizada em maio de 2018.

Wang JY, Chia KS, Liew JYR, Zhang MH. Flexural performance of fiber-reinforced ultra lightweight cement composites with low fiber content. Cement and Concrete Composites 2013;43:30-47.

# MANUSCRITO 2 - IMPACT OF THE ADDITION OF SUPERABSORVENT POLYMER IN THE PERFORMANCE OF EXTRUDED CEMENT COMPOSITES SUBMITTED TO AGING CYCLES

Manuscript to be submitted to Construction and Building Materials (2018). Can be modified according the suggestions of the reviewers.

Danillo Wisky Silva [a*], Alan Pereira Vilela [a], Saulo Rocha Ferreira [b], Camila Soares Fonseca [b], Maria Alice Martins [c], Juliano Elvis Oliveira [b], Gustavo Henrique Denzin Tonoli [a], Lourival Marin Mendes [a]

[a] Federal University of Lavras, Department of Forestry Sciences, Campus Universitário, Caixa postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil. *danilowisky@hotmail.com (corresponding author)

[b] Federal University of Lavras, Department of Engineered, Campus Universitário, Caixa postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil.

[c] LNNA, Brazilian Agricultural Research Corporation (EMBRAPA Instrumentação), Rua XV de Novembro, 1452, caixa postal 741, CEP 13565-970, São Carlos, São Paulo, Brazil.

## Abstract

The aim of this research was to evaluate the impact of the addition of superabsorbent polymer (SAP) on extruded cemented matrixes subjected to accelerated aging. A simple cement matrix (70% cement and 30% limestone) was used. In the composites was added 0.5 to 2.0% SAP per cement matrix mass and compared with Control (0.0% SAP) and fiber-cement (5% pulp in the SAP-free matrix). The composites were tested after 28 days of curing in a wet room (99% RH) and after 30 cycles of accelerated aging. The physical properties were evaluated by water absorption (WA), porosity (VA) and apparent density (BD). Three-point bending test was performed. The results indicate a gradual increase of WA and AV with the increase of SAP. On the other hand, a decrease in DB was observed. A decrease in mechanical strength was also observed with increasing SAP concentration, however, there was no interference in the tenacity (TO) of the composites. The composites with 0.5% of SAP presented mechanical strength similar to fiber reinforcement, however, they did not present reinforcement characteristics (TO equal to fiber less composites). After aging, there was a general reduction of the physical-mechanical properties of the composites. Only the density presented gains and the modulus of elasticity was similar to the non-aged composites. In general, the use of SAP in cementitious matrices decreases the mechanical resistance due to the formation of voids, however, it presents similar degradation when exposed to accelerated aging. The fiber-cements presented higher resistance to aging compared to non-reinforced composites with fibers.

**Keywords:** Cement microstructure, physical-mechanical properties, polyacrylamide, accelerated aging.

## Introduction

According to Teixeira et al. (2012), the extrusion process allows the production of cohesive cementitious composites, forcing them through the matrix (mouthpiece) that can be adjusted to various shapes configurations (flat, structural, hollow). In addition to the low cost of implantation, one of the main advantages of this method of production is the possibility of incorporating a variety of residual materials, including lignocellulosic fibers (SANTOS et al., 2011). These characteristics have encouraged the development of numerous researches aimed production of extruded fiber cement reinforced with vegetable fibers (SANTOS et al., 2014; SILVA et al., 2016; FONSECA et al., 2016, CORREA et al., 2018). Due to the pressure exerted on the molding, the extruded cementitious composites have an apparent density varying from 1,500 to 1,900 kg.m-3 (SILVA et al., 2016; FONSECA et al., 2016, CORREA et al., 2018). However, fiber cement produced by other processes have an apparent density ranging from 1,100 to 1,400 kg.m-3 (TONOLI et al., 2010; PIZZOL et al., 2014; TONOLI et al., 2016).

Superabsorbent polymers (SAP) may be an alternative to decrease the density of these composites. These SAPs, also known as hydrogels, are crosslinked polymers which have the ability to absorb a disproportionately large amount of liquids (500 to 1500 times their weight), expand and retain these liquids in the spaces between the polymer chains and cross-links without being dissolved in solution (SNOECK et al., 2014; MECHTCHERINE; REINHARDT, 2012; LEE et al., 2016). The main application of SAP is personal hygiene products (diapers). Other uses include biomedical (bandages), pharmaceutical (drug delivery), agricultural (soil conditioning), waste solidification, meat packaging and water blocking tapes for undersea cables (LEE et al., 2016; BUCHHOLZ; GRAHAM, 1998). Studies with SAPs in cementitious matrices are largely focused on reducing autogenous contraction through internal cure (JENSEN; HANSEN, 2001; JENSEN; HANSEN, 2002; SCHROEFL et al., 2012; HASHOLT et al., 2012; SOLIMAN; NEHDI, 2013), increased durability against freezing and thawing (MONNIG; LURA, 2007; MONNIG, 2005), autogenous scarring (LEE et al., 2010; SNEECK et al., 2012), and as an alternative method of incorporating air (RIYAZI et al., 2018), for concretes and mortars.

However, information about behavior of SAPs in mechanical properties, pore formation, and the durability of extruded cementitious matrices is scarce. The durability of cement matrices is related in part to the formation of microcracks from the autogenous contraction (HASHOLT et al., 2012; SOLIMAN; NEHDI, 2013), internal pressures caused by freezing and thawing of water inside the cement matrix (YANTURINA et al., 2017; POGOROLEV; SEMENYAK, 2016), dimensional stability and degradation of reinforcement materials (TONOLI et al., 2016), exposure to environmental, among others. The accelerated aging test to simulate natural aging with exposure to UV-B irradiation cycles, water spray and vapor condensation can contribute to the generation of information about the changes promoted by the composition in mineralogical phase, formation of microcracks and degradation of other materials inside in matrix. Understanding these degradation processes may allow new strategies to predict the evolution of microstructure and properties and, ultimately, microstructure and overall performance. The aim of this research was to evaluate the impact of the addition of superabsorbent polymer (SAP) on extruded cemented matrixes subjected to accelerated aging.

## Materials and methods

### *Materials*

The bleached eucalyptus pulp by Kraft process, was obtained by an industrial unit of Klabin, São Paulo / SP, Brazil. Physical and chemical characteristics of the bleached eucalyptus pulp are showed in Table 1.

Table 1 – Physical and chemical characteristics of the eucalyptus pulp (RAABE et al., 2018).

| | |
|---|---|
| Length (µm) | 650.00 |
| Fiber diameter (µm) | 16.60 |
| Aspect ratio | 39.10 |
| ISO whiteness (%) | 90.90 |
| Extractives in acetone (%) | 0.09 |
| Ash (%) | 0.30 |
| Water retention index (%) | 152.00 |
| Apparent density (kg.m$^{-3}$) | 800.00 |

A matrix with mix design of 1:0.5:0.3 (binder: filler: water/binder) by weight was used. The cementitious matrix consisted of cement CPV ARI (ABNT, 1983), corresponding to ASTM-C150, Type I (ASTM, 2011) and filler limestone. Ordinary Portland cement was selected because of its finer particles size and higher reactivity. Additionally, this type of cement contains higher levels of tricalcium silicate ($C_3S$) and dicalcium silicate ($C_2S$) for the formation of C-S-H. The main chemical and physical characteristics of these cement and filler limestone can be observed in Santos et al. (2014). To assist in the extrusion process, two rheological modifiers, Hydroxypropyl methylcellulose (HPMC) and polyether carboxylic acid (ADVA 175) supplied by the multinational company Grace Construction Products-BR.

The super absorbent polymer (SAP) to be used in the cementitious matrix has in its basic composition polyacrylamide and potassium acrylate (see Table 2), this polymer was supplied by the company Hydroplan EB.

Table 2 – Superabsorbent polymer physical characteristics.

| | |
|---|---|
| Appearance | White powder |
| Particle Size | < 1 mm |
| Ionic characteristics | Anionic |
| Active ingredient (% solid content) | 100 |
| Solubility | Insoluble in water |
| Theoretical absorption (g for 1g) | 500 |
| Practical Absorption (g to 1g) | 350 |
| Specific weight (in g / $cm^3$) | 1.0 |
| Absorption time to 60% equilibrium (in minutes) | 30 |

It is expected that this polymer presents air incorporation characteristics, seeking to reduce the bulk density of the cementitious composites.

### *Extrusion of the cement-based composites*

Prior to the composite production process, SAP was hydrated in deionized water; the amount of water to be used was 0.40 in relation to the mass of the cement. The hydration process consisted in adding the SAP in the water, where it remained at rest for 6 hours to guarantee the total hydration of the polymer, according to previous pre-tests.

The cementitious matrix consisted of cement CPV ARI [ABNT, 1983] and filler limestone. The mixture for extrusion was prepared with the addition of 1% (by mass) of rheology modifiers: hydroxypropyl-methylcellulose (HPMC) and self-compacting additive for concrete polyether carboxylic (commercially named ADVA 175 and provided by Grace-BR). The final water:cement ratio was of around 0.40. The dry powders (cement, filler and

HPMC) were mixed together in a planetary mixer for 10 minutes, and then the pulp and hydrated SAP were gradually added in order to obtain a good distribution into the mixture. The ADVA was mixed with water (ratio was around 0.1) and subsequently added to the mixture until the final stage of the mixing process, which took about 5 min. Then, the mass was introduced in the helical extruder for obtaining the extruded composites with 20 x 30 x 200 mm nominal dimensions. The composites were produced on a laboratory scale by extrusion (Figure 1) in a VERDES 051 model helical extruder. The mix-design formulations of the composites are described in Table 3. Seven replicates were produced for each treatment.

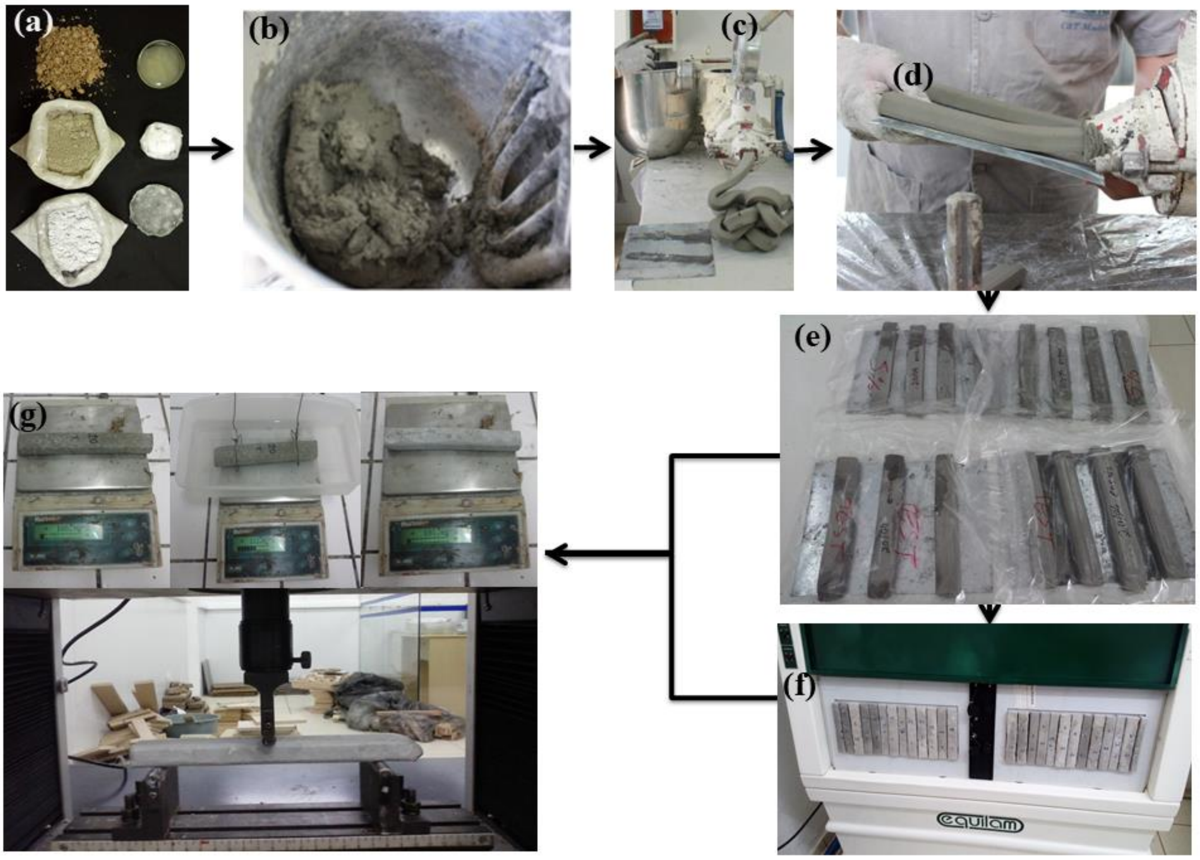


Figure 1 – (a) Materials used; (b) mixing of materials for 10 minutes; (c) one cycle of mixing through extruder for homogenization; (d) production of extruded composites; (e) curing of the composites for 28 days in a humidity saturated (>95%) environment; (f) accelerated aging cycles; (g) evaluation of physical and mechanical properties after 28 days of cure and after 30 cycles of accelerated aging.

Table 3 – Experimental design of the extruded cement composites.

| Treatments | Cement | Limestone | SAP | Pulp |
|---|---|---|---|---|
| | ---------------------- | (% in mass) | -------------------- | |
| Control | 70.00 | 30.00 | - | - |
| SAP 0.5 | 69.65 | 29.85 | 0.50 | - |
| SAP 1.0 | 69.30 | 29.70 | 1.00 | - |
| SAP 1.5 | 68.95 | 29.55 | 1.50 | - |
| SAP 2.0 | 68.60 | 29.40 | 2.00 | - |
| Pulp | 66.50 | 28.50 | - | 5.00 |

*Accelerated ageing cycles*

Accelerated aging is intended to simulate the eventual degradation of materials by prolonged exposure to natural elements. For such treatment, an accelerated aging chamber was used through was to perform exposure cycles simulating solar irradiation, rainfall and dew. The accelerated aging cycle was adapted from ASTM G154-6 (ASTM, 2006) for coating materials (Test type 5) and corresponds to 19:30 hours of irradiation in a UV-B 313 lamp, with 0.62 W / m² / nm irradiance and 80 ° C; 0:15 hours of spray and UV-B 313 with 0.62 W / m² / nm of irradiation and 25 ° C; 4:00 hours of condensation of steam at 50 ° C; and 0:15 hours spray at 25 ° C, totaling 24 hours. In total, a total of 30 aging cycles per treatment were performed.

*Thermogravimetry analysis (TG)*

To verify the effect of the addition of SAP on the carbonation of the composites to the non-aging and after 30 aging cycles, thermogravimetric (TG) analysis was recorded with a Netzsch equipment with STA 409 simultaneous analysis system using 30 mg samples and a dynamic nitrogen stream (flow rate = 100 $cm^3$/min) at a heating rate of 10°C/min. It was used the same mass (around 30 mg) for all samples, in order to reduce inaccurate results from heterogeneous mass quantity (HOPPE FILHO, 2008; TAYLOR, 1997).

*Scanning Electron Microscopy (SEM)*

The micro structural properties of cementitious composites were evaluated after 28 days of cure and after accelerated aging. The analyses were performed on the rupture surface of the plates that were tested by static bending. This observation aims to evaluate the effect of SAP on physical-mechanical properties. The composites samples were coated with golden conducting films in the vacuum coating machine using the vaporization method. The SEM (JEOL® JMS – 6510 type) was employed to observe the samples microstructures. In this experiment, the interface between the SAP and cement matrix was located under the center of the SEM so that the interfacial transition zone would be observable.

### *Physical-mechanical characterization of the composites and data analysis*

Apparent porosity (AP), bulk density (BD), and water absorption (WA) of the composites were determined following the procedures described in ASTM C 948-81 (1981) standard. Mechanical test was performed using the universal testing machine EMIC DL30000 equipped with a 0.5 kN load cell. Three-point bending was performed. Modulus of rupture (MOR), modulus of elasticity (MOE), limit of proportionality (LOP) and toughness (TO) were evaluated (RILEM, 1984) and are described in detail in previous works (TONOLI et al., 2010; TONOLI et al., 2011). Data analysis was performed using a randomized design. The ANOVA and the Scott-Knott mean test were performed at 5% of significance.

## Results and discussion

### *Thermogravimetric analysis (TG/DTG)*

Fig. 2 depict the differential weight loss on the thermogravimetric (TG) curves of the composites at the different of air-entraining types and dosages. Endothermic effects can be identified in the three main zones of decomposition: 50–250 °C (hydrated phases), 400–450 °C (portlandite) and 500–800 °C (carbonates) and weight losses are respectively summarized in Table 4.

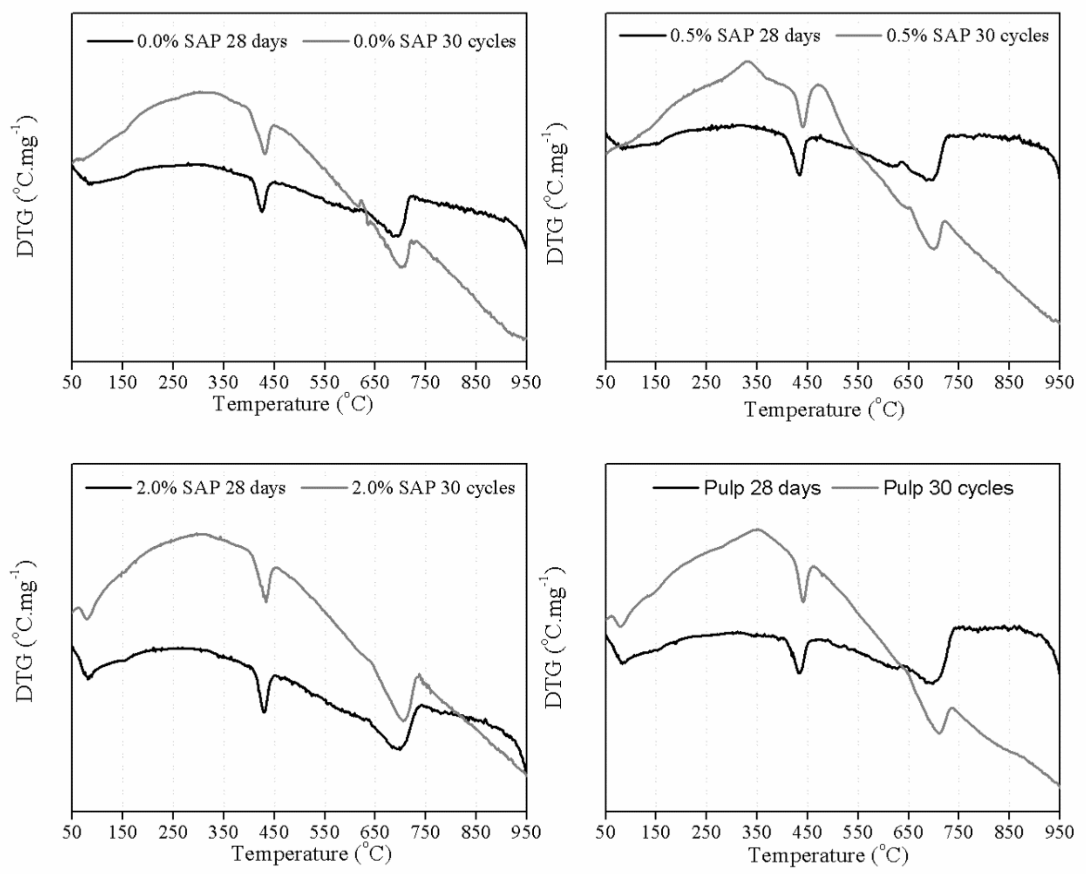


Figure 2. DTG curves of the fiber-cements composites. Before aging and after 30 accelerated ageing cycles.

Table 4. Weight loss of the composites in three different temperature ranges.

| | All hydrated phases | Portlandite [$Ca(OH)_2$] | Calcite ($CaCO_3$) |
|---|---|---|---|
| Composites | 50-250 °C | 400-450 °C | 500-800 °C |
| | ----------------------------------------- Weight loss (%) ------------------------- | | |
| Control | 6.4 | 8.4 | 40.7 |
| Control Env | 6.3 | 9.3 | 35.3 |
| SAP 0.5 | 8.8 | 11,7 | 41.3 |
| SAP 0.5 Env | 6.8 | 9.6 | 38.9 |
| SAP 2.0 | 7.2 | 9.1 | 37.3 |
| SAP 2.0 Env | 7.9 | 9.1 | 37.2 |
| Pulp | 8.2 | 10.5 | 39.8 |
| Pulp Env | 8.2 | 10.1 | 37.31 |

### *Physical properties of the composites*

Fig. 3 describes the influence of hydrated SAP concentration on the physical properties of cementitious composites after 28 days of curing and after 30 cycles of accelerated aging.

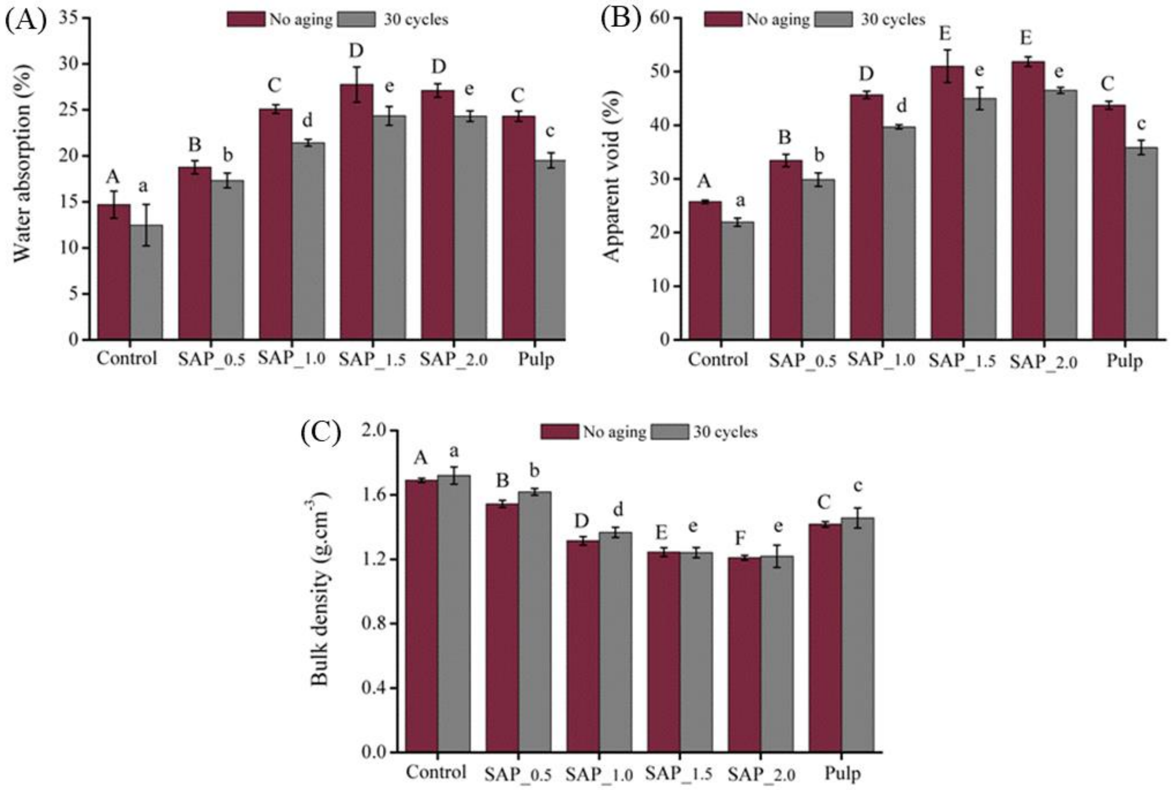


Figure 3 – Average and standard deviation values of: (A) water absorption, (B) apparent void, and (C) bulk density in cementitious composites with the addition of SAP samples at 28 days and 30 accelerated ageing cycles.

Water absorption (27.7 to 88.7% higher) and apparent void (29.8 to 101.3% higher) increased substantially as a function of the hydrated SAP concentration in the cementitious matrix. In contrast, a decrease in apparent density (8.6 to 28.4% lower) occurred in composites containing SAP hydrated (Fig. 3). This is mainly due to the physical mechanism of retraction of the polymer at its original size, after SAP loses water to the medium. As a result was observed, an increasing of AV and WA and a decrease of DB as a function of voids formation. The fact that the basic density of the SAP is substantially lower than the density of the cementitious matrix also corroborates in the explanation of the results (WANG et al., 2013; JUSTS et al., 2015). The physical properties of the composite SAP_1.0 were similar to the fiber cement (Pulp). However, in the micrographs (SEM) of the fracture large voids (arrow 1 in Fig. 4c and arrow 2 in Fig. 4d) are visible in the composites with SAP, these voids are not visible in the fiber cement (arrow 4 in Fig. 4b).

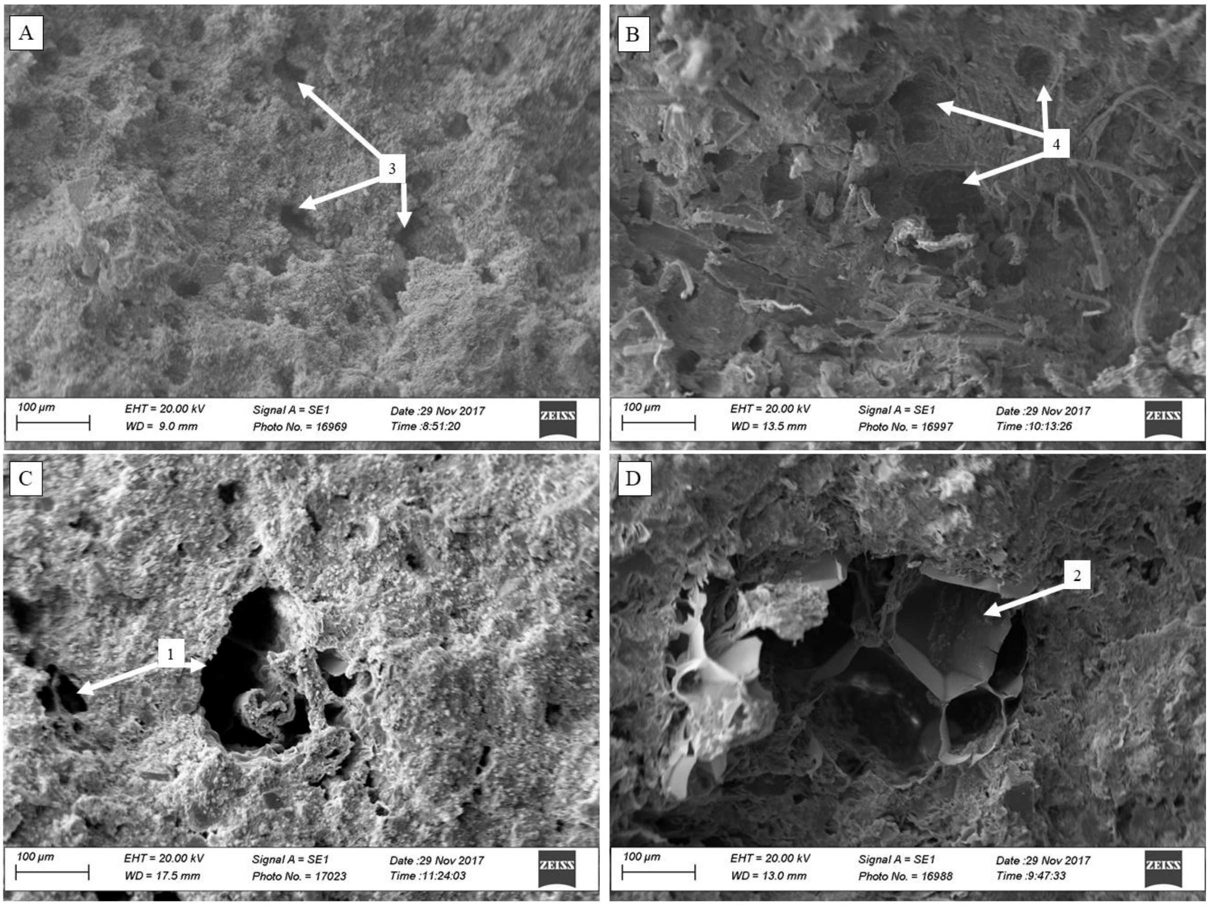


Figure 4 – Scanning electron microscopy (SEM) micrographs of the surface of fracture of test specimens at non-aging: (A) Control; (B) Pulp; (C) 0.5% of SAP; and (D) 2.0% of SAP.

The cementitious composites presented the same behavior for WA, AV and DB, after the 30 cycles of accelerated aging. However, there was a decrease in WA and AV and a brief increase in BD of composites in general. In arrow 4 of the Fig. 5d it is possible to verify the filling of the pores with AFt needles after the 30 aging cycles. According to Tonoli et al. (2010) and Pizzol et al. (2014), in the accelerated aging occurs a reintroduction of water in the cement matrix after the curing period, which reactivates the dissolution of ions (mainly $Ca^{2+}$) of anhydrous grains and less stable cement phases such as $Ca(OH)_2$. As a result, these ions are transported and reprecipitated in the porous regions of the cementitious matrix. Thus, accelerated aging cycles promote the continued hydration of the composite, and consequent densification of the matrix.

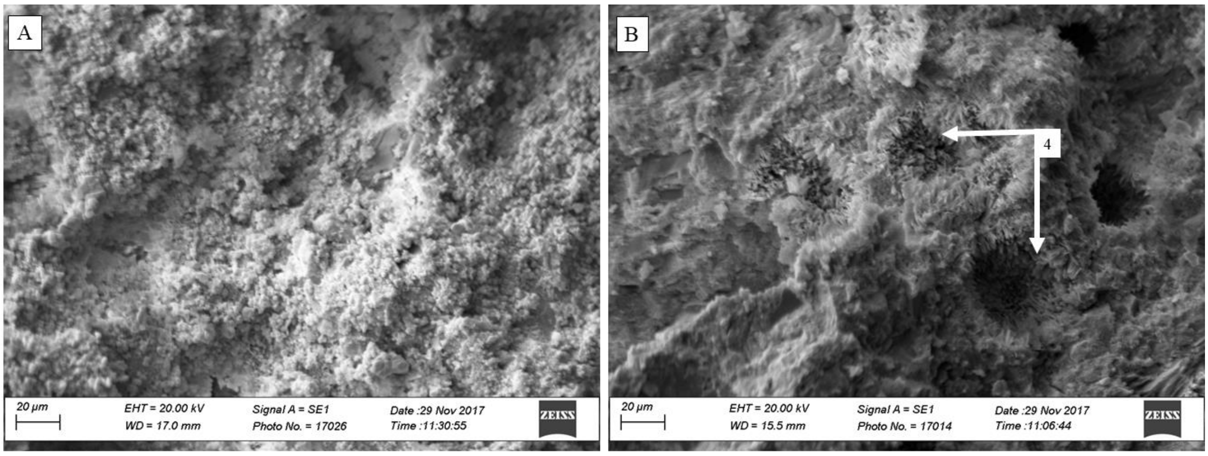


Figure 5 – Scanning electron microscopy (SEM) micrographs of the surface of fracture of Control composite. (A) non-aging; and (B) after 30 cycles of accelerated aging.

*Mechanical properties of the composites*

Fig. 6 describes the influence of hydrated SAP concentration on the mechanical properties of cementitious composites after 28 days of curing and after 30 cycles of accelerated aging.

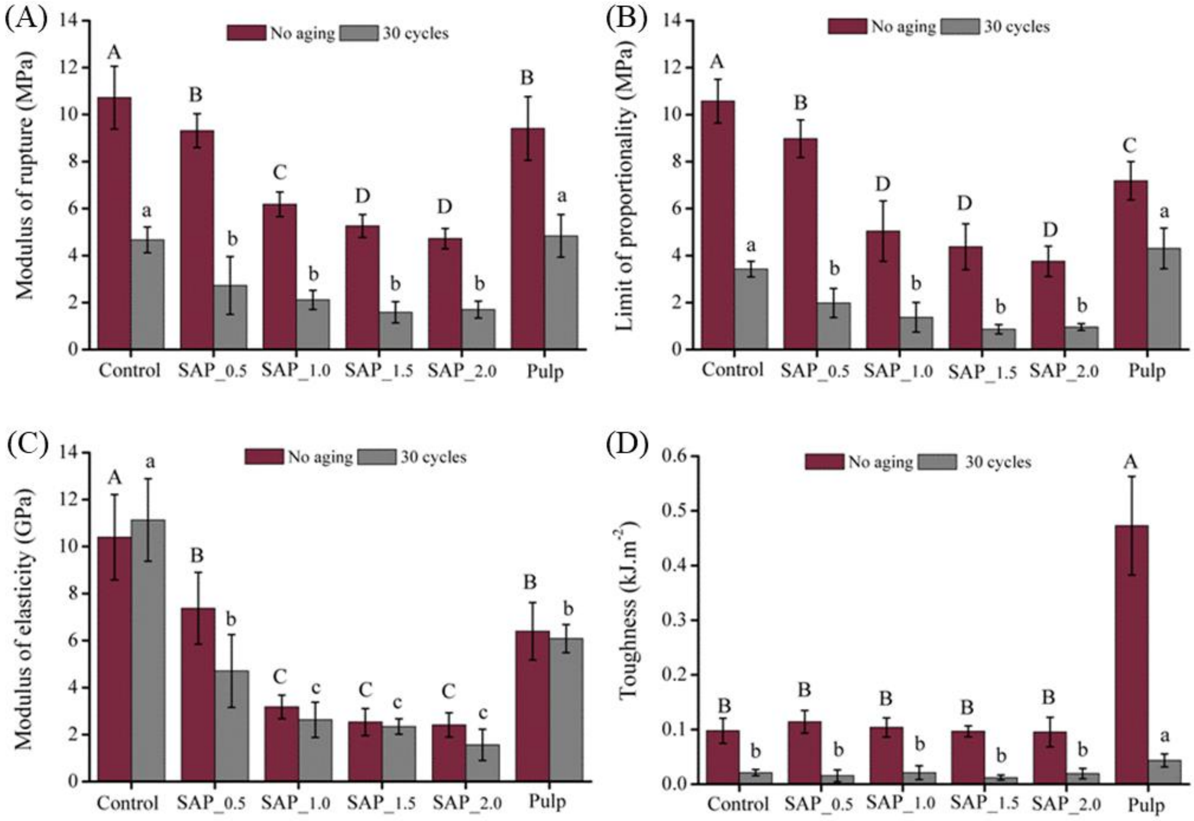


Figure 6 – Average and standard deviation values of: (A) modulus of rupture, (B) proportionality limit, (C) modulus of elasticity, and (D) toughness in cementitious composites with the addition of SAP samples at 28 days and 30 accelerated ageing cycles.

The increase of the SAP content led to a significant decrease of modulus of rupture (13.1 to 55.9% lower), limit of proportionality (15.2 to 64.5% lower) and modulus of elasticity (29.1 to 76.8% lower) and did not modified of the toughness of the composites at 28 days of cure (see Figure 6). The lower mechanical strength of the composites with hydrated SAP is related to the increase of porosity (Fig. 3) and formation of large voids that can be observed in Fig. 4c and d. For the mechanical properties of cement matrices are directly influenced by pore volume, size and morphology (JENNINGS et al., 2008). The relationship between porosity and strength in cement composites is inverse, where, in general, pores are damaging to force (CORREIA et al., 2018). Another aspect elucidated in the literature is the low mechanical resistance of the SAP particle in comparison to the cement grain which also provide loss in mechanical resistance of the composites (LURAS et al., 2006). Among the composites with hydrated SAP, SAP_0.5 was the one that presented mechanical resistance similar to fiber cement (Pulp). However, it is important to point out that SAP presents no reinforcement characteristics (Fig. 6d), unlike cellulosic fibers that act on the fracture of the composite through debond, pull-out, bridging and fracture mechanisms of the fibers.

As cement hydration and carbonation continues during accelerated aging, the apparent porosity decreases due the filling of permeable pores (Fig. 5) with the hydration products and natural carbonation. Thus, the aged matrices of SAP composites and of fiber cement were densified (Fig. 3) and consequently, presented a higher stiffness, which is certified by increasing the MOE results. However, a substantial decrease in MOR, LOP and TO was also observed, even with the densification of the microstructure of the cementitious matrix. Likely, the loss of mechanical resistance (MOR, LOP and TO) is related to defects (microcracks) caused by fatigue during the accelerated aging cycles. These defects, observed by Correia et al. (2018), in immersion and drying cycles. The fact that the rain simulation (water at 25°C) causes a thermal shock in the composites that are on the effect of UV-B irradiation with a temperature of 80 °C, also influences the generation of microcracks and the loss of resistance. In fiber cement the loss of mechanical strength (MOR, LOP and TO) is also related to the fiber mineralization process, as can be observed in arrow 3 of the Fig. 7. This process consists of the accumulation of reprecipitates of the cement phases in the cell walls of the fibers and inside of the internal cavities of the fibers, making them fragile and brittle (MOHR et al., 2005; MOHR et al., 2006).

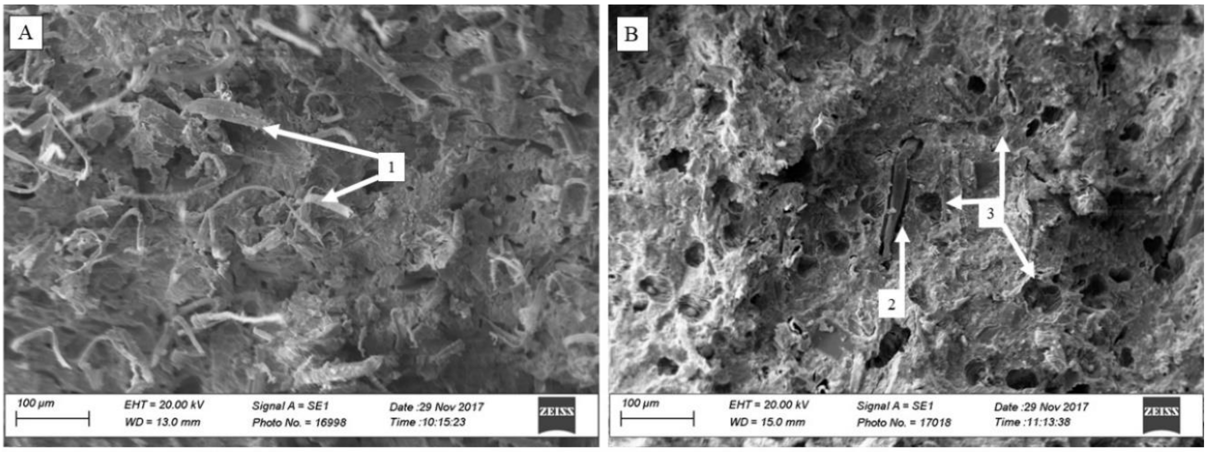


Figure 7 – Scanning electron microscopy (SEM) micrographs of the surface of fracture of Pulp composite. (A) non-aging; and (B) after 30 cycles of accelerated aging.

## Conclusion

The results of this work showed that, in general, at 28 days the extruded composites with addition of hydrated SAP influenced the microstructure of cement phases. Due to the loss of water and consequent contraction of the polymers inside the cementitious matrix, large voids were formed. As a result, there was an increase in the WA and AV properties and a decrease in DB, MOR, MOE and LOP properties. The different concentrations of SAP did not influence TO property. After the aging cycles there was a general decrease in WA, AV, MOR, LOP and TO properties and a small increase in BD. However, the EOM did not show major changes. Among the evaluated composites, the fiber cement obtained lower losses in the mechanical resistance, even with the mineralization and degradation of the cellulosic fibers.

In general, the behavior of the composites with SAP before the aging cycles were similar to the Control composites. However, due to the presence of voids and pores, these composites presented a substantial decrease in mechanical strength, which restricts their applications to materials subjected to small loads. The use of SAP matrices in the production of asbestos cement by extrusion may be interesting, however, characterization studies are required

## Acknowledgements

Thanks to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Rede Brasileira de Compósitos e Nanocompósitos Lignocelulósicos (RELIGAR), Federal University of Lavras (UFLA), and Grace Construction Products-BR for the donation of surfactants and superplasticizer used in this research.

## References

American Society for Testing and Materials – ASTM 949-81. Test method for dry and wet bulk density, water absorption, and apparent porosity of thin sections of glass-fiber reinforced concrete. West Conshohocken, 1981.

American Society for Testing and Materials - ASTM C150/C150M-11 Standard Specification for Portland Cement, 2011

American Society for Testing and Materials – ASTM G 154-6. Standard practice for operating fluorescent light apparatus for UV exposure of Nonmetallic materials. West Conshohocken, 2006.

Bezerra EM, Joaquim AP, Savastano Jr. H, John VM, Agopyan V. The effect of different mineral additions and synthetic fiber contents on properties of cement based composites. Cement & Concrete Composites. 28 (2006) 555-563.

Brazilian Association of Technical Standards – NBR5733. Cement Portland high early strength, specification, 1983.

Buchholz FL, Graham AT. (Eds.), Modern Superabsorbent Polymer Technology, WILEY-VCH, New York, 1998.

Correia VdaC, Santos SF, Teixeira RS, Savastano Jr H. Nanofibrillated celulose and cellulosic pulp for reinforcement of the extruded cement based materials. Construction and Building Materials 2018;160:376-84.

Fonseca CS, Silva TFDA, Silva MT, Oliveira IRC, Mendes RF, Hein PRG, Mendes LM, Tonoli GHD. Micro/nanofibrilas celulósicas de Eucalyptus em fibrocimento extrudados. Cerne, v. 22, n. 1, p. 59-68, 2016.

Hasholt MT, Jensen OM, Kovler K, Zhutovsky S. Can superabsorbent polymers mitigate autogenous shrinkage of internally cured concrete without compromising the strength?, Constr Build. Mater. 2012;31:226–30.

Hoppe Filho J (2008) Sistemas cimento, cinza volante e cal hidratada: mecanismo de hidratação, microestrutura e carbonatação de concreto. Tese (Doutorado em Engenharia Civil) — Escola de Engenharia, Universidade de São Paulo, São Paulo (in Portuguese).

Jennings HM, Bullard JW, Thomas JJ, Andrade JE, Chen JJ, Scherer GW. Characterization and Modeling of Pores and Surfaces in Cement Paste: Correlations to Processing and Properties, J. Adv. Concr. Technol. 2008;6:5–29.

Jensen OM, Hansen PF. Water-entrained cement-based materials: I. Principles and theoretical background, Cem. Concr. Res. 2001;31(4):647–54.

Jensen OM, Hansen PF. Water-entrained cement-based materials: II. Experimental observations, Cem. Concr. Res. 2002;32(6):973–8.

Justs J, Wyrzykowski M, Bajare D, Lura P. Internal curing by superabsorbent polymers in ultra- high performance concrete. Cement and concrete Research 2015;76:82-90.

Lee HXD, Wong HS, Buenfeld NR. Potential of superabsorbent polymer for self-sealing cracks in concrete, Adv. Appl. Ceram. 2010;109:296–302.

Lee HXD, Wong HS, Buenfeld NR. Self-sealing of cracks in concrete using superabsorbent polymers. Cement and Concrete Research 2016;79:194-208.

Mechtcherine V, Reinhardt H. Application of Super Absorbent Polymers (SAP) in Concrete Construction, State-of-the-Art Rep., Springer, 2012.

Mönnig S, Lura P. Superabsorbent polymers – an additive to increase the freeze-thaw resistance of high strength concrete, in: C.U. Grosse (Ed.), Advances in Construction Materials, Springer Berlin Heidelberg, Berlin, 2007:351–8.

Mönnig S. Water saturated super-absorbent polymers used in high strength concrete, Otto-Graf J. 2005;16:193–202.

Mohr BJ, Biernacki JJ, Kurtis KE. Microstructural and chemical effects of wet/dry cycling on pulp fiber–cement composites. Cement and Concrete Research 2006;36(7):1240-51.

Mohr BJ, Nanko H, Kurtis KE. Durability of kraft pulp fiber-cement composites to wet/dry cycling. Cem Concr Compos 2005;27:435-48.

Pizzol VD, Mendes LM, Savastano Jr H, Frías M, Davila FJ, Cincotto MA, John VM, Tonoli GHD. Mineralogical and microstructural changes promoted by accelerated carbonation and ageing cycles of hybrid fiber-cement composites. Construction and Building Materials 2014;68:750-6.

Pogorolov SN, Semenyak GS. Frost resistence of the steel fiber reinforced concrete containing active mineral additives. Procedia Engineering 2016;150:1491-95.

Raabe J, Santos LPdos, Del Menezzi CHS, Tonoli GHD. Effect of nano-silica deposition on cellulose fibers on the initial hydration of the Portland cement. BioResources 2018;13(2):3525-44.

Rilem Technical Committee 49 TFR. Testing methods for fibre reinforced cement-based composites. Mat Struc 1984;17:441-456.

Riyazi S, Kevern JT, Mulheron M. Super absorbent polymers (SAPs) as physical air entrainment in cement mortars. Construction and Building Materials 2017;147:669-76.

Santos SF, Rodrigues JdeA, Tonoli GHD, Almeida AEFdeS, Savastano Jr H. Effect of coloidal sílica on the mechanical properties of fiber-cement reinforced with cellulosic fibers. J. Mater. Sci. 2014. DOI 10.1007/s10853-014-8455-1.

Santos SF, Tonoli GHD, Savastano Jr. H. Materias-primas e procesos de fabricación para fibrocemento. In: Universidad Politécnica de Valencia, editor. Aprovechamiento de residuos agro-industriales como fuente sostenible de materiales de construcción. España 2011;327-43.

Schroefl C, Mechtcherine V, Gorges M. Relation between the molecular structure and the efficiency of superabsorbent polymers (SAP) as concrete admixture to mitigate autogenous shrinkage, Cem. Concr. Res. 2012;42:865–73.

Silva DW, Mendes RF, Freire C, Vilela B, Tonoli GHD, Teixeira RS, Santos SF, Savastano Jr. Cementitious composites reinforced with Kraft pulping waste. Key Engin Mater 2016;668:390-8.

Snoeck D, Schaubroeck D, Dubruel P, De Belie N. Effect of high amounts of superabsorbent polymers and additional water on the workability, microstructure and strength of mortars with a water-to-cement ratio of 0.50. Constr. Build. Mater. 2014;72:148–57.

Snoeck D, Steuperaert S, Van Tittelboom K, Dubruel P, De Belie N.Visualization of water penetration in cementitious materials with superabsorbent polymers by means of neutron radiography, Cem. Concr. Res. 2012;42:1113–21.

Soliman AM, Nehdi ML. Effect of partially hydrated cementitious materials and superabsorbent polymer on early-age shrinkage of UHPC, Constr. Build. Mater. 2013;41:270–5.

Taylor HFW (1997) Cement chemistry, 2nd edn. Thomas Telford Pub, London.

Teixeira RS, Tonoli GHD, Santos SF, Fiorelli J, Savastano Jr. H, Lahr RFA. Extruded cement based composites reinforced with sugar cane bagasse fibres. Key Eng Mat 2012;517:450-7.

Tonoli GHD, Belgacem MN, Bras J, Pereira-da-Silva MA, Lahr FR, Savastano Jr. H. Impact of bleaching pine fibre on the fibre/cement interface. J of Materials Science 2012;47:4167-77.

Tonoli GHD, Pizzol VD, Urrea G, Santos SF, Mendes LM, Santos V, John VM, Frías M, Savastano Jr H. Rationalizing the impact of aging on fiber-matrix interface and stability of cement-based composites submitted to carbonation at early ages. J. Mater. Sci. 2016;51:7929-43.

Tonoli GHD, Santos SF, Joaquim AP, Savastano Jr. H. Effect of accelerated carbonation on cementitious roofing tiles reinforced with lignocellulosic fibre. Constru Build Mater 2010;24:193-201.

Tonoli GHD, Savastano Jr. H, Santos SF, Dias CM, John VM, Larh FAR. Hybrid reinforcement of sisal and polypropylene fibres in cement based composites. J Mat Civil Eng 2011;23:177-87.

Wang JY, Chia KS, Liew JYR, Zhang MH. Flexural performance of fiber-reinforced ultra lightweight cement composites with low fiber content. Cement and Concrete Composites 2013;43:30-47.

Yanturina RA, Trofimov BYa, Ahmedjanov RM. The influence of grafite-containing nano-additives on thermo-frost resistence of concrete. Procedia Engineering 2017;206:869-74.

# MANUSCRITO 3 – IMPACT OF DIFFERENT AIR-ENTRAINING ADDITIVES ON THE PROPERTIES OF EXTRUDED FIBER CEMENTS

Manuscript to be submitted to Cement & Concrete Composites (2018). Can be modified according the suggestions of the reviewers.

Danillo Wisky Silva [a*], Alan Pereira Vilela [a], Camila Soares Fonseca [b], Saulo Rocha Ferreira [b], Maria Alice Martins [c], Juliano Elvis Oliveira [b], Gustavo Henrique Denzin Tonoli [a], Lourival Marin Mendes [a]

[a] Federal University of Lavras, Department of Forestry Sciences, Campus Universitário, Caixa postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil. *danilowisky@hotmail.com (corresponding author).

[b] Federal University of Lavras, Department of Engineered, Campus Universitário, Caixa postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil.

[c] LNNA, Brazilian Agricultural Research Corporation (EMBRAPA Instrumentação), Rua XV de Novembro, 1452, caixa postal 741, CEP 13565-970, São Carlos, São Paulo, Brazil.

## Abstract

The objective of this work was to evaluate the impact of air-entraining admixtures (surfactants) and superabsorbent polymer (SAP) on the properties of extruded fibrocement. A simple matrix of cement (70% cement and 30% limestone) reinforced with 3% unbleached eucalypt Kraft pulp was used. In the fiber cement Darafill EXP300 (0.6; 0.8; and 1.2% by mass); Drycast (0.6 and 1.2% by mass); and SAP (0.3; 0.5; and 0.7% by mass); were added and compared with the Control (fiber cement without admixtures). The fiber cements were tested after 28 days of curing in a humid chamber (99% RH). The different additives influenced the microstructure of the cement phases. Commercial surfactants were responsible for increased hydration after 28 days of curing. Fiber cements with 0.7% of SAP presented high $CaCO_3$ rates due to natural carbonation. The commercial surfactants improved the wettability, thus, a smaller number of voids occurred inside the matrix, unlike the fiber cement with SAP that influenced in the increase of these voids. As a consequence of the modification of the cement phases and voids formation, commercial surfactants caused a decrease in water absorption (WA) and porosity (AV) and a gain in mechanical performance. While the use of SAP increased WA and AV and substantially reduced the mechanical performance of fiber cement. In general, surfactants did not incorporate air into the matrix, however, they showed substantial gains in mechanical performance. SAP was effective in incorporating air, however, forming large voids that detracted from the mechanical performance of fiber cement.

**Keywords:** Superabsorbent polymer, surfactants, cement microstructure, unbleached Kraft pulp, extrusion process.

## Introduction

The extrusion process involves the formation of cohesive fiber cement composites, forcing it through the matrix (mouthpiece) that can be adjusted to various shape configurations (TEIXEIRA et al., 2012). The advantage of extrusion is that it is an economical method of mass production capable of producing not only flat shapes, but also structural and hollow forms. This process allows the use of a variety of residual materials that can be successfully incorporated into the matrix, including the use of lignocellulosic fibers as a reinforcement in fiber cement composites (SANTOS et al., 2011). Due to the pressure exerted in the molding, the extrusion produced fiber cements have an apparent density ranging from 1,500 to 1,900 kg.m$^{-3}$ (SILVA et al., 2016; FONSECA et al., 2016; CORREIA et al., 2018), however, fiber cement produced by other processes have an apparent density ranging from 1,100 to 1,400 kg.m$^{-3}$ (TONOLI et al., 2010; PIZZOL et al., 2014; TONOLI et al., 2016).

One way of decreasing the density of the extruded fiber cement would be to incorporate air into the cementitious matrix. The use of air-entraining admixtures (surfactants) in concretes and mortars is already well elucidated. The surfactants introduce small bubbles of air dispersed throughout the matrix (MENDES et al., 2017). These homogeneously distributed microbubbles improve the cohesion and workability of cement-based composites, prevent water penetration, and reduce the tendency for segregation (MEHTA; MONTEIRO, 2014). Surfactants reduce the surface tension of substances due to the balance of forces between their molecules at the interface. In general, the surfactant molecules contain a hydrophobic (or non-polar) chain and one or more hydrophilic (or polar) groups (DU; FOLLIARD, 2005; MENDES et al., 2017). However, it is difficult to predict the behavior of these substances in the extruded fibrocement. Since the cohesive force applied at the time of molding can damage these microbubbles.

The superabsorbent polymers (SAPs) can also be used as air incorporators in cementitious matrixes (RIYAZI et al., 2017). These were first developed in the 1980s and are mainly used in convenience products, food packaging, and sanitary and medical industry eg care articles or smart pills (BUCHHOLZ; GRAHAM, 1998, FRIEDRICH, 2012). SAPs have high water absorption capacity (500 to 1500 times their weight), expansion and retention of liquid in the spaces between the polymer chains and cross-links without being dissolved in solution (SNOECK et al., 2014; MECHTCHERINE; REINHARDT, 2012). Studies with SAPs in cementitious matrices are largely focused on reducing autogenous contraction through internal cure (JENSEN; HANSEN 2001; JENSEN; HANSEN, 2002; SCHROEFL et al., 2012; HASHOLT et al., 2012; SOLIMAN; NEHDI, 2013), increased durability against freezing and thawing (MONNIG; LURA, 2007; MONNIG, 2005), autogenous healing (LEE et al., 2010; SNEECK et al., 2012), among others. There are few researches that aim to use SAPs as an alternative method of incorporating air (RIYAZI et al., 2017).

The effects of surfactants and SAPs on extrusion fiber cements is still scarce. It is an area that requires research to clarify how these additives influence the incorporation of air, the microstructure and the mechanical behavior of the extruded fiber cements. The objective of this work was to evaluate the impact of air-entraining admixtures (surfactants) and superabsorbent polymer (SAP) on the properties of extruded fiber cement.

## Material and methods

### *Raw materials*

The unbleached pulp used in this research was extracted from Eucalyptus spp. (around 7 years old) by Kraft process (Table 1). The pulp was obtained by an industrial unit of Klabin, São Paulo / SP, Brazil.

Table 1 – Average values of the morphological characteristics and chemical components of the eucalyptus fibers (provided by Klabin-BR).

| Characteristics | Values (μm) |
|---|---|
| Length | 782 |
| Diameter | 20.64 |
| Components (%) | Values (%) |
| Ash | 1.07 |
| Total extractives | 0.323 |
| Insoluble lignin | 16.05 |
| Soluble lignin | 2.807 |
| Holocellulose | 79.75 |

A matrix with mix design of 1:0.5:0.4 (binder: filler: water/binder) by weight was used. The binder used was Brazilian ordinary Portland cement CPV ARI (ABNT, 1983), corresponding to ASTM-C150, Type I (ASTM, 2011) and filler limestone (calcium carbonate). Ordinary Portland cement was selected because of its finer particles size and higher reactivity. Additionally, this type of cement contains higher levels of tricalcium silicate ($C_3S$) and dicalcium silicate ($C_2S$) for the formation of C-S-H. The main chemical and physical characteristics of these cement and ground limestone are presented in Santos et al. (2014).

The super absorbent polymer (SAP) to be used in the cementitious matrix has in its basic composition polyacrylamide and potassium acrylate (Table 2), with an absorption capacity of 350 to 500 times its weight in water and can increase its volume by up to 100 times; this SAP was supplied by the company Hydroplan EB. It is expected that this polymer presents air incorporation characteristics, seeking to reduce the apparent density of the cementitious composites.

Table 2 – Superabsorbent polymer physical characteristics.

| | |
|---|---|
| Appearance | White powder |
| Particle Size | < 1 mm |
| Ionic characteristics | Anionic |
| Active ingredient (% solid content) | 100 |
| Solubility | Insoluble in water |
| Theoretical absorption (g for 1g) | 500 |
| Practical Absorption (g to 1g) | 350 |
| Specific weight (in g / $cm^3$) | 1.0 |
| Absorption time to 60% equilibrium (in minutes) | 30 |

Two commercial surfactants from Grace Construction Products-BR (air-entraining) were also tested to decrease the density of the extruded cementitious composites, the Darafill EXP 300 (chemical essence in sodium lauryl ether sulfonate) and the Drycast (chemical essence in sodium lauryl ether sulfonate combined with sodium polycarboxylate).

### *Extrusion of the cement-based composites*

Before the production process of the composites, the SAP will be hydrated in deionized water; the amount of water to be used will be 0.40 in relation to the mass of the cement. The hydration process consists in adding the SAP in water, where it will remain at rest for 6 hours to guarantee the total hydration of the polymer.

The cementitious matrix consisted of cement CPV ARI (ABNT, 1983) and ground agricultural limestone. The mixture for extrusion was prepared with the addition of 1% (by mass) of rheology modifiers: hydroxypropyl-methylcellulose (HPMC) and self- compacting additive for concrete polyether carboxylic (commercially named ADVA 175 and provided by Grace-BR). The final water:cement ratio was of around 0.40. The dry powders (cement, filler and HPMC) were mixed together in a planetary mixer for 5 minutes, and then the unbleached pulp was gradually added in order to obtain a good distribution into the mixture. The ADVA was mixed with water (ratio was around 0.1) and subsequently added to the mixture, the air-entraining agents (SAP, Darafill EXP 300, and Drycast) have also been added, until the final stage of the mixing process which took about 10 min. Then, the mass was introduced in the helical extruder for obtaining the extruded composites with 20 x 30 x 200 mm nominal dimensions.

The composites were produced on a laboratory scale by extrusion in a VERDES 051 model helical extruder. The mix-design formulations of the composites are described in Table 3. Seven replicates were produced for each treatment.

Table 3. Experimental plan of treatments

| Treatments | Cement | Limestone | SAP | Pulp | Darafill | Drycast |
|---|---|---|---|---|---|---|
| | ---------------------------------- | ------------ | (% in mass) | ------------ | ---------------------------------- | |
| Control | 70.0 | 30.0 | - | 3.0 | - | - |
| SAP_0.3 | 69.8 | 29.9 | 0.3 | 3.0 | - | - |
| SAP_0.5 | 69.7 | 29.9 | 0.5 | 3.0 | - | - |
| SAP_0.7 | 69.5 | 29.8 | 0.7 | 3.0 | - | - |
| DAF_0.6 | 69.6 | 29.8 | - | 3.0 | 0.6 | - |
| DAF_0.8 | 69.6 | 29.8 | - | 3.0 | 0.8 | - |
| DAF_1.2 | 69.6 | 29.8 | - | 3.0 | 1.2 | - |
| DRY_0.6 | 69.6 | 29.8 | - | 3.0 | - | 0.6 |
| DRY_1.2 | 69.6 | 29.8 | - | 3.0 | - | 1.2 |

*Thermogravimetry analysis (TG)*

To verify the effect of the addition of SAP on the carbonation of the composites to the non-aging and after 30 aging cycles, thermogravimetric (TG) analysis was recorded with a Netzsch equipment with STA 409 simultaneous analysis system using 20 mg samples and a dynamic nitrogen stream (flow rate = 100 $cm^3$/min) at a heating rate of 10 C/min.

### *X-ray tomography (XRT)*

Tomographic scans were performed at the Embrapa Instrumentação Agropecuária, São Carlos - SP, Brazil. Depending on the sample age, the beam energy was set to values from 100 kV, the intensity being kept constant at 100 µA. 1000 projections with an angle step of 0.20° and an exposure time of 2.876 s each were acquired on a Hamamatsu 10Mp camera. The pixel resolution under these conditions was 11.32 µm. Reconstructed slices (tomograms) were computed using the DataViewer. The short exposure times and configuration of the line ensure that there is no significant heating or drying of the sample during the acquisition of the images.

### *Characterization of the composites and data analysis*

Apparent porosity (AP), bulk density (BD), and water absorption (WA) of the composites were determined following the procedures described in ASTM C 948-81 (ASTM, 1981) standard. Mechanical test was performed using the universal testing machine EMIC DL30000 equipped with a 0.5 kN load cell. Three-point bending was performed. Modulus of rupture (MOR), modulus of elasticity (MOE), limit of proportionality (LOP) and toughness (TO) were evaluated (Rilem, 1984) and are described in detail in previous works (Tonoli et al., 2010; Tonoli et al., 2011). Data analysis was performed using a randomized design. The ANOVA and the Scott-Knott mean test were performed at 5% of significance.

## **Results and discussion**

### *Thermogravimetry analysis (TG) and X-ray tomography (XRT)*

Fig. 1 a and b depict the differential weight loss on the thermogravimetric (TG) curves of the composites at the different of air-entraining types and dosages. Endothermic effects can be identified in the three main zones of decomposition: 50–250 °C (hydrated phases), 400–450 °C (portlandite) and 500–800 °C (carbonates) and weight losses are respectively summarized in Table 4. The changes in the weight loss between 90 and 200 °C correspond to the interaction of C–S–H, ettringite ($C_3AS_3H_{32}$-AFt), monosulfoaluminate ($C_3ASH_{12}$-AFm), monocarboaluminate ($C_4AcH_{11}$-Mc) with CO2 as also observed by Almeida et al. (2010;

2013) and Frías and Goñi (2013) adopting different curing conditions and cement matrixes. The variation in air-entraining type and dosage influenced the formation of hydrated phases (50-250 ° C) after 28 days of cure (Table 4).

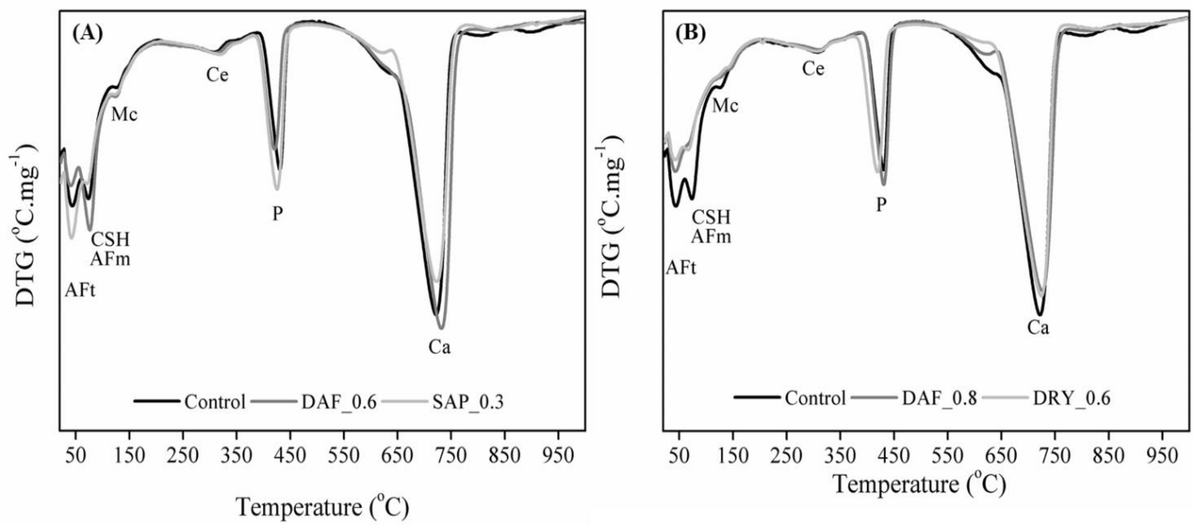


Fig. 1. DTG curves of the fiber-cements composites. (a) Control sample, DAF_0.6, and SAP_0.3; (b) Control sample, DAF_0.8, and DRY_0.6. AFt = ettringite; AFm = monosulfoaluminate; CSH = calcium silicate hydrate; Mc = noncarbonated; Ce = cellulosic pulp; P = portlandite; and Ca = calcite.

Table 4. Weight loss of the composites in three different temperature ranges.

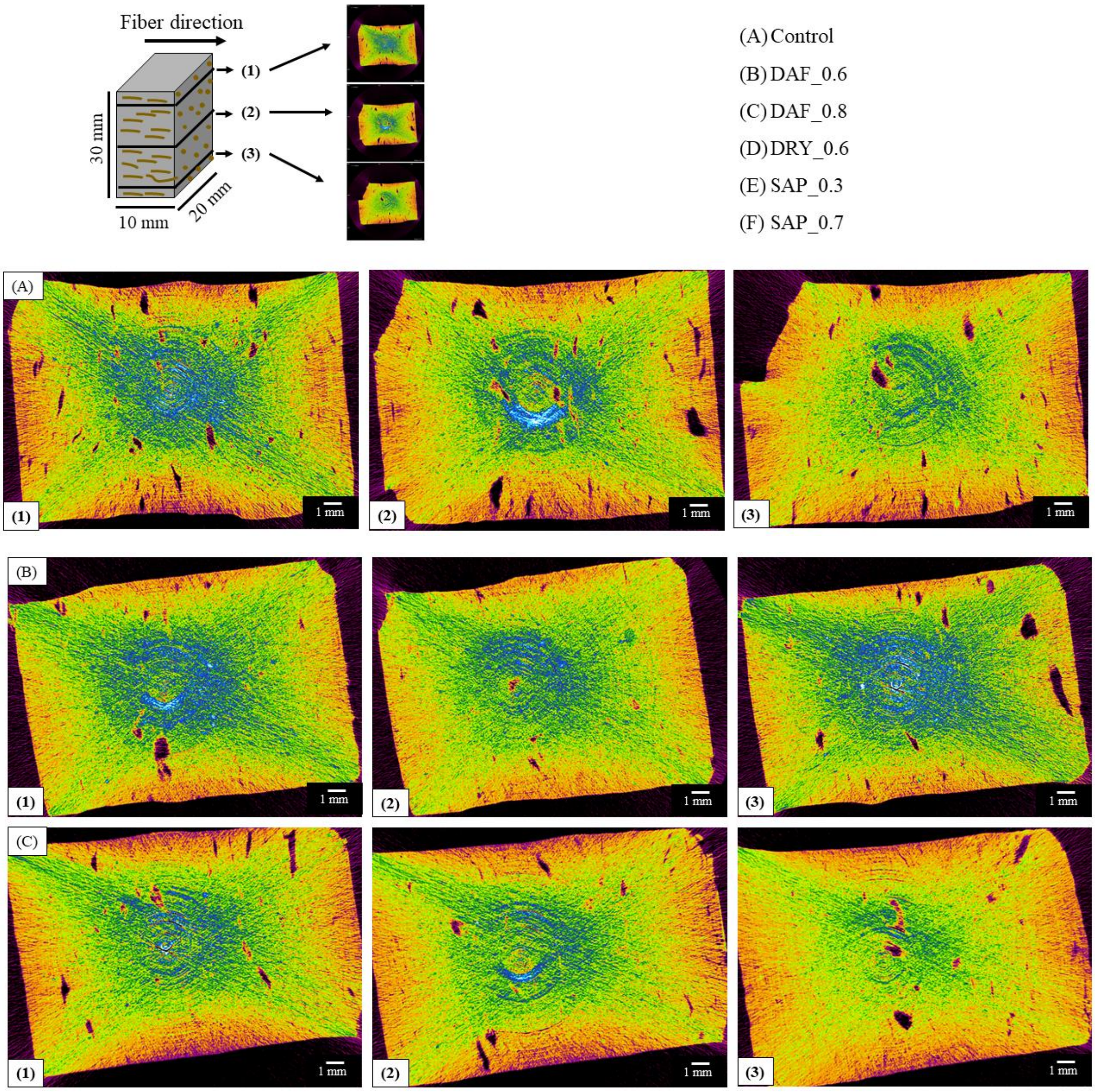
| Composites | All hydrated phases<br>50-250 °C | Portlandite [$Ca(OH)_2$]<br>400-450 °C | Calcite ($CaCO_3$)<br>500-800 °C |
|---|---|---|---|
| | ---------------------------------- Weight loss (%) | | -------------------------- |
| Control* | 11.7 | 11.2 | 38.7 |
| DAF_0.6 | 12.3 | 9.9 | 39.8 |
| DAF_0.8 | 9.8 | 12.8 | 35.3 |
| DAF_1.2 | 9.9 | 12.6 | 34.0 |
| DRY_0.6 | 9.5 | 11.7 | 34.4 |
| DRY_1.2 | 11.0 | 10.0 | 38.8 |
| SAP_0.3 | 12.3 | 13.9 | 34.1 |
| SAP_0.5 | 12.8 | 13.9 | 35.2 |
| SAP_0.7 | 12.0 | 10.2 | 41.5 |

*The darker the shade of gray, the greater the MOR.

In the composites DAF_0.8; DAF_1.2; and DRY_0.6; smaller percentages of the initial phases (50-250 °C) of cement hydration were observed. These results indicate a more effective initial hydration of the anhydrous cement grains in comparison to the control and other treatments, due to an increase of the wettability in these composites. In relation to percentages of portlandite (400-450 °C) and calcite (500-800 °C), composites DAF_0.8; DAF_1.2; and DRY_0.6 also presented close values (Table 4). However, for the other composites it was not possible to observe a pattern.

When the porosity in the fiber–cement is sufficiently high to permit constant $CO_2$ diffusion, the $Ca(OH)_2$ (portlandite) is further reduced and the calcium ions released from C–S–H react with carbon dioxide to form $CaCO_3$ (FERNÁNDEZ-BERTOS et al., 2004). This may explain the higher percentage of calcite ($CaCO_3$) in SAP_0.7 composites due to natural carbonation.

Fig. 2 illustrates the variation in pore size and quantity, of composites from computed tomography (CT) photomicrographs.



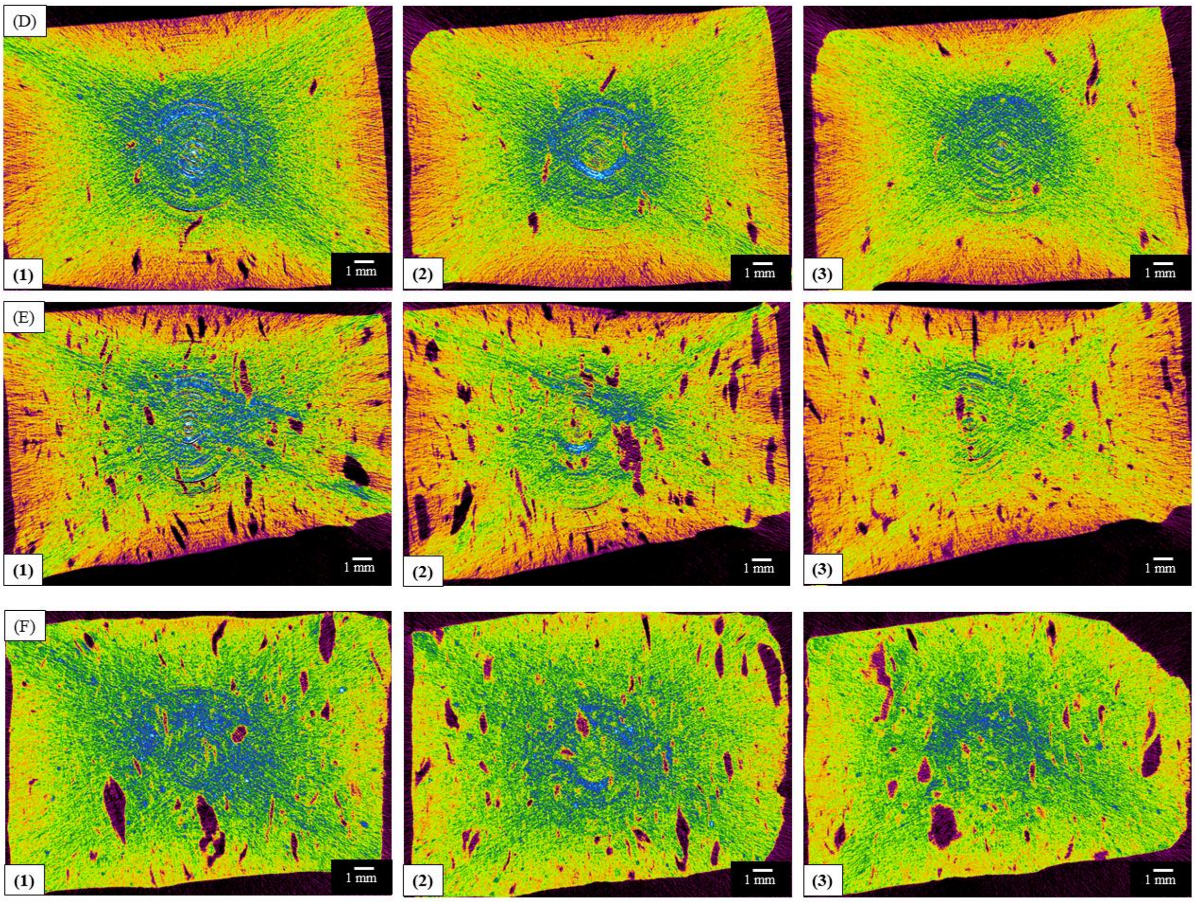


Fig. 2. X-ray tomography of the composites after 28 days of cure. (A) Control; (B) DAF_0.6; (C) DAF_0.8; (D) DRY_0.6; (E) SAP_0.3; and (F) SAP_0.7.

The surfactants facilitate the transfer of the water present in the fibers and limestone to the cement particles, due to their dispersing effect, which in turn improves the workability and wettability of the mixture (ATAHAN et al., 2008; MANGANE et al., 2018). In X-ray tomography images (Fig. 2a, b, c and d), the difference in the number of voids at the macro scale is visible when compared to the Control composite (Fig. 2a). The superabsorbent polymer has a large capacity to expand its volume (100 times) in the hydrated state, returning to its natural size after losing water to the medium. This characteristic was responsible for a significant increase of the voids in macro scale inside the composites (Fig. 2 e and f).

X-ray tomography also made it possible to qualitatively verify a density gradient in the composites. Where the surfaces (in red) are denser than the core (in green) of the fibro-cement, this is due to the compressive force that the extruder promotes at the moment of molding the cement paste. However, the SAP_0.7 composites do not present this densification gradient (Fig. 2f). Due in particular to its greater hydrophilicity compared to the cement particles (JUSTS et al., 2015), promoting an expansion of the composites after extrusion molding. What did not occur in the SAP_0.3 composites (Fig. 2e) because the SAP concentration in the blend was insufficient to overcome the compaction force applied in the extrusion molding. The observed results for the composite SAP_0.7 corroborate with the results of the thermogravimetry, and it helps in the understanding of the theory that the natural carbonation was more intense in these composites.

*Physical properties of the composites*

Fig. 3 shows the variation of water absorption properties (WA), apparent porosity (VA), and bulk density (BD) in the different cementitious composites produced.

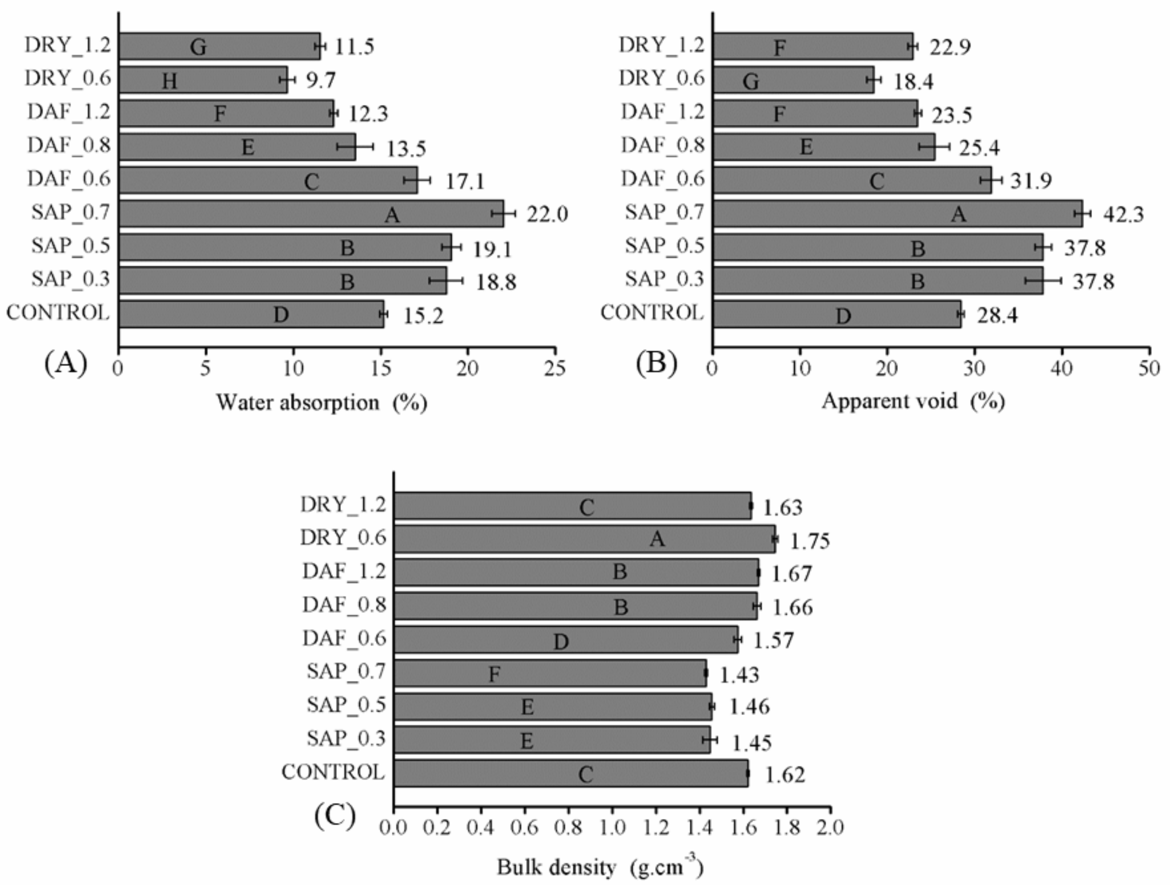


Fig. 3. Average and standard deviation values of: (a) water absorption, (b) apparent void, and (c) bulk density in fiber-cement composites. Means of the same letter do not statistically differ by the Scott-Knott mean test, at 5% of significance.

Air-entraining admixtures contain surface active molecules (surfactant), consisting of a hydrophilic head (polar) and a hydrophobic (radical) tail (MYERS, 2006). The attraction between the water molecules is reduced as the air-entraining molecules are inserted in between. Bubbles are formed as the surface tension is lowered and the bubbles are stabilized against physical deformation (SAHIN et al., 2017). The air-entraining from SAP occurs by physical mechanism, the hydrated (expanded) polymer inside the cement matrix releases water into the medium, returning to its original size, thus forming the voids.

The use of 0.6% of Darafill EXP 300 in the extruded fibrocement allowed a minimum increase in porosity (12.3%) and a decrease of 3.1% in bulk density compared to Control. The other dosages of Darafill, as well as the Drycast surfactant, did not air-entraining into the fibro-cements, probably due to the compaction force applied by the extruder at the time of molding. However, due to the dispersing characteristics of the commercial air-entraining admixtures, the cement paste became more homogeneous and with fewer voids than the Control composite (Fig. 2). Consequently, there was a decrease in AV (10.6 to 35.2% lower) and WA (11.2 to 36.2% lower), and an increase in DB (2.5 to 8.0% higher) in the composites containing commercial surfactants compared to the Control composites.

The SAP in the different dosages evaluated was effective regarding the air-entraining in the cementitious matrix. As can be seen from the properties WA (23.7 to 44.7% higher), AV (33.1 to 48.9% higher), and BD (9.9 to 11.7% lower), both shown in Fig. 3. However, unlike surfactants, SAP produces large amounts of millimetric voids in the cementitious matrix (Fig. 2e and f). These voids cause matrix failure and consequent loss in mechanical strength (CORREIA et al., 2018). The use of 0.7% of hydrated SAP blend in the cementitious matrix causes an expansion of the composites after extrusion, this expansion facilitates the natural carbonation process, because the composites do not present a densified layer on the external surfaces (Fig. 2f). Corroborating, one has the results of thermogravimetry in Table 4, in that the composites SAP_0.7 presented the highest percentage of $CaCO_3$.

### *Mechanical properties of the composites*

Fig. 4 describes the variation of mechanical properties: modulus of rupture (MOR), modulus of elasticity (MOE), limit of proportionality (LOP), and toughness (TO); depending on the different air-entraining admixture types and dosages.

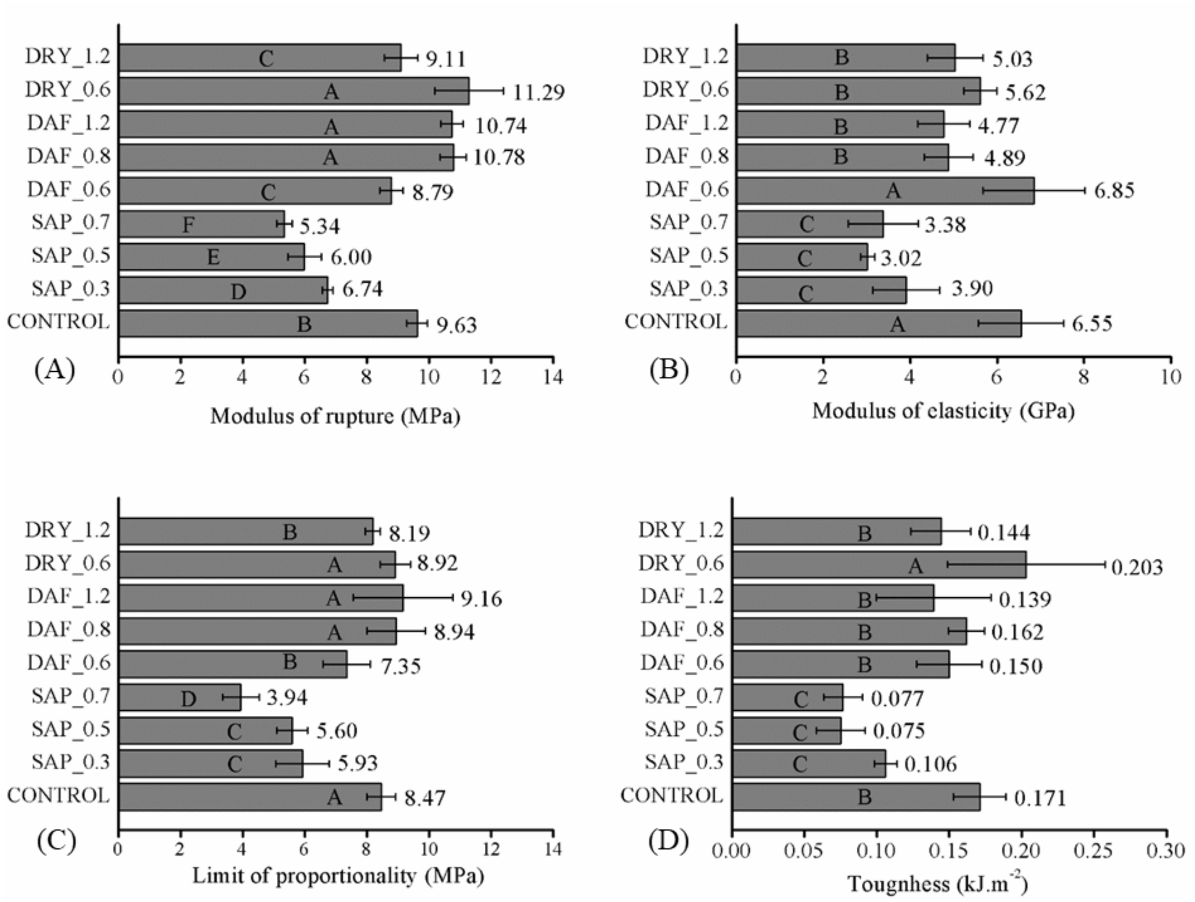


Figure 3 – Average and standard deviation values of: (A) modulus of rupture, (B) modulus of elasticity, (C) limit of proportionality, and (D) toughness in fiber-cement composites. Means of the same letter do not statistically differ by the Scott-Knott mean test, at 5% of significance.

Monosulfoaluminates, such as ettringite $[(CA_6(Al\ (OH)_6)_2(SO_4)_3(H_2O)_{25.7})]$ consume large amounts of water of crystallization, which results in a large increase in volume. Fissures appear in the hardened cement paste around the ettringite. As a result, increased porosity and cracking generation at the fiber / matrix interface (PIZZOL et al., 2014). It is important to highlight that MOR indicates the joint participation of the matrix and the fibers, that is, this mechanical property is related to the mechanical strength of the matrix and the mechanisms of tenacification between the fibers and the matrix (BENTUR; MINDE, 2007). Toughness is related to the tenacity mechanisms associated to fibers, which act in the composite fracture process, such as debond, pull-out, bridging and fracture of the fibers. Thus, the mechanical properties of the cement matrices are influenced by the microstructure of the cement phases.

It is also known that the mechanical properties of cement matrices are directly influenced by pore volume, size and morphology (JENNINGS et al., 2008). The relationship between porosity and strength in cement composites is inverse, where, in general, pores are damaging to force (CORREIA et al., 2018). This is due to the concentration of stress and subsequent rupture in the application of charge that starts in the large capillary pores and microcracks, which are present in the matrix (MEHTA; MONTEIRO, 2006).

Thus, the highest values of MOR observed for the composites DAF_0,8; DAF_1.2; and DRY_0.6 (11.5 to 17.2% higher) are related to the lower concentration of the initial cement hydration phases (Fig. 1 and Table 4) and the lower porosity of these composites in comparison with the Control (Fig. 3). These aspects were also significant in the increase of the toughness of the composite DRY_0.6 in relation to the other composites, mainly due to the lower porosity that influenced the fiber / matrix interface. The higher values of MOE observed in the Control and DAF_0.6 composites may be related to the higher $CaCO_3$ contents (Table 4) that present densified crystalline microstructure in comparison with $Ca(OH)_2$. As a result, there is an increase in the stiffness of the cementitious matrix.

The lower mechanical strength of the composites with SAP addition is related to the increase of porosity (Fig. 3) and formation of large voids (Fig. 2) inside the cementitious matrix. Due to the absence of a densified surface layer (Fig. 2f) in the SAP_0.7 composite, a more severe natural carbonation occurred, which increased the concentration of $CaCO_3$ (Table 4). As a result, even with a 44.7% increase in porosity, formation of large voids and a decrease of 44.5% in MOR, the composite presented similar MOE with a slight increasing tendency to the other composites with SAP.

## Conclusion

The commercial surfactants and SAP influenced the microstructure and the formation of large voids within the cement matrix. It was possible to verify an expansion of the composites with 0.7% SAP, which consequently released the compacting stresses exerted by the extrusion molding. As consequence, the permeability of the composites increased, and, by the action of the natural carbonation, an increasing of the concentration of CaCO3 was observed.

Only the composites with 0.6% of Darafill and with SAP were effective in the incorporation of air in the composites. However, due to the increase of large voids in the composites with SAP, there was a substantial increase of WA and AV and a substantial decrease in the mechanical performance of the composites. The composites DAF_0.8, DAF_1.2 and DRY_0.6 presented lower concentrations of the initial phases of hydration, which together with the reduction of voids were responsible for an increase in DB and mechanical performance, besides a decrease in WA and AV of composites.

In general, commercial surfactants did not obtain efficiency in the incorporation of air in the extrusion molded fibro-cements, due to the compressive forces that the extruder exerts in the molding of the composites. However, these surfactants modified the microstructure and the formation of voids in the matrix, causing in gain of mechanical performance and decrease of the permeability, being able to positive influence in the durability of the composites. The hydrated SAP obtained efficiency in the incorporation of air due to the physical mechanism of expansion and contraction. However, it was responsible for the formation of large voids that resulted in substantial losses in mechanical performance, which restricted its applications.

## Acknowledgements

Thanks to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Rede Brasileira de Compósitos e Nanocompósitos Lignocelulósicos (RELIGAR), Federal University of Lavras (UFLA), and Grace Construction Products-BR for the donation of surfactants and superplasticizer used in this research.

## References

Almeida AEFS, Tonoli GHD, Santos SF, Savastano Jr H. Carbonatação acelerada efetuada nas primeiras idades em compósitos cimentícios reforçados com polpas celulósicas. Amb Constr 2010;10(4):233–46.

Almeida AEFS, Tonoli GHD, Santos SF, Savastano Jr H. Improved durability of vegetable fiber reinforced cement composite subject to accelerated carbonation at early age. Cem Concr Compos 2013;22:49–58.

American Society for Testing and Materials – ASTM 949-81. Test method for dry and wet bulk density, water absorption, and apparent porosity of thin sections of glass-fiber reinforced concrete. West Conshohocken, 1981.

American Society for Testing and Materials - ASTM C150/C150M-11 Standard Specification for Portland Cement, 2011

Atahan HN, Carlos Jr C, Chae S, Monteiro PJM, Bastacky J. The morphology of entrained air voids in hardened cement paste generated with different anionic surfactants. Cement and Concrete Composites 2008;30:566-75.

Bentur A, Mindess S. Fibre reinforced cementitious composites. 2nd ed. London: Taylor & Francis, 2007.

Brazilian Association of Technical Standards – NBR5733. Cement Portland high early strength, specification, 1983.

Buchholz FL, Graham AT. (Eds.), Modern Superabsorbent Polymer Technology, WILEY-VCH, New York, 1998.

Correia VdaC, Santos SF, Teixeira RS, Savastano Jr H. Nanofibrillated celulose and cellulosic pulp for reinforcement of the extruded cement based materials. Construction and Building Materials 2018;160:376-84.

Du L, Folliard KJ. Mechanisms of air entrainment in concrete, Cem. Concr. Res. 2005;35:1463–71.

Fernández-Bertos M, Simons SJR, Hills CD, Carey PJ. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2. J Hazard Mater 2004;B112:193–205.

Fonseca CS, Silva TFDA, Silva MT, Oliveira IRC, Mendes RF, Hein PRG, Mendes LM, Tonoli GHD. Micro/nanofibrilas celulósicas de Eucalyptus em fibrocimento extrudados. Cerne, v. 22, n. 1, p. 59-68, 2016.

Frías M, Goñi S. Accelerated carbonation effect on behavior of ternary Portland cements. Compos Part B 2013;48:122–8.

Friedrich S. Superabsorbent polymers (SAP), in: Mechtcherine V, Reinhardt HW (Eds.), Appl. Super Absorbent Polym. Conc. Constr. State-of-the-Art Rep., Springer, 2012:13–19.
H. Cementitious composites reinforced with Kraft pulping waste. Key Engin Mater 2016;668:390-8.

Hasholt MT, Jensen OM, Kovler K, Zhutovsky S. Can superabsorbent polymers mitigate autogenous shrinkage of internally cured concrete without compromising the strength?, Constr Build. Mater. 2012;31:226–30.

Jennings HM, Bullard JW, Thomas JJ, Andrade JE, Chen JJ, Scherer GW. Characterization and Modeling of Pores and Surfaces in Cement Paste: Correlations to Processing and Properties, J. Adv. Concr. Technol. 2008;6:5–29.

Jensen OM, Hansen PF. Water-entrained cement-based materials: I. Principles and theoretical background, Cem. Concr. Res. 2001;31(4):647–54.

Jensen OM, Hansen PF. Water-entrained cement-based materials: II. Experimental observations, Cem. Concr. Res. 2002;32(6):973–8.

Justs J, Wyrzykowski M, Bajare D, Lura P. Internal curing by superabsorbent polymers in ultra- high performance concrete. Cement and concrete Research 2015;76:82-90.

Lee HXD, Wong HS, Buenfeld NR. Potential of superabsorbent polymer for self-sealing cracks in concrete, Adv. Appl. Ceram. 2010;109:296–302.

Mangane MBC, Argane R, Trauchessec R, Lecomte A, Benzaazoua M. Influence of superplasticizers on mechanical properties and workability of cemented paste backfill. Minerals Engineering 2018;116:3-14.

Mechtcherine V, Reinhardt H. Application of Super Absorbent Polymers (SAP) in Concrete Construction, State-of-the-Art Rep., Springer, 2012.

Mehta P, Monteiro PJM. Concrete: Microstructure, Properties and Materials, second ed., IBRACON, São Paulo, 2014.

Mehta PK, Monteiro PJM. Concrete: Microstructure, Properties, and Materials, third ed., McGraw-Hill Professional Publishing, New York, 2006. https://doi.org/10.1036/0071462899.

Mendes JC, Moro TK, Figueiredo AS, Silva KDdoC, Silva GC, Silva GJB, Peixoto RAF. Mechanical, rheological and morphological analysis of cement-based composites with a new LAS-based air entraining agent. Construction and Building Materials 2017;145:648-61.

Mönnig S, Lura P. Superabsorbent polymers – an additive to increase the freeze-thaw resistance of high strength concrete, in: C.U. Grosse (Ed.), Advances in Construction Materials, Springer Berlin Heidelberg, Berlin, 2007:351–8.

Mönnig S. Water saturated super-absorbent polymers used in high strength concrete, Otto-Graf J. 2005;16:193–202.

Myers D. Surfactant Science and Technology, third ed., John Wiley & Sons, New Jersey, 2006.

Pizzol VD, Mendes LM, Savastano Jr H, Frías M, Davila FJ, Cincotto MA, John VM, Tonoli GHD. Mineralogical and microstructural changes promoted by accelerated carbonation and ageing cycles of hybrid fiber-cement composites. Construction and Building Materials 2014;68:750-6.

Rilem Technical Committee 49 TFR. Testing methods for fibre reinforced cement-based composites. Mat Struc 1984;17:441-456.

Riyazi S, Kevern JT, Mulheron M. Super absorbent polymers (SAPs) as physical air entrainment in cement mortars. Construction and Building Materials 2017;147:669-76.

Şahin Y, Akkaya Y, Boylu F, Taşdemir MA. Characterization of air entraining admixtures in concrete using surface tension measurements. Cement and Concrete Composites 2017;82:95-104.

Santos SF, Rodrigues JdeA, Tonoli GHD, Almeida AEFdeS, Savastano Jr H. Effect of coloidal sílica on the mechanical properties of fiber-cement reinforced with cellulosic fibers. J. Mater. Sci. 2014. DOI 10.1007/s10853-014-8455-1.

Santos SF, Tonoli GHD, Savastano Jr. H. Materias-primas e procesos de fabricación para fibrocemento. In: Universidad Politécnica de Valencia, editor. Aprovechamiento de residuos agro-industriales como fuente sostenible de materiales de construcción. España 2011;327-43.

Schroefl C, Mechtcherine V, Gorges M. Relation between the molecular structure and the efficiency of superabsorbent polymers (SAP) as concrete admixture to mitigate autogenous shrinkage, Cem. Concr. Res. 2012;42:865–73.

Silva DW, Mendes RF, Freire C, Vilela B, Tonoli GHD, Teixeira RS, Santos SF, Savastano Jr. Cementitious composites reinforced with Kraft pulping waste. Key Engin Mater 2016;668:390-8.

Snoeck D, Schaubroeck D, Dubruel P, De Belie N. Effect of high amounts of superabsorbent polymers and additional water on the workability, microstructure and strength of mortars with a water-to-cement ratio of 0.50. Constr. Build. Mater. 2014;72:148–57.

Snoeck D, Steuperaert S, Van Tittelboom K, Dubruel P, De Belie N.Visualization of water penetration in cementitious materials with superabsorbent polymers by means of neutron radiography, Cem. Concr. Res. 2012;42:1113–21.

Soliman AM, Nehdi ML. Effect of partially hydrated cementitious materials and superabsorbent polymer on early-age shrinkage of UHPC, Constr. Build. Mater. 2013;41:270–5.

Teixeira RS, Tonoli GHD, Santos SF, Fiorelli J, Savastano Jr. H, Lahr RFA. Extruded cement based composites reinforced with sugar cane bagasse fibres. Key Eng Mat 2012;517:450-7.

Tonoli GHD, Belgacem MN, Bras J, Pereira-da-Silva MA, Lahr FR, Savastano Jr. H. Impact of bleaching pine fibre on the fibre/cement interface. J of Materials Science 2012;47:4167-77.

Tonoli GHD, Pizzol VD, Urrea G, Santos SF, Mendes LM, Santos V, John VM, Frías M, Savastano Jr H. Rationalizing the impact of aging on fiber-matrix interface and stability of cement-based composites submitted to carbonation at early ages. J. Mater. Sci. 2016;51:7929-43.

Tonoli GHD, Santos SF, Joaquim AP, Savastano Jr. H. Effect of accelerated carbonation on cementitious roofing tiles reinforced with lignocellulosic fibre. Constru Build Mater 2010;24:193-201.

Tonoli GHD, Savastano Jr. H, Santos SF, Dias CM, John VM, Larh FAR. Hybrid reinforcement of sisal and polypropylene fibres in cement-based composites. J Mat Civil Eng 2011;23:177-87.