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Departamento de Engenharia de Alimentos

Reologia de suspensões-modelo: efeito da concentração de sólidos e da matriz dispersante

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Você pode ter defeitos, viver ansioso e ficar irritado algumas vezes, mas não se esqueça de que sua vida é a maior empresa do mundo.
E você pode evitar que ela vá a falência.

Há muitas pessoas que precisam, admiram e torcem por você.
Gostaria que você sempre se lembrasse de que ser feliz não é ter um céu sem tempestade, caminhos sem acidentes, trabalhos sem fadigas, relacionamentos sem desilusões.

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É ter ousadia para dizer "me perdoe".
É ter sensibilidade para expressar "eu preciso de você".
É ter capacidade de dizer "eu te amo".
É ter humildade da receptividade.

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Tese de Doutorado**AUTORA:** Ana Carla Kawazoe Sato**Título:** Reologia de suspensões-modelo: efeito da concentração de sólidos e da matriz dispersante**ORIENTADORA:** Rosiane Lopes da Cunha**Depto. de Engenharia de Alimentos – FEA – UNICAMP**

RESUMO GERAL

A influência das características físicas e químicas do meio dispersante sobre a reologia de suspensões-modelo foi avaliada visando o entendimento do comportamento de sistemas reais como as polpas de frutas. Para isto, o trabalho foi dividido em duas etapas: 1) estudo do efeito da composição de sistemas-modelo de soro de polpas de frutas no comportamento reológico, e 2) estudo de suspensões-modelo de diferentes partículas dispersas em matrizes com diferentes propriedades físicas e químicas. Na primeira etapa, foi verificado o efeito da presença de pectinas de alto e baixo grau de metoxilação, assim como de suas misturas. Os resultados mostraram um efeito sinérgico da mistura destes diferentes tipos de pectinas, devido à maior viscosidade e pseudoplasticidade dos sistemas mistos quando comparados aos sistemas com um único tipo de pectina. Assim, ressaltou-se a importância dos diferentes tipos de ligação no comportamento reológico destes sistemas. A segunda etapa permitiu a compreensão das interações entre partículas e partícula-solvente e a sua influência no comportamento reológico de suspensões-modelo. De um modo geral, as interações entre partículas e partícula-solvente foram maiores nos meios menos viscosos e polares. Tais resultados foram refletidos pelo valor ajustado da fração máxima de empacotamento (ϕ_m) por diferentes modelos, dado que foi possível a adição de maior

quantidade de sólidos para os sistemas com menos interações. Xantana foi adicionada às matrizes dispersantes para promover pseudoplasticidade, indicando comportamentos distintos quando adicionadas em água pura e em soluções aquosas de glicerina. No primeiro caso, as matrizes apresentaram comportamento altamente pseudoplástico, enquanto que a adição de mesma quantidade de xantana nas soluções aquosas de glicerina levou a um grande aumento na viscosidade, com menor influência no valor do índice de comportamento de escoamento. A adição de sólidos nestes dois tipos de matrizes levou a comportamentos distintos. No primeiro caso verificou-se uma leve desestruturação do sistema, refletido principalmente pela maior influência do módulo complexo com a frequência e menor variação na viscosidade relativa das suspensões. Por outro lado, o aumento na fração de sólidos nos sistemas compostos com xantana, glicerina e água levou a suspensões mais estruturadas. Assim, os resultados apresentados mostram que além das características das partículas, as propriedades químicas e reológicas da matriz dispersante são essenciais na determinação do comportamento estrutural e de escoamento de suspensões e portanto, não deveriam ser desprezadas pelos modelos existentes.

Ph. D. Thesis**AUTHOR:** Ana Carla Kawazoe Sato**TITLE:** Model suspensions rheology: effect of solids concentration and dispersing matrix characteristics.**SUPERVISOR:** Rosiane Lopes da Cunha**Depto. de Engenharia de Alimentos – FEA – UNICAMP**

ABSTRACT

The influence of the physical and chemical properties of dispersing matrices on the rheological behavior of model-suspensions was evaluated, aiming the understanding of real suspensions such as fruit pulps. The present research was divided into two parts: 1) influence of composition of serum of fruit pulps on their rheological characteristics, through the study of model-systems, and 2) evaluation of model-suspensions of different particles dispersed into matrices with distinct characteristics (physical and chemical). In the first part, the effects of low and high methoxy pectins were evaluated, as well as their mixture. Results indicated a synergistic effect on the mixture of different sorts of pectin, which was observed by the higher viscosity and pseudoplasticity of mixed systems as compared to pure pectin ones. Such results allowed emphasizing the importance of different binding characteristics on the rheological properties of these systems. The second part allowed for the comprehension of interparticle and particle-matrix interactions, and their influence on the rheological behavior of model suspensions. Generally, interactions were more pronounced at low viscous and polar matrices, which reflected the lower maximum packing fraction (ϕ_m) fitted by different models. Xanthan was added to dispersing matrices to impart pseudoplasticity, showing distinct behaviors when mixed in pure water and aqueous glycerin solutions. In the first case, matrices

showed highly shear thinning behavior, while the addition of the same amount of xanthan in glycerin aqueous solutions promoted a significant increase on viscosity, with lower influence on the flow index behavior (n). Thus, distinct behavior was observed when increasing solids concentration on these two matrices. In the first case, the increase of the dependency of complex modulus with frequency and the lower influence of the relative viscosity reflected a slight loss of structure with solids addition. On the other hand, increasing solids content on systems composed with xanthan, glycerin and water increased structuring. Thus, results indicated that beyond particles characteristics, which have already been widely studied in literature, the knowledge of the chemical and rheological properties of dispersing matrix is of great importance on structural behavior of suspensions.

CAPÍTULO 1 - *INTRODUÇÃO E*
OBJETIVOS

1.1 INTRODUÇÃO

Suspensões são sistemas multifásicos nos quais uma fase sólida encontra-se dispersa em um meio líquido. Dentre as diversas áreas industriais, suspensões são encontradas em linhas de processamento dos mais variados produtos, desde a matéria prima até o produto final. Como exemplos bastante estudados na literatura, podem ser citados o cimento, tintas, argila, sangue, além de diversos produtos alimentícios como sucos, polpas e purês de frutas, chocolate e molhos para salada. Por se tratar de um sistema com duas fases distintas, a instabilidade pode ser um fator crítico no processamento e decisivo na aceitação de suspensões. A natureza das partículas e suas características como tamanho, formato e distribuição de tamanho são fatores que influenciam a estabilidade e, conseqüentemente, as propriedades de escoamento das suspensões.

Diversos trabalhos na literatura estudam o efeito da fração volumétrica de sólidos e da distribuição do tamanho de partículas no comportamento reológico de uma suspensão, sendo que a maioria deles foca em interações partícula-partícula. Gulmus & Yilmazer (2005) avaliaram o efeito da fração volumétrica de sólidos e do tamanho de partículas no escoamento de suspensões poliméricas e verificaram que a baixas taxas de deformação as partículas escorregam umas sobre as outras, levando à redução da viscosidade, enquanto que altas taxas aumentam o contato entre as partículas. Chang & Powell (1994) demonstraram que, mantendo uma mesma fração volumétrica, a viscosidade de suspensões com dois tamanhos predominantes de partículas altamente concentradas é reduzida, em comparação à encontrada para uma suspensão com um único tamanho. No entanto, além das características físicas das partículas, a sua afinidade com o meio dispersante e as propriedades do solvente são fatores que podem influenciar fortemente as propriedades reológicas das suspensões.

O estudo do comportamento reológico de “suspensões ideais”, utilizando esferas rígidas em meios Newtonianos já foi amplamente explorado na literatura, e pode ser descrito por uma série de modelos, como o de Einstein e de Maron & Pierce (1956) . No entanto, à medida que os sistemas se aproximam do real, o comportamento passa a ser mais complexo. Na área de alimentos, a maioria das suspensões não apresenta características ideais. Frequentemente, as partículas encontradas não são esféricas e, muitas vezes, o meio de dispersão é não-Newtoniano. Além disso, a diferença na composição dos variados sistemas, pode influenciar bastante as características reológicas de uma suspensão. Em particular, as frutas apresentam composições e características distintas e, conseqüentemente, as suas polpas contêm diferentes teores de sólidos, açúcares, ácidos, lipídeos, etc., além de apresentar diferentes pHs e características reológicas (SHARMA et al., 1996; BHATTACHARYA,1999; FREITAS, 2002), além de apresentar diferentes teores de partículas sólidas em suspensão. Estas partículas são formadas, principalmente, por carboidratos e proteínas, que são insolúveis no pH do suco (BENÍTEZ et al., 2007), além de outros componentes maiores como fibras insolúveis, pedaços de casca e semente de diferentes formatos e tamanhos, que podem se agregar com o cisalhamento, tornando bastante difícil o estudo reológico destes sistemas (SATO, 2005). A pectina, um dos principais componentes da parede celular, é um polissacarídeo naturalmente presente em grande parte dos frutos, podendo também ser adicionada para melhorar a estabilidade de sucos e polpas de frutas. Além disso, a adição de outros hidrocolóides que aumentem a ainda mais a estabilidade destes produtos é comum, o que leva a alterações no seu comportamento reológico, tornando estes sistemas ainda mais complexos.

Assim, a utilização de sistemas-modelo no estudo fundamental de suspensões é de extrema importância para o entendimento das interações que podem ocorrer entre

partículas e partículas-solvente em sistemas reais. A partir do estudo de sistemas com formulação controlada (modelo), torna-se possível a avaliação da influência de cada parâmetro avaliado, facilitando o entendimento das interações e, conseqüentemente, o processamento de suspensões reais.

1.2 OBJETIVOS

Este trabalho teve como objetivo principal avaliar a influência das características físicas e químicas do meio dispersante sobre a reologia de suspensões-modelo, visando o entendimento do comportamento de polpas de frutas. Para isto, foram avaliados meios com diferentes propriedades reológicas (viscosidade e pseudoplasticidade) e polaridades, além de partículas com diferentes características morfológicas.

1.2.1 Objetivos específicos

- Avaliar o efeito da mistura de diferentes pectinas no comportamento reológico de sistemas-modelo visando entender a influência dos ingredientes no comportamento da fase contínua de polpa de frutas (“serum”);

- Estudar o efeito da fração volumétrica de sólidos (ϕ) no comportamento reológico de suspensões com partículas de diferentes formatos e natureza (sílica e celulose);

- Avaliar a influência do comportamento reológico e da natureza do meio dispersante (polaridade) nas propriedades de escoamento de suspensões-modelo, em matrizes Newtonianas e não-Newtonianas.

1.3 ORGANIZAÇÃO DA TESE EM CAPÍTULOS

A fim de se compreender melhor o comportamento de escoamento de suspensões alimentícias, optou-se pelo estudo de suspensões-modelo. Por se tratar de um universo bastante amplo com suspensões com características distintas, focou-se nas polpas de frutas como sistemas-modelo a serem estudados. Assim, tornou-se necessário o estudo dos diferentes fatores que poderiam influenciar o comportamento reológico destes sistemas. Deste modo, o estudo foi dividido em duas partes onde, primeiramente, foram estudados sistemas-modelo do meio contínuo (soro da polpa de fruta) (Capítulo 3) e, depois, o comportamento reológico das suspensões propriamente ditas (Capítulo 4). Assim, o presente trabalho encontra-se estruturado da seguinte forma:

Capítulo 1 – Introdução geral

Capítulo 2 – Revisão bibliográfica

Capítulo 3 – Comportamento reológico de sistemas-modelo de soro de polpas de frutas: neste capítulo estudou-se o efeito de algumas variáveis que poderiam influenciar o comportamento reológico de soro de polpas de frutas como a concentração de pectina, de sacarose e a mistura de diferentes tipos de pectinas (duas pectinas de alto teor de metoxilação e uma pectina de alto com uma de baixo teor de metoxilação). O efeito simultâneo destas variáveis foi estudado através da metodologia de superfície de resposta e os resultados obtidos foram publicados no artigo intitulado “*Rheology of mixed pectin solutions*” (*Food Biophysics* (2008), v. 3, p. 100-109), como requisito para a realização da qualificação geral desta tese de doutorado.

Capítulo 4 – Comportamento reológico de suspensões-modelo: este capítulo apresenta os resultados obtidos do estudo do comportamento reológico de suspensões

dispersas em meios com diferentes características. Para isto, partículas de sílica e celulose foram dispersas em meios com diferentes propriedades físicas e químicas, e a influência da fração volumétrica de sólidos (ϕ) foi avaliada em cada caso. Os resultados obtidos foram divididos em dois trabalhos (Parte 1 e Parte 2), sendo que no primeiro foi avaliado o efeito da viscosidade e da polaridade do meio dispersante no comportamento de escoamento, visando a existência de suspensões alimentícias com diferentes composições, enquanto que o segundo focou o efeito do comportamento não-Newtoniano da matriz dispersante nestes sistemas, através da adição de hidrocolóides freqüentemente utilizados em suspensões alimentícias para a obtenção de produtos mais estáveis ou com outras características sensoriais desejadas. Nesta etapa, optou-se pela utilização de xantana que, mesmo em baixas concentrações, promove grande pseudoplasticidade aos sistemas, sendo muito utilizada para melhorar a estabilidade de polpas e derivados de frutas.

Capítulo 5 - Conclusões gerais

CAPÍTULO 2 - REVISÃO
BIBLIOGRÁFICA

2.1 SUSPENSÕES

Suspensões são sistemas multifásicos, nos quais uma fase sólida encontra-se dispersa em um meio líquido. Nestes sistemas pode ou não haver contato entre as partículas, que podem estar estruturadas de diferentes maneiras: diluídas sem interação entre si; estabilizadas estericamente; floculadas e estruturadas, parcialmente estáveis ou sedimentando (Figura 1). A formação do tipo de estrutura em cada sistema pode depender de diversos fatores, entre eles: a composição química das duas fases, o tamanho e formato de partículas, os efeitos de superfície e/ou da presença de aditivos (FERGUSON & KEMBLOWSKI, 1991). Entre estes fatores, o tamanho das partículas suspensas é o que geralmente define o tipo de interação entre elas, enquanto que a concentração de partículas definirá como estas interações irão afetar a formação de estruturas e as propriedades de escoamento destes sistemas. Durante o escoamento de suspensões, existem três tipos de forças predominantes que dependem principalmente do tamanho e da natureza das partículas (Tabela 1). Em relação ao tamanho, suspensões com partículas menores que 10 μm são consideradas coloidais, enquanto que sistemas com partículas maiores são denominadas não-coloidais. Neste caso, a presença de partículas maiores (10 - 100 μm) pode ser o resultado de agregados de partículas coloidais (BEVERIDGE, 1997). Para estas partículas maiores, o movimento Browniano e forças interpartículas, determinantes para partículas coloidais, são insignificantes, quando comparadas às forças hidrodinâmicas.

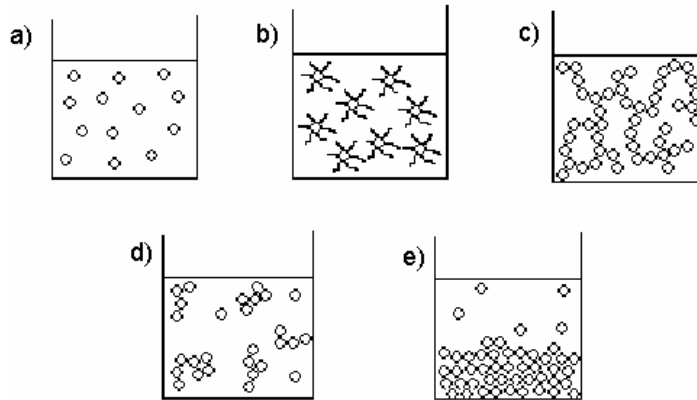


Figura 1 - Estrutura das partículas em uma suspensão: (a) diluídas sem interação entre as mesmas; (b) estabilizadas estericamente; (c) floculadas; (d) parcialmente estáveis com alguma estrutura formada; (e) sedimentando.

Tabela 1- Classificação das dispersões.

Tamanho das partículas	Partículas	Forças que determinam a viscosidade
~ 1 nm	Molecular/coloidal	Sistemas diluídos: intermolecular- Browniano. Sistemas concentrados: entrelaçamentos e reptação.
1 nm – 10µm	Microscópica/coloidal	A baixas taxas de deformação: hidrodinâmicas, interpartículas e Brownianas. A altas taxas de deformação: hidrodinâmicas.
10µm - 100µm	Microscópica/não-coloidal	Hidrodinâmicas.
> 100µm	Macroscópica/não-coloidal	Hidrodinâmicas.

Fonte: GENOVESE et al, 2007.

Além do tamanho das partículas suspensas, também é bastante importante considerar parâmetros como formato, deformabilidade e distribuição do tamanho das partículas, além das propriedades interfaciais entre as partículas sólidas e o meio dispersante, que podem afetar a estrutura do sistema e, conseqüentemente, o comportamento das suspensões durante o escoamento e sua estabilidade (TSAI & ZAMMOURI, 1988; WINDHAB, 2000).

2.1.1 Caracterização da fase dispersa

Em sistemas reais, como é o caso de alimentos, é comum encontrar suspensões de partículas não-esféricas, com os mais diversos formatos. Neste caso, pode-se representar o tamanho desta partícula de diversas maneiras. Uma vez que a esfera é o único formato que pode ser representado por um único número, costuma-se relacionar as dimensões da partícula aos diâmetros de esferas de diferentes tamanhos. Deste modo, as dimensões de uma partícula podem ser expressas em termos do diâmetro da esfera equivalente de mesma área superficial, mesmo volume, mesma massa, etc. (Figura 2). Assim, as diferentes técnicas utilizadas para a determinação de tamanho de partículas de uma suspensão também podem fornecer resultados bastante distintos, uma vez que determinarão as dimensões das partículas de diferentes pontos de vista. Os valores de diâmetros obtidos a partir das diferentes técnicas deveriam ser bastante similares se a partícula medida fosse uma esfera perfeita. Assim, à medida que o formato da partícula se afasta do formato esférico, os resultados obtidos a partir das diferentes metodologias passam a mostrar variações mais marcantes.

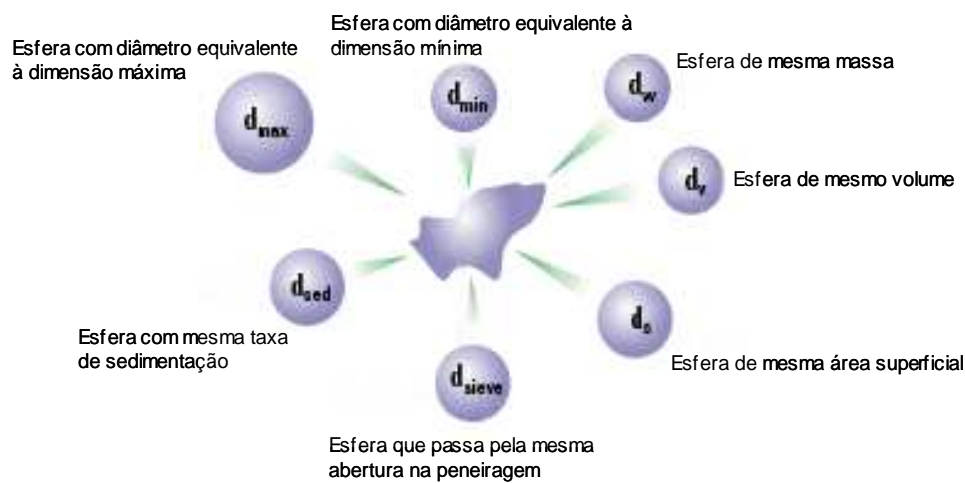


Figura 2 - Esferas de diversos diâmetros equivalentes a diferentes características de uma partícula.

Diversas metodologias são encontradas na literatura para a determinação de tamanho de partículas em alimentos, dentre as quais podem ser citadas a peneiragem, microscopia, difração de luz, fotometria de sedimentação, entre outras (DEN OUDEN & VAN VLIET, 1997; GENOVESE & LOZANO, 2000; VALENCIA et al., 2002). Recentemente, a técnica de difração de luz (LS), também denominada de difração a laser, tem sido amplamente empregada para a caracterização dos mais variados produtos. Este método é baseado no princípio de que partículas com diferentes tamanhos têm um padrão único de intensidade e ângulo da luz difratada, sendo que o ângulo de difração é inversamente proporcional ao tamanho da partícula. Neste caso, um feixe de luz é incidido na amostra, e refratado a diferentes ângulos, dependendo do tamanho da partícula. Com o auxílio de lentes de Fourier, estes feixes são convergidos em um detector, que acoplado a um computador, é capaz de determinar o tamanho das partículas de uma determinada amostra (Figura 3). A difração a laser permite a obtenção da curva de distribuição do tamanho de partículas rapidamente, podendo ser utilizada em linhas de processo. No entanto, alguns fatores devem ser considerados na aplicação desta técnica, principalmente quando são avaliados sistemas com partículas não esféricas (TINKE et al., 2008), que podem se orientar no decorrer dos ensaios. Neste caso, o padrão de difração de uma partícula não-esférica não pode ser relacionado a um único tamanho, o que também é influenciado pela orientação das partículas durante a realização da análise (HEFFELS et al., 1995; MUHLENWEG & HIRLEMAN, 1998; TINKE et al, 2008). Assim, deve-se considerar que os resultados obtidos através desta técnica são altamente influenciados pela escolha do índice de refração durante a conversão dos padrões de difração em curvas de distribuição do tamanho de partículas (SAVEYN et al., 2006).

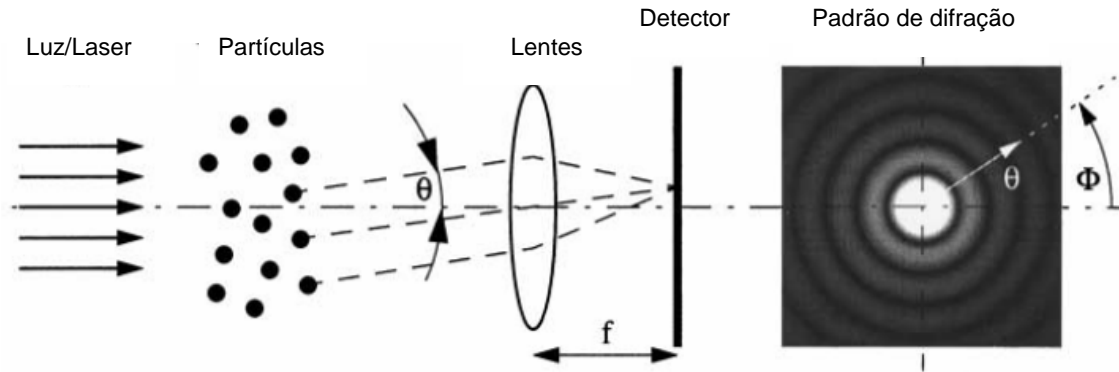


Figura 3 – Esquema óptico para determinação do tamanho de partículas por difração a laser, onde: f = distância focal; θ = ângulo de difração; Φ = coordenada esférica polar do padrão de difração. (Fonte: MÜHLENWEG & HIRLEMAN, 1998)

Por outro lado, a microscopia é uma técnica relativamente barata que permite a observação direta das partículas, de maneira que o formato das partículas e a presença de aglomerados podem ser avaliados. Neste caso, as dimensões das partículas podem ser determinadas através da análise das imagens obtidas com o auxílio de *softwares* adequados. No entanto, para uma boa visualização das imagens, é preciso que a amostra seja pequena para evitar sobreposição das partículas e, para se obter um resultado adequado, é necessária a determinação das dimensões de um grande número de unidades, o que torna esta técnica bastante trabalhosa e demorada (BARREIROS et al., 1996; BOWEN et al, 2002).

Além das diferentes características das partículas que podem ser utilizadas na caracterização de seu tamanho, deve-se também considerar o tipo de distribuição resultante de cada análise. Dependendo da técnica utilizada, uma amostra composta com uma única partícula com 100 μm de diâmetro e 1.000.000 partículas de 1 μm poderia apresentar distribuição de tamanho bastante distintas. Considerando o resultado de análises que levam em consideração a distribuição volumétrica de uma amostra, como é o caso de peneiragem ou difração de luz, esta única partícula de 100

μm ocuparia o mesmo volume que as 1.000.000 partículas de $1 \mu\text{m}$, resultando em uma distribuição igual de volume (50% para cada tamanho) (Figura 4). No entanto, se este mesmo conjunto de partículas fosse analisado através de técnicas que considerassem a distribuição numérica, como a microscopia, a distribuição de tamanhos seria completamente desigual, com mais de 99,99% de partículas de $1 \mu\text{m}$ e menos de 0,01% de partículas de $100 \mu\text{m}$.



Figura 4 - Distribuição volumétrica de partículas esféricas com diferentes diâmetros.

Avaliando diferentes técnicas para análise de distribuição do tamanho de partículas, SAVEYN et al. (2006) ressaltaram que é necessário o conhecimento das possibilidades e limitações de cada técnica utilizada. Estes autores recomendam a utilização de diferentes técnicas, condições de preparo de amostra ou de configurações de *software*, para a detecção de anomalias nos resultados de tamanho de partículas, de modo a obter resultados mais precisos e confiáveis.

2.1.2 Suspensões em alimentos

Uma grande quantidade de materiais das mais diversas áreas apresenta-se como suspensão de partículas sólidas em um meio líquido, sendo que o meio pode apresentar diferentes características de escoamento e de afinidade com as partículas adicionadas. Preenchimento de polímeros, fabricação de papel, cerâmica, concreto,

cosméticos, além de alimentos, são alguns exemplos de suspensões produzidas/processadas por indústrias de diferentes setores. Cimento, tinta, argila e sangue são exemplos de suspensões bastante estudadas na literatura, além de diversos produtos alimentícios, como sucos, polpas e purês de frutas, molhos de salada, chocolate, ketchup e produtos lácteos, como o iogurte (RAO, 1977).

Em particular, os alimentos são sistemas complexos, geralmente constituídos por uma grande variedade de componentes, tais como carboidratos, proteínas, lipídeos, sais, fibras e água. Além da sua composição, a presença de diferentes fases em sistemas multifásicos, como no caso de emulsões e suspensões, aumenta ainda mais a complexidade, dificultando o entendimento do comportamento físico destes sistemas.

2.1.2.1 Polpas de frutas

Dentre as diversas suspensões encontradas em alimentos, os produtos derivados de frutas como as polpas e purês são exemplos de grande importância para a indústria nacional. Eles permitem a substituição da fruta *in natura*, como matéria-prima em diversos produtos industrializados, sendo uma alternativa para a conservação das frutas em época de safra e para a sua utilização durante a entressafra.

Sucos e polpas de frutas naturais são sistemas multicomponentes opalescentes ou turvos devido à presença de sólidos insolúveis em suspensão. Estes sólidos são compostos principalmente de carboidratos e proteínas, insolúveis no pH natural do suco, além de partículas maiores como pedaços de casca e fibras insolúveis. Acredita-se que as partículas de proteína suspensas em sucos sejam cobertas por uma camada protetora de pectina negativamente carregada no pH do suco, que se ligam à pectina dissolvida, promovendo estabilidade aos sistemas (SORRIVAS et al., 2006). No entanto, a presença de outros componentes macromoleculares provenientes da parede

celular pode prejudicar a estabilidade dos sucos durante o processamento industrial. Isto mostra que as propriedades físicas de sucos e polpas de frutas, como o comportamento reológico, dependem do conteúdo e da natureza dos sólidos solúveis, polpa em suspensão e pectina destes sistemas (CARBONELL et al., 1991).

No estudo de sistemas complexos, como é o caso de suspensões e, mais especificamente, as polpas de frutas, é freqüente o uso de sistemas-modelo para melhor entendimento do comportamento de sistemas reais. Sistemas-modelo são compostos por frações definidas e conhecidas de “ingredientes” de interesse, de modo que as substâncias escolhidas para a formulação de soluções modelo devem apresentar composição semelhante à do sistema em estudo. O estudo de sistemas-modelo tem grande importância na interpretação das propriedades físicas de alimentos, permitindo o esclarecimento/entendimento de alterações micro e macroscópicas de sistemas complexos quando submetidos a diferentes condições de processo, como no caso de alimentos.

2.1.2.1.1 Pectina

A pectina é um polissacarídeo presente na parede celular e na região intercelular da lamela média dos tecidos da planta, de grande importância na consistência de frutas e vegetais processados. Quimicamente, as pectinas são compostas por uma cadeia linear de ácido galacturônico ligado por associação $\alpha(1,4)$ formando uma cadeia polissacarídea (Figura 5) (LOOTENS et al., 2003). As unidades de ácido galacturônico são esterificadas com metanol, sendo que o grupo éster pode ser facilmente removido pela ação de enzimas (MAY, 1997). Na natureza, as pectinas apresentam mais de 50% dos grupos esterificados (pectinas de alto teor de metoxilação – HM), sendo que pectinas com menos de 50% de grupo esterificados (pectinas de baixo teor de metoxilação) podem ser obtidas por uma desesterificação controlada das

HM em meio alcoólico, com ácido ou amônia (Figura 6) (AXELOS & THIBAUT, 1991; THO et al., 2005). Quando a desesterificação é realizada em meio com amônia, parte dos grupos metil-éster é substituída pelos grupos amida resultando na pectina denominada amidada (AXELOS & THIBAUT, 1991).

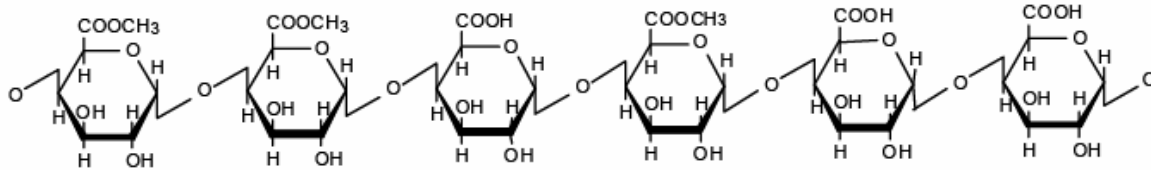


Figura 5 - Estrutura molecular da pectina.

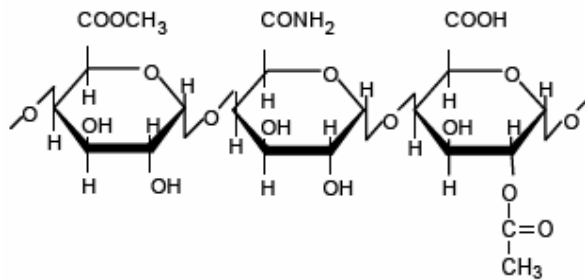


Figura 6 - Representação dos diferentes substituintes potencialmente presentes em pectinas comerciais: metil-éster, grupo amida e grupo acetil, respectivamente.

Devido à sua propriedade em formar gel em diferentes condições, a pectina é comumente utilizada como agente espessante e/ou gelificante em alimentos, podendo alterar fortemente o comportamento reológico do meio no qual se encontra. De um modo geral, as pectinas são classificadas de acordo com o seu grau de esterificação (DE), o que determina as condições necessárias para a sua gelificação: em pectinas com alto teor de metoxilação ($DE > 50\%$), a formação de gel ocorre em baixo pH ($< 3,5$) e elevada concentração de açúcar através de ligações hidrofóbicas e pontes de hidrogênio (OAKENFULL, 1991), enquanto que a formação de gel por pectina com

baixo teor de metoxilação (DE<50%) ocorre na presença de íons de cálcio ou outro metal bi ou tri-valente, pelo mecanismo não-covalente do tipo “caixa de ovo” (AXELOS & THIBAUT, 1991). Na falta destes íons, as pectinas de baixo teor de metoxilação também podem gelificar em pH bastante baixo (em torno de 1,6), quando as cadeias deixam de ter cargas. Neste caso, a gelificação é atribuída à protonação dos grupos carboxilas que promovem uma ordenação conformacional e associação destes grupos por dois mecanismos distintos: i) supressão da repulsão eletrostática e ii) favorecimento da formação de pontes de hidrogênio entre os grupos carboxilas protonados (GILSENAN et al., 2000). Além das ligações entre os grupos carboxílicos da molécula de pectina, a presença de grupos amida na estrutura da molécula amidada permite a estabilização das zonas de junção através de pontes de hidrogênio, permitindo a gelificação do sistema em uma faixa mais ampla de concentração de cálcio (10-80 mg/g de pectina), quando comparada à pectina de baixo teor de metoxilação não amidada (20-40 mg/g pectina) (CHRISTENSEN, 1986; MAY, 1990).

2.1.2.1.2 Xantana

A goma xantana é um polissacarídeo microbiano, extracelular, produzido pela bactéria *Xanthomonas campestris*. A estrutura fundamental ou primária da molécula de xantana é composta de uma cadeia central de 1,4-β-D-glucose com substituições laterais contendo duas manoses e um ácido glucurônico (Figura 7) (BORN et al., 2005).

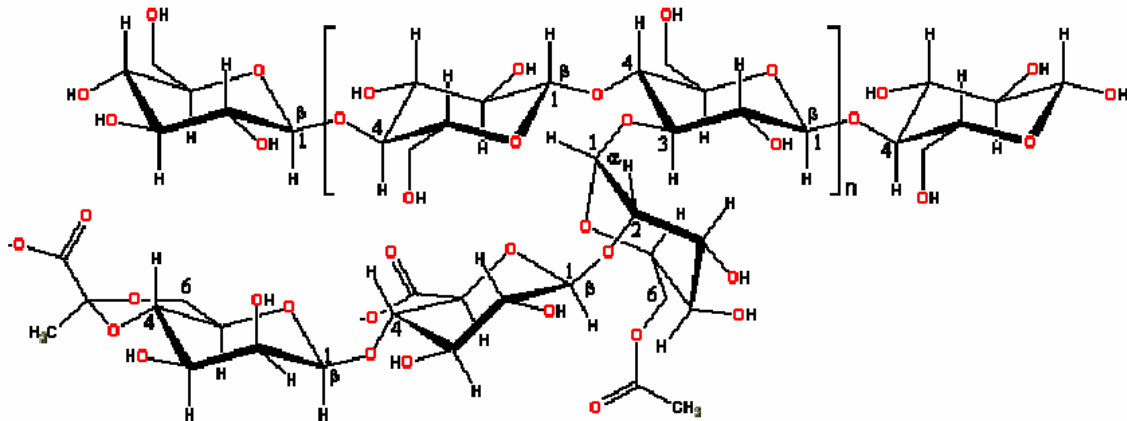


Figura 7 – Estrutura molecular da xantana.

A goma xantana se destaca por ser um polissacarídeo com propriedades reológicas características. Apresenta um *plateau* Newtoniano, que permite uma boa estabilização de partículas e gotas dispersas, em suspensões e emulsões, respectivamente. Além disso, possui a propriedade de ser altamente pseudoplástica, escoando facilmente com a aplicação de taxas de deformações baixas, sendo bastante utilizada em diversos produtos alimentícios como molhos, bebidas molhos para salada e maionese, entre outros (WILLIAMS & PHILLIPS, 2003)

2.2 REOLOGIA

Reologia é a ciência que estuda a deformação e o escoamento de materiais, ou seja, o modo como os materiais respondem à aplicação de uma tensão ou deformação. O conhecimento das propriedades reológicas de alimentos é muito importante para o projeto de tubulações e equipamentos, no controle de qualidade, no desenvolvimento de novos produtos, na aceitação por parte do consumidor, bem como em um melhor entendimento do comportamento estrutural dos produtos (BARNES et al., 1989; STEFFE, 1996).

Ensaio reológico que envolve grandes deformações são de enorme valor prático, pois proporcionam informação sobre a consistência do alimento durante o consumo e sua resistência a processos tais como agitação e bombeamento. Os dados obtidos em estado estacionário são úteis na obtenção da curva de escoamento (viscosidade em função da taxa de deformação), pois, dependendo das condições experimentais, permitem a avaliação da influência de diversos fatores como temperatura, concentração e presença e tamanho de partículas em suspensão, sobre a viscosidade.

Em função do comportamento reológico viscoso, os fluidos podem ser basicamente classificados em Newtonianos e não-Newtonianos (Figura 8). Em fluidos Newtonianos, a tensão de cisalhamento é diretamente proporcional à taxa de deformação, como é observado na Equação (1), de modo que a viscosidade (η) do sistema independe da taxa de deformação aplicada.

$$\sigma = \eta * \dot{\gamma} \quad (1)$$

Fluidos não Newtonianos são caracterizados como aqueles cuja relação entre tensão de cisalhamento e taxa de deformação não é linear e/ou não passa pela origem, podendo ser classificados como dependentes ou independentes do tempo. No primeiro caso, a viscosidade aparente do fluido varia tanto com a taxa de deformação quanto com a duração de sua aplicação, podendo ser classificados como tixotrópicos ou reopéticos. A diminuição da viscosidade aparente com o tempo de cisalhamento, a uma condição constante de temperatura e taxa de deformação, caracteriza um material tixotrópico, enquanto que fluidos que têm a sua viscosidade aparente aumentada com o tempo são denominados reopéticos. Grande parte dos fluidos alimentícios como pastas de frutas e vegetais, “ketchup”, mostarda e comida de bebê apresentam comportamento

tixotrópico (BARBOSA-CÁNOVAS et al.,1993; CHOI & YOO, 2004), enquanto que a reopexia não é muito comum em alimentos, podendo ser observada em soluções de amido altamente concentradas (SHARMA et al., 2000).

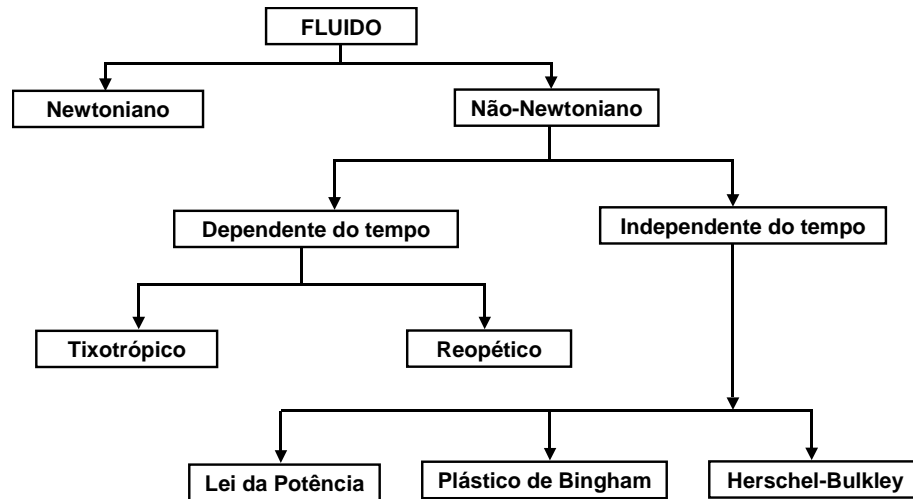


Figura 8 – Classificação do comportamento reológico de fluidos.

Nos fluidos independentes do tempo, a viscosidade aparente é somente função da taxa de deformação, podendo apresentar ou não tensão residual (σ_0) para o início do escoamento (Figura 9).

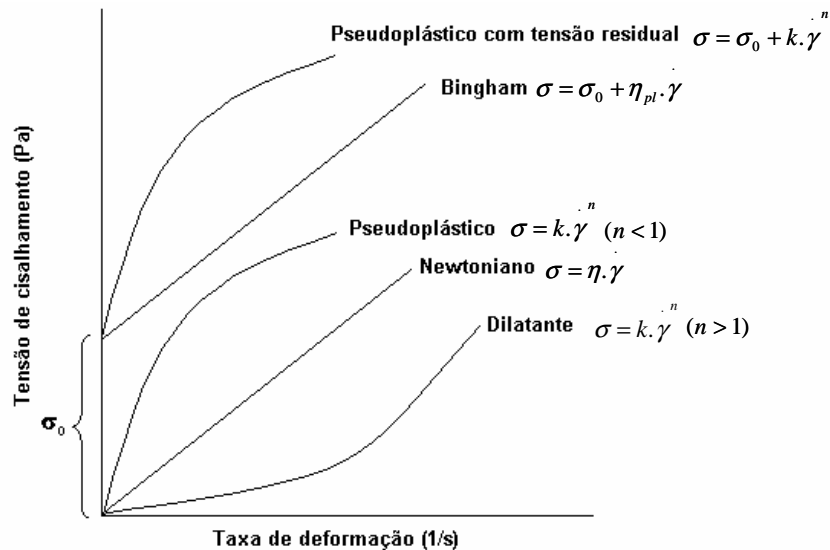


Figura 9 - Curvas de escoamento típicas de fluidos.

De maneira geral, o modelo Herschel-Bulkley (Equação 2) pode ser usado para descrever o comportamento de fluidos não-Newtonianos independentes do tempo, pois, dependendo do valor das constantes, é possível representar o comportamento reológico de diferentes tipos de fluidos (Tabela 2).

$$\sigma = \sigma_0 + k * \dot{\gamma}^n \quad (2)$$

Onde: σ_0 = tensão residual (Pa); k = índice de consistência (Pa.sⁿ); n = índice de comportamento de escoamento

Tabela 2– Fluido newtoniano, pseudoplástico, dilatante e plástico de Bingham como casos especiais do modelo Herschel-Bulkley (STEFFE, 1996).

Fluido	k	n	σ_0	Exemplos típicos
Herschel-Bulkley	> 0	$0 < n < \infty$	> 0	Pasta de peixe picada, pasta de uva passa
Newtoniano	> 0	1	0	Água, suco de fruta clarificado, leite, mel, óleo vegetal
Pseudoplástico	> 0	$0 < n < 1$	0	Molho de maçã, purê de banana, sucos e polpas de frutas
Dilatante	> 0	$1 < n < \infty$	0	Alguns tipos de mel, solução de 40% de amido de milho
Plástico de Bingham	> 0	1	> 0	Pasta de dente, pasta de tomate

De maneira geral, a maior parte dos alimentos mostra comportamento pseudoplástico e tixotrópico, ou seja, a viscosidade aparente diminui à medida que a taxa de deformação e o tempo de cisalhamento aumentam, devido à orientação das moléculas na direção do escoamento e à quebra de agregados, que tornam a resistência ao movimento cada vez menor (Figura 10) (BARNES et al., 1989). No entanto, suspensões concentradas apresentam comportamento pseudoplástico e dilatante a baixas e altas taxas de deformação, respectivamente. A baixas taxas, as partículas escorregam umas sobre as outras, de modo que a viscosidade do sistema

diminui com o aumento do cisalhamento, enquanto que, a altas taxas, o contato entre as partículas é maior, fazendo com que elas interajam entre si, resultando no aumento da viscosidade com a taxa de deformação (GULMUS & YILMAZER, 2005). Em soluções concentradas, durante o início do cisalhamento, as partículas em suspensão passam por um mecanismo de coagulação e fragmentação, antes de atingirem o estado estacionário. De acordo com Barthelmes et al. (2003), em suspensões inicialmente livres de agregados, o cisalhamento leva à formação de pequenos agregados devido a pequenas colisões. Posteriormente, com a formação de agregados maiores, o volume de colisão entre as partículas aumenta, causando quebra de alguns agregados e conseqüente redução do tamanho das partículas, até que o equilíbrio entre a coagulação e a fragmentação dos agregados/partículas seja atingido. Segundo Huang et al. (2004), taxas de deformação elevadas levam ao aumento da força hidrodinâmica do sistema, que promove a colisão entre as partículas, impedindo-as de manter a sua organização. Assim, o contato entre as partículas é maior fazendo com que elas interajam entre si, resultando no aumento da viscosidade com a taxa de deformação (GULMUS & YILMAZER, 2005). Assim, para frações volumétricas de sólidos muito altas, o comportamento do sistema é aparentemente dilatante (BARNES, 1989).

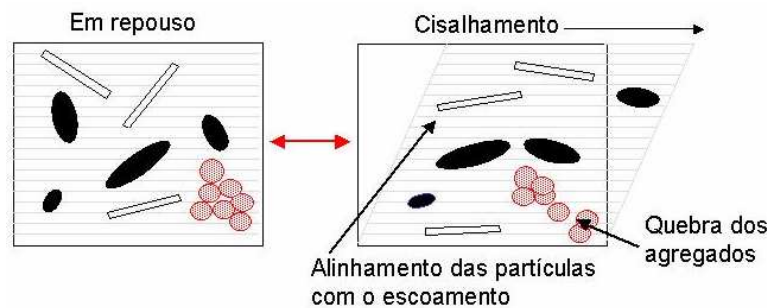


Figura 10 – Efeito do cisalhamento sobre o comportamento de partículas e agregados.

2.2.1 Reologia de suspensões

As características de escoamento das suspensões podem ser definidas tanto pela fase contínua, como pela particulada, além da influência de uma fase na outra, pois mudanças na estrutura formada entre as partículas da fase dispersa também afetam o comportamento do fluido (FERGUSON & KEMBLAWSKI, 1991).

As suspensões mais simples consistem em uma dispersão diluída de partículas não-Brownianas, rígidas e esféricas, sem interação entre si, dispersas em um meio Newtoniano. Neste caso, as partículas suspensas devem estar suficientemente diluídas de modo que as interações hidrodinâmicas possam ser desprezadas e o comportamento reológico da suspensão seja basicamente determinado pela fase contínua (FERGUSON & KEMBLAWSKI, 1991).

Einstein definiu que a viscosidade de sistemas altamente diluídos, com fração volumétrica de sólidos (ϕ) inferior a 0,03, escoando ao redor de uma esfera rígida pode ser predita pela equação (3).

$$\eta = \eta_s(1 + k_E \cdot \phi) \quad (3)$$

onde η é a viscosidade da suspensão, η_s a viscosidade da fase contínua, ϕ a fração volumétrica de sólidos e k_E o coeficiente de Einstein. Em soluções suficientemente diluídas, quando o escoamento ao redor de uma esfera não é influenciado pelas partículas vizinhas, o valor de k_E equivale a 2,5 (LARSON, 1999). Estudando partículas elípticas isoladas (de paredes e de outras partículas) dispersas em um meio Newtoniano, Jeffery (1922) observou que, em casos nos quais o movimento Browniano pode ser ignorado, a trajetória da partícula é periódica, sendo definida pela chamada *órbita de Jeffery* (Figura 11). Considerando o escoamento de partículas fibrosas, estas passam a maior parte do tempo alinhadas no sentido do

escoamento quando, repentinamente, rotacionam meia revolução, até se alinharem novamente. Mais recentemente, Ingber & Mondy (1994) concluíram que a teoria de Jeffery permite uma boa aproximação da orientação de trajetória para o movimento orbital de partículas alongadas, mesmo em regiões próximas à parede ou na presença de outras partículas, e em condições de escoamento em tubos com perfil parabólico, completamente desenvolvido.

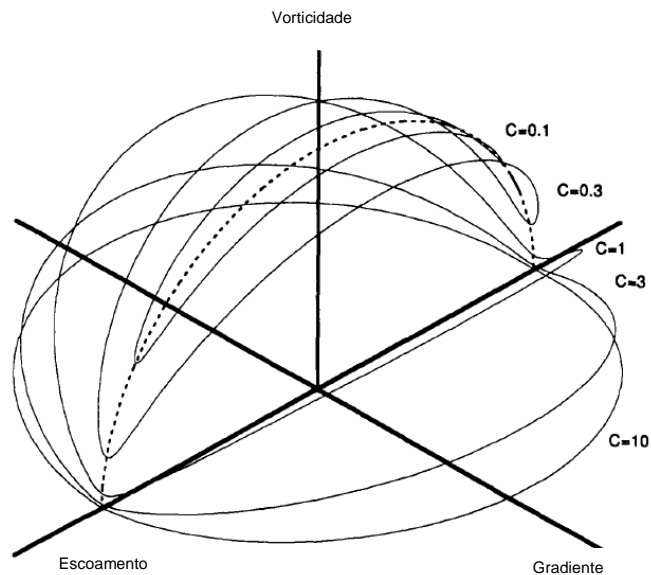


Figura 11 - Ilustração da órbita de Jeffery para uma fibra. As linhas sólidas indicam a trajetória de uma extremidade de uma partícula centrada na origem enquanto que a linha pontilhada representa o plano de escoamento, perto do qual as fibras passam a maior parte do tempo. C representa uma constante relacionada à órbita da partícula: quando $C=0$ a fibra está orientada na direção da vorticidade do escoamento; quando $C=\infty$ a fibra rotaciona no plano da direção da velocidade e do gradiente de velocidade. (Fonte: ISO et al., 1996)

À medida que a fração de sólidos do sistema (ϕ) aumenta, o movimento de uma partícula passa a ser influenciado pelas outras partículas presentes, podendo ocorrer interações. Neste caso, a viscosidade deixa de seguir a relação linear com o aumento

da fração volumétrica de sólidos (ϕ), proposta por Einstein (Equação 3). Neste caso, para suspensões de esferas, termos de maior ordem da fração volumétrica ($\phi^2, \phi^3 \dots$) podem ser adicionados à Equação de Einstein, de modo que as interações entre as partículas passam a ser contabilizadas (Equação 4) (HSUEH & BECHER, 2005; THOMAS & MUTHUKUMAR, 1991).

$$\eta = \eta_s (1 + k_1 \cdot \phi + k_2 \cdot \phi^2 + k_3 \cdot \phi^3 \dots) \quad (4)$$

Alguns modelos semi-empíricos foram desenvolvidos e permitem descrever a viscosidade de suspensões em regime não diluído em função da fração volumétrica de sólidos no sistema (ϕ). Dentre os modelos mais utilizados, encontra-se o modelo de Maron & Pierce (Equação 5), para suspensões de partículas esféricas monomodais (MARON & PIERCE, 1956). Baseados neste modelo, outros modelos empíricos foram propostos, permitindo um bom ajuste aos dados experimentais de suspensões com maior fração de sólidos, como é o caso dos modelos de Krieger & Dougherty (KRIEGER & DOUGHERTY, 1959) (Equação 6) e Eilers (FERRINI et al., 1979) (Equação 7).

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \quad (5)$$

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \quad (6) \quad \eta_r = \left(1 + \frac{\frac{1}{2}[\eta]\phi}{1 - \frac{\phi}{\phi_m}}\right)^2 \quad (7)$$

Onde, $[\eta]$ representa a viscosidade intrínseca, ϕ_m a fração máxima de empacotamento e o expoente $([\eta] \cdot \phi_m)$ também pode ser representado pela constante a , que, normalmente, tem um valor entre 1,4 e 3 (SERVAIS et al., 2002).

Levando-se em conta os extremos de concentração de sólidos de uma suspensão, pode-se considerar que a viscosidade intrínseca representa a viscosidade do sistema a baixas concentrações de sólidos (Equação 8). Com o aumento na fração de sólidos, interações e/ou agregações das partículas passam a ser observadas, podendo haver a formação de uma rede que leva ao aparecimento do comportamento não-Newtoniano pseudoplástico no sistema. A medida que ϕ se aproxima da ϕ_m , a viscosidade da suspensão tende ao infinito (comportamento de sólido) (Equação 9) (STICKEL & POWELL, 2005).

$$\lim_{\phi \rightarrow 0} \frac{\eta_r - 1}{\phi} = [\eta] \quad (8)$$

$$\lim_{\phi \rightarrow \phi_m} \eta_r = \infty \quad (9)$$

Onde: η_r equivale à viscosidade relativa da suspensão; $[\eta]$ à viscosidade intrínseca; ϕ à fração volumétrica de sólidos e ϕ_m à fração máxima de empacotamento.

Fisicamente, ϕ_m representa a fração máxima de partículas sólidas que é possível adicionar em uma suspensão, levando-se em consideração a composição da suspensão, o formato e, conseqüentemente, o arranjo das partículas. Alguns valores de fração máxima de empacotamento para suspensões monomodais observados na literatura são apresentados na 0, para partículas rígidas de diferentes formatos e arranjos. No entanto, no estudo prático de suspensões, este valor é freqüentemente utilizado como parâmetro de ajuste em modelos, como os das Equações 5-7.

Tabela 3- Influência do formato das partículas na fração máxima de empacotamento (ϕ_m) de suspensões monomodais.

Formato das partículas	ϕ_m
Cúbicas	0,52
Hexagonal	0,74
Esferas em arranjo cúbico	0,52
Esferas em arranjo tetragonal	0,70
Esferas em arranjo piramidal	0,74
Fibras (eixo maior/eixo menor = 27)	0,18

Quando a fração de sólidos atinge uma determinada concentração, o movimento das partículas passa a ser influenciado diretamente por outras, e aglomerados de partículas podem ser formados de modo a permitir mais “espaços livres” para a movimentação das partículas. Se não for possível a formação destas estruturas ordenadas, um conjunto de partículas pode impedir o escoamento da suspensão (MENG & HIGDON, 2008), levando à formação de uma estrutura sólida (que não escoar).

2.2.1.1 Influência do solvente nas propriedades reológicas das suspensões

Dependendo da matéria prima, as polpas de frutas podem ter características físicas e químicas bastante distintas. Teor de sólidos em suspensão, sólidos solúveis, açúcares, ácidos orgânicos, lipídeos e pH são alguns fatores que variam bastante conforme a fruta utilizada e podem levar a grandes variações no comportamento de escoamento destas polpas. Avaliando a reologia do soro de diversas frutas, Freitas (2002) observou que a remoção dos sólidos em suspensão conferiu comportamento Newtoniano às polpas, com viscosidade variando entre 1 e 10 mPa.s, a 25 °C (Tabela 4).

A grande maioria dos trabalhos encontrados na literatura utiliza fluidos Newtonianos como matriz dispersante. No entanto, a adição de hidrocolóides que modifiquem a característica reológica do meio contínuo em suspensões é bastante comum, sendo utilizada para melhorar as características sensoriais e de estabilidade de diversos produtos como molhos para salada e sucos de frutas. A presença de solutos de alto peso molecular é a principal responsável pelo comportamento não-newtoniano das soluções (MIZRAHI, 1979). A adição de biopolímeros como estabilizantes e/ou espessantes altera significativamente o comportamento reológico do meio que, além de modificar as propriedades da fase contínua, pode influenciar o comportamento das partículas dispersas durante o escoamento. No entanto, deve-se considerar que a grande variação na composição das polpas de frutas pode afetar as propriedades dos biopolímeros de formas distintas, levando a diferentes efeitos no seu comportamento reológico (FREITAS, 2002).

Tabela 4- Viscosidade do soro da polpa de diversas frutas a 25°C, determinada por Freitas, 2002.

Fruta	η (mPa.s)	Fruta	η (mPa.s)
Abacaxi	2,16	Maracujá	3,42
Açaí	1,61	Melão	1,54
Acerola	2,47	Morango	4,77
Cajá	6,48	Pitanga	4,06
Caja	1,46	Tangerina	2,90
Coco	10,10	Uva	3,58
Graviola	2,47		

A medida que a elasticidade da matriz contínua aumenta, a orientação das partículas durante o escoamento tende a ser mais complexa (BARTRAM et al., 1975; JOHNSON et al., 1990). GUNES et al. (2008) estudaram a orientação em cisalhamento de suspensões de partículas diluídas em diversos fluidos viscoelásticos e observaram que quando os efeitos elásticos passam a ser significativos, a rotação das partículas

diminui, de modo que a sua órbita tende a se direcionar no sentido do vórtice. Sepehr et al. (2004) demonstraram que o aumento no teor de fibras em um meio Newtoniano levou somente a um leve aumento na viscosidade do sistema, tornando-o levemente pseudoplástico, enquanto que a adição das mesmas partículas em um fluido do tipo Boger levou a alterações muito mais significativas.

2.2.1.2 Influência das partículas nas propriedades reológicas da suspensão

A estabilidade e as propriedades reológicas de suspensões são fortemente dependentes das propriedades das partículas como tamanho, formato e distribuição de tamanhos, assim como das forças entre as partículas e da concentração de sólidos do sistema, sendo que a variação destes parâmetros determina as alterações nas propriedades da suspensão (GRECO et al., 2007).

Os sistemas dispersos mais simples são constituídos por esferas rígidas e inertes nas quais a única interação existente entre as partículas são repulsões rígidas que ocorrem quando as partículas se colidem (LARSON, 1999). De um modo geral, a viscosidade de suspensões aumenta com o aumento na fração volumétrica de sólidos (MEWIS & MACOSCO, 1993). Marti et al. (2005) observaram que, em soluções concentradas de esferas ocas de vidro, o aumento na concentração da fração de sólidos levou ao aumento nas interações entre partículas, permitindo a estruturação do sistema.

Suspensões concentradas contendo partículas esféricas rígidas com distribuição monomodal e bimodal foram extensivamente estudadas na literatura (SHIKATA et al., 1998; CHANG & POWELL, 1994; LUCKHAM & UKEJE, 1999). De modo geral, mantendo-se uma mesma fração volumétrica de sólidos (ϕ), o aumento na polidispersão dos sistemas quase sempre levou à redução da viscosidade das suspensões. É

possível reduzir até 50 vezes a viscosidade aparente mantendo a mesma quantidade de sólidos, somente com alterações na distribuição do tamanho das partículas. A adição controlada de partículas de tamanhos extremos da distribuição pode ser empregada para aumentar ou reduzir a viscosidade do sistema, o que é conhecido como *efeito Farris* (BARNES et al., 1989).

Em sistemas reais, a maioria das suspensões encontradas, especialmente na área de alimentos, não possui partículas rígidas nem esféricas. Entre as partículas não-esféricas, uma grande variedade de formatos pode ser encontrada. Os formatos não-esféricos de partículas mais simples são simétricos, ou seja, possuem um eixo rotacional de simetria, dentre os quais podem ser citados discos, esferóides achatados ou alongados e fibras. Quando as partículas em suspensão não são esféricas, elas costumam se orientar no sentido do escoamento, promovendo efeitos elásticos mais pronunciados que em suspensões esféricas com frações volumétricas similares (LARSON, 1999). De um modo geral, suspensões de fibras apresentam maior viscosidade que partículas esféricas com a mesma fração de sólidos, o que dificulta o seu manuseio industrial. O comportamento reológico das fibras depende não só das características destas partículas, mas também da sua orientação e das características da matriz.

Pena et al. (1995) observaram que partículas com formato de disco tendem a se mover em conjunto, se alinhando facilmente na direção do cisalhamento, pois promovem pouca resistência ao escoamento, enquanto que partículas esféricas tendem a se agrupar fortemente, levando a um aumento na resistência ao escoamento. Marti et al. (2005) estudaram a reologia de suspensões concentradas de misturas de esferas e fibras rígidas em diferentes frações volumétricas, e observaram que, para uma mesma fração de sólidos (ϕ), o aumento na proporção de fibras resultou em suspensões

altamente viscosas, com predominância do escorregamento durante o cisalhamento. Estes mesmos autores observaram que a rotação e alinhamento das fibras no sentido do escoamento não foram influenciados pelas partículas esféricas presentes no sistema.

Sabe-se que a viscosidade de suspensões é fortemente influenciada pelo formato e atrito entre as partículas. No caso de fibras, este atrito tem maior efeito na viscosidade de suspensões com fibras ramificadas que para sistemas com fibras lineares (SWITZER III & KLINGENBERG, 2003). De um modo geral, a adição de fibras pode afetar drasticamente o comportamento de escoamento de um fluido, independente da sua natureza, sendo que a magnitude deste efeito depende da orientação das partículas durante o escoamento, da concentração de sólidos, da razão entre o seu comprimento e diâmetro (*aspect ratio*) e das interações entre as partículas e o meio dispersante (EBERLE et al., 2008).

Por outro lado, sólidos em grandes quantidades podem provocar um grande aumento na viscosidade de suspensões. Polpas de frutas como tomate, manga, acerola, cajá, graviola, melão e morango foram caracterizadas na literatura como sendo fluidos pseudoplásticos com tensão residual (SHARMA et al., 1996; BHATTACHARYA, 1999; FREITAS, 2002). Freitas (2002) observou que amostras com maior teor de polpa em suspensão apresentaram menor índice de comportamento de escoamento (n) e maior de tensão de cisalhamento inicial (σ_0). Qiu & Rao (1988) também observaram que as propriedades reológicas do purê de maçã foram influenciadas pelo conteúdo de polpa, sendo que os valores de tensão residual eram proporcionais ao quadrado do conteúdo de polpa presente. Segundo Servais et al. (2002), um pequeno aumento na quantidade de sólidos em uma suspensão de 50% (em

volume) de concentração de partículas esféricas que não interagem (entre si nem com o sistema), pode duplicar a viscosidade do fluido.

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**CAPÍTULO 3 – COMPORTAMENTO
REOLÓGICO DE SISTEMAS-
MODELO DE SORO DE POLPAS DE
FRUTAS**

RHEOLOGY OF MIXED PECTIN SOLUTIONS

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ABSTRACT

The effects of sucrose (S) and pectin (P) concentrations and the ratio between two distinct pectins (R) on the rheological behavior of diluted pectin systems were evaluated simultaneously using surface response methodology. The systems were composed of a mixture of two high methoxy pectins with different DE values (HM1/HM2) and of a mixture of a high with an amidated low methoxy pectin (HM1/LMA). For the HM1/HM2 systems, the multivariate analysis showed that the sucrose and pectin concentrations exerted statistically significant ($p < 0.05$) linear effects on the consistency index k and viscosity, the influence of pectin about 5 times higher than that of sucrose. The pectin concentration and the ratio between the different pectins were shown to be significant with respect to the rheological parameters of the HM1/LMA systems. Evaluating the influence of the ratio between the different pectins, a synergistic effect on the structure reinforcement was observed when mixing HM1 and LMA in similar proportions, indicating the importance of the presence of hydrophobic interactions between methyl ester groups in addition to the stronger hydrogen bonding in junction

zone stabilization. In general, the conditions in which hydrogen bonds were favored in relation to hydrophobic interactions, led to systems with higher pseudoplasticity.

Keywords: rheological behavior, dilute solutions, high methoxy pectin, amidated low methoxy pectin.

1. INTRODUCTION

Pectin is a complex polysaccharide found in most plant tissues and fruits. This polysaccharide has been widely studied due to its ability to form gels in certain concentrations and under determined solvent conditions. It consists of α -(1-4)-D-galacturonic acid (GalA) units, interrupted by the insertion of rhamnose units and with side chains of neutral sugars attached to the backbone (Lootens et al., 2003). The carboxyl groups of pectin are often esterified with methanol (Fig.1), and the percent of groups esterified allows for the classification of pectins according to their degree of methoxylation or degree of methyl esterification (DE). In nature, pectins are usually highly methoxylated (HM), with more than 50% of the carboxyl groups esterified, low methoxylated (LM) pectins (<50% esterified) generally being obtained by controlled acid de-esterification of HM pectins. De-esterification using ammonia produces a different type of LM pectins in which some carboxylic acid groups have been amidated, referred to as amidated LM pectins (LMA) (Axelos & Thibault, 1992; Tho et al., 2005) (Fig.2).

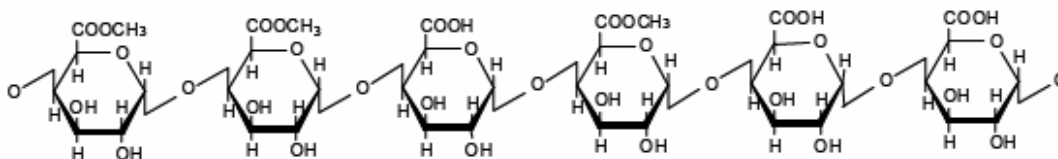


Fig.1 - Structural formula of partially methylated poly-galacturonic acid

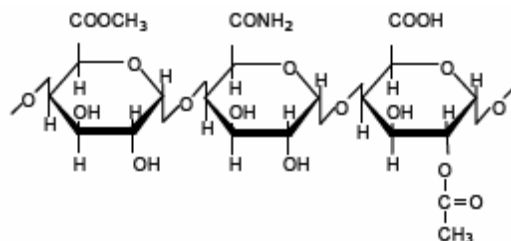


Fig.2 - Representation of the different substituents potentially present in commercial pectins (respectively, methyl-ester and amide group).

In general, the degree of methyl esterification determines the gelling mechanism of pectins. High-methoxyl (HM) pectins form gels mainly by hydrophobic interactions and hydrogen bonds at acidic pH values, due to the reduction of electrostatic repulsion, and in the presence of more than 55% sugar or similar co-solute, which decreases polymer-water interactions leading to junction zone stabilization by promoting hydrophobic interactions between ester methyl groups (Oakenfull & Scott, 1984). On the other hand, LM pectins have the ability to form gels in the presence of Ca^{2+} ions over a wider range of pH values, with or without sugar, by the “egg –box” mechanism (Axelos & Thibault, 1992). In this case, sections of two pectic chains, which must be free of ester groups, are held together by calcium ions. For LM pectins, the combined effect of pH and sugar promotes gelation at a lower calcium level despite the decrease in the number of sequences of carboxyl groups for calcium binding, due to the specific effect of sugar on the water activity, promoting hydrophobic interactions (Thakur et al., 1997). Although not completely understood, it is believed that the gelation of LMA pectins also occurs by the “egg-box” mechanism, in addition to the formation of hydrogen bonds by amide groups, which are responsible for stabilizing the junction zones between different pectin molecules (Alonso-Mougan et al., 2002).

The gelling properties of pure LM or HM pectins in systems that favour gelation of these polysaccharides (with Ca^{2+} or different co-solutes and low pH, respectively) have been widely explored in the literature (Löfgren et al., 2005; Tsoga et al., 2005; Evageliou et al., 2000; Grosso & Rao, 1998). More recently, mixed HM/LM pectin gelled systems were studied in the presence of more than 30% sucrose and Ca^{2+} , which favoured HM and LM pectin gelation, respectively (Löfgren et al., 2002; Löfgren & Hermansson, 2007), but the strongest synergistic effect in the rheological properties was obtained for a mixed HM/LM pectin gel in the presence of Ca^{2+} and 60% sucrose at pH 3. In this way, the study of mixtures of different pectins may be of great interest in food applications, in order to obtain products with well known functionalities, without the addition of excess co-solute, just exploiting a possible synergy between both polysaccharides.

Although the study of gelled systems is quite important, there is little information about the behaviour of more dilute polysaccharide systems, despite their crucial role in the food industry, since they comprise liquid foods and beverages, such as fruit juices, pulps and pastes. Moreover, only a few papers deal with the rheological behaviour of dilute pectin solutions (non gelled systems) and none of them deal with mixed HM/LM systems (Kjønriksen et al., 2005).

2. MATERIAL AND METHODS

2.1. Materials

Pectin HM2 (P9135, 60.97%DE) was purchased from Sigma (Sigma-Aldrich, St. Louis, MO, USA), while the HM1 (GENU® pectin type B Rapid Set-Z, 72% DE) and LMA (GENU® pectin type L21102AS-FS, 30% DE, 19% degree of amidation - DA) pectins

were kindly provided by Kelco Biopolymers (cPKelco, San Diego, CA, USA). Analytical sucrose and citric acid were purchased from Synth (Labsynth, São Paulo, Brazil).

2.2. Methods

Intrinsic viscosity

The intrinsic viscosities of the pure pectins were measured using a size 100 Cannon-Fenske semi-micro capillary viscometer (Cannon Instrument Co., USA). The viscometer was immersed in a water bath maintained at $25.0 \pm 0.5^\circ\text{C}$. A water run was used to calibrate the instrument, and the viscosity values were based on at least 3-4 efflux time readings taken for various concentrations of aqueous pectin solutions. All measurements were made in the concentration range from about 0.2 to 1% (w/v). The relative viscosity of a given solution η_{rel} (defined as the ratio between the solution and solvent viscosities) was determined by measuring the relative efflux times in the capillary. The relative viscosity values were converted to specific viscosities (η_{sp}) using Equation (1) (Ng et al., 1999).

When the solution concentration approaches zero, the reduced viscosity (η_{sp}/C) approaches the intrinsic viscosity, which is an indirect measurement of the hydrodynamic volume of the polysaccharide. The reduced viscosity was plotted against the concentration and the intrinsic viscosity was obtained by extrapolation of the reduced viscosity to zero polymer concentration using the Staudinger Equation (2) (Pagan & Ibarz, 1999).

$$\eta_{sp} = \eta_{rel} - 1 \quad (1)$$

$$[\eta] = \lim_{C \rightarrow 0} \left(\frac{\eta_{sp}}{C} \right) \quad (2)$$

where C is the concentration of the pectin solution (g/ml), η_{sp} is the specific viscosity (-) and $[\eta]$ is the intrinsic viscosity (ml/g).

Sample preparation

The rheological behaviour of pure pectin solutions (HM1, HM2 and LMA) were evaluated using fixed sugar and pectin concentrations at 10 and 1.25g/100g water, respectively. Pectin and sucrose, previously weighed, were added to a determined amount of deionized water and stirred for 2 hours until complete dissolution at room temperature. The pH of this solution was then measured (pH1) and 0.5% of citric acid added. The samples were then stirred for at least 15 minutes until completely homogenised and the solutions stored at 10 °C for 48 hours before reading the final pH (pH2) and performing the rheological measurements.

In order to study the rheological properties of mixed pectin solutions, a five level, three variables, central composite rotatable design (CCRD) was used to evaluate the simultaneous influence of sucrose (S), pectin (P) concentration and the ratio between the different pectins (R). The range and levels of the variables studied are shown in Table 1 and the samples were prepared in the same way as the samples of pure pectin solutions, described above. This design required seventeen sets of experiments including eight factorial points, three central points and six extra axial points. These conditions allowed for the description of the behaviour of the properties studied according to a second-order polynomial equation (Equation 3). The final pH, viscosity and rheological parameters of the best-fitting model (Newtonian, Power-law and Herschel-Bulkley) were taken as the responses to the design experiments.

$$y = b_0 + b_1S + b_2P + b_3R + b_{11}S^2 + b_{22}P^2 + b_{33}R^2 + b_{12}SP + b_{13}SR + b_{23}PR \quad (3)$$

where y is the response calculated by the model; S, P and R are the coded sucrose and pectin concentrations and the ratio between the different pectins, respectively, and b_i , b_{ii} , b_{ij} are the coefficients estimated by the model representing the linear, quadratic and the 2-factor-interactions of the response, respectively.

Table 1 - Experimental range and levels of both coded and real values of the independent variables. (A) Axial points; (C) Central points.

	Coded values			Real values		
	Sucrose concentration	Total pectin concentration	Ratio (HM1/HM2 or HM1/LMA)	Sucrose concentration (g/100g water)	Total pectin concentration (g/100g water)	Ratio (HM1/HM2 or HM1/LMA)
1	-1	-1	-1	5.0	0.200	0.524
2	1	-1	-1	15.0	0.200	0.524
3	-1	1	-1	5.0	0.500	0.524
4	1	1	-1	15.0	0.500	0.524
5	-1	-1	1	5.0	0.200	1.476
6	1	-1	1	15.0	0.200	1.476
7	-1	1	1	5.0	0.500	1.476
8	1	1	1	15.0	0.500	1.476
9 (A)	-1.68	0	0	1.6	0.350	1.000
10 (A)	1.68	0	0	18.4	0.350	1.000
11 (A)	0	-1.68	0	10.0	0.098	1.000
12 (A)	0	1.68	0	10.0	0.602	1.000
13 (A)	0	0	-1.68	10.0	0.350	0.200
14 (A)	0	0	1.68	10.0	0.350	1.800
15 (C)	0	0	0	10.0	0.350	1.000
16 (C)	0	0	0	10.0	0.350	1.000
17 (C)	0	0	0	10.0	0.350	1.000

The analysis of variance (ANOVA) was used to verify the regression significance, and the proportion of variance explained by the fitted model was given by the coefficient of determination (R^2). Three extra systems randomly chosen were formulated for each design (HM1/HM2 and HM1/LMA) in conditions within the studied range, in order to validate the models. Moreover, additional systems with expanded pectin ratios were evaluated in order to identify any possible synergy between different pectins.

Rheological measurements

The rheological properties of the pectin solutions were obtained using a Carri-Med CSL² 500 controlled stress rheometer (TA Instruments, New Castle, USA) at 25 °C. A double walled concentric cylinder consisting of an inner rotating acrylic cylinder (inner radius = 20.38 mm, outer radius = 21.96 mm) and an outer fixed stainless steel cup (inner radius = 20 mm, outer radius = 22.38 mm) was used for the measurements. Flow curve measurements were carried out with a shear rate ranging from 0 to 300 s⁻¹, in 3 sweeps (up, down and up-cycles), in order to eliminate thixotropy. The data obtained in the third sweep were fitted to different flow equations (Newtonian, Power-law and Herschel-Bulkley), to find the best fitting model, using the software Statistica v.5.0 (StatSoft Inc., Tulsa, USA).

3. RESULTS AND DISCUSSION

3.1. Intrinsic viscosity

Fig.3 shows typical Huggins plots of reduced viscosity (η_{red} (-)) against pectin concentration for LMA and HM-pectins in deionized water. All the pectin solutions showed a continual increase in molecular volume with dilution, exhibiting a pseudo-hyperbolic pattern. Such behaviour can be attributed to expansion of the molecules with dilution, due to the formation of large spherical networks or an increase in charge-charge repulsions along the chain. In this case, a smaller variation in the $[\eta]$ values was observed when η_{red} was fitted against the concentration of the pectin solution (C) using a fourth order regression method (Yoo et al., 2006) and the values for intrinsic viscosity $[\eta]$ of the different pectin solutions were obtained (Table 2). It can be observed that $[\eta]$ increased with decrease in the degree of methyl esterification (DE), varying from 1500 to

2500 ml/g, which was coherent with the values found by Yoo et. al (2006). Although $[\eta]$ is considered to be a measure of molecular weight, being the higher the molecular weight the higher the viscosity, it is in fact a measure of the hydrodynamic volume occupied by a molecule. In this sense, Morris et al. (2000) related the increase in DE to a decrease in intrinsic viscosity $[\eta]$, indicating a decrease in molecular rigidity. Thus, among the evaluated pectin, the LMA should be less rigid as compared to the HM-pectins.

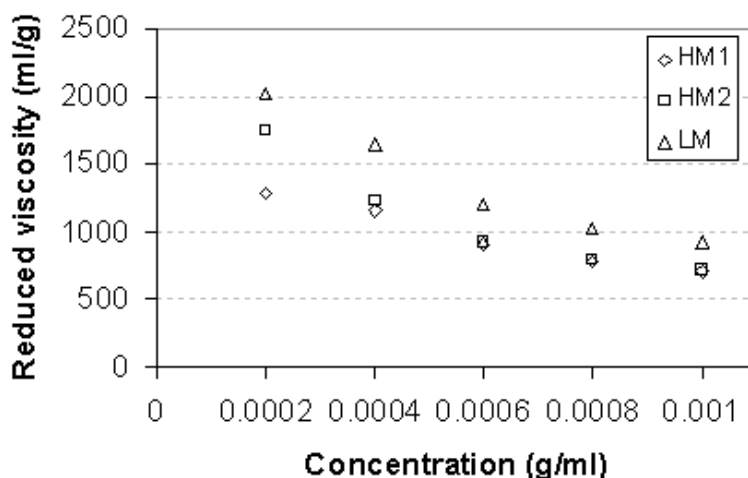


Fig.3 - Huggins plot of pectins in deionized water.

3.2. Characterization of the pure pectin solutions

Table 2 shows the rheological parameters, natural pH of the pure pectin samples (pH1) and the pH of the acidified systems (pH2). The addition of citric acid led to a decrease in the pH value of up to 1.26 units, greater pH variation being related to higher intrinsic viscosity values and higher initial pH values.

Table 2 – Degree of methyl esterification, rheological parameters and pH of the pure pectin solutions.

	DE	pH1	pH2	Δ pH	$[\eta]$ (ml/g)	k (Pa.s ⁿ)	n (-)
HM1	72	3.38	2.71	0.67	1517	0.0978	0.8702
HM2	61	3.96	2.96	1.00	2132	0.0526	0.9439
LMA	30	4.50	3.24	1.26	2450	0.6329	0.6341

The flow behaviour of all the pure pectin solutions with 1.25g of pectin and 10g of sucrose/100g water was shear thinning, showing a good fit to the power law model ($R^2 > 0.98$), being the consistency index k and the flow index behaviour n the rheological parameters fitted. The pure LMA solution showed the highest k value and pseudoplasticity (lowest n), while the HM2 solution showed behaviour closer to Newtonian ($n \sim 1$) and the lowest viscosity (directly related to k). Despite the fact that the polysaccharide concentration studied for the pure pectin solutions was higher than those studied in the mixed systems (Section 3.3), the results of the pure systems are an indication of how each pectin influences the rheological behaviour. In this sense, the results shown in Table 2 indicate that LMA pectin promotes greater modifications in system viscosities.

Comparing both HM pectins, it can be observed that the pectin with the lower pH at the same citric acid concentration was more viscous (higher k). The addition of citric acid led to a reduction in pH, which suppressed the dissociation of the carboxylic groups, promoting a reduction in the electrostatic repulsion between carbohydrate ions and, consequently, enhancing the interaction between pectin molecules (Thakur et al., 1997). Even though low-methoxyl pectins are known for their ability to form gels in the presence of Ca^{2+} and low co-solute concentration, Gilsenan et al. (2000) have reported that LM may also gel in the absence of calcium at pH values below 3.0. In such a case, the

unexpected gel formation of the LM pectin was a result of protonation of the carboxyl groups, promoting conformational ordering as a result of the association between the suppression of electrostatic repulsion with the liberation of the carboxyl groups to act as hydrogen-bond donors. Under these conditions, the LM pectin can aggregate and eventually gel. Since the conditions studied in this work were non-gelling favourable (low sucrose concentration and no Ca^{2+}), gelation was not expected, but the enhancement of the system viscosity could be associated with a conformational change of this pectin to the ordered form. In addition it should be emphasized that the presence of amide groups in the LM studied (amidated LM pectin), responsible for the formation of hydrogen bonds at low pH (≤ 3.5) (Lootens et al., 2003), and consequently a more structured system with a higher k value, although at a higher pH than the HM solutions.

3.3. Mixed pectin solutions

HM1/HM2 mixture

All the mixed HM1/HM2 solutions fitted the power law model well ($R^2 > 0.96$), except the sample with the lowest pectin concentration (run 11 - Table 1) that showed Newtonian behaviour ($n = 1$). Thus the rheological parameters evaluated as responses in this experimental design were the parameters fitted from the power law model: consistency index, k , and the flow index behaviour, n , as well as the viscosities at 10 and 100s^{-1} .

The statistical significance of the fitted model equations was evaluated by the F-test analysis of variance (ANOVA). The statistical model allowed for a good fit of all the rheological parameters and pH values, with a good R^2 ($R > 0.91$) value and with F_{model} much higher than F_{tab} (Table 3). The multivariate analysis showed that the sucrose and pectin concentrations exerted statistically significant ($p < 0.05$) linear effects on the

prediction of the consistency index and the viscosities for mixed HM1/HM2 systems, the influence of pectin being about 5 times higher than that of sucrose. Moreover the flow index behaviour showed a good fit to the quadratic model, with a clear increase in pseudoplasticity with increasing pectin concentration, but a non-linear and more complex influence of sucrose on this property. An increase in the sucrose content leads to a reduction in the system water activity, facilitating hydrophobic interactions between the pectin methyl ester groups of HM pectin (Löfgren & Hermansson, 2007), promoting more viscous and structured solutions.

Preliminary experiments showed that the amount and type of pectin influenced the final pH value, not allowing it to remain fixed. This fact can be attributed to the fraction of hydrogen ions used to neutralize the pectin, which depends on the amount of H^+ added to the system and the pKa of both pectins (Lootens et al., 2003). Thus in the present study the amount of acid was fixed at 0.5g/100g water, such that the final pH of the samples was only dependent on the amount of polysaccharide (P) and the ratio between the different pectins (R), as can be seen in 0. A positive regression coefficient for P indicated that the pH increased with an increase in pectin concentration at the same ratio between different pectins, while an increase in the amount of HM1 (+R) reduced the final solution pH. The higher the DE of the pectin, the less the amount of carboxyl ions available to bind to the added H^+ , such that there will be a greater amount of available H^+ , leading to a lower pH.

Table 3 - Model fitted for the rheological parameters and final pH of mixed HM1/HM2 solutions: coefficient of determination (R^2) and F-model/F-table.

	Model	R^2	$F_{\text{model}}/F_{\text{tab}}$
k =	$0.0065+0.0006*S+0.0030*P$	0.9196	818.07
n =	$0.9662+0.0030*S^2-0.0109*P+0.0054*P^2+0.0033*R^2+0.0031*S*P$	0.9473	29.21
η_{10}=	$0.0061+0.0006*S+0.0027*P$	0.9242	3441.84
η_{100}=	$0.0057+0.0005*S+0.0024*P$	0.9278	2667.50
pH =	$2.45+0.05*P-0.02*P^2-0.02*R$	0.9243	85.00

In order to observe the non-linear effects on the flow index behaviour, the response surfaces in Fig.4 represent the predicted models for mixed HM1/HM2 systems as a function of the sucrose and pectin concentrations and the ratio between HM1/HM2 and pectin concentration, respectively. It can be observed that the flow index behaviour tended to be closer to 1 (Newtonian behaviour) with increase in sucrose concentration and decrease in polysaccharide content. On the other hand, a more shear thinning behaviour (lower n value) was reached at lower sucrose concentrations (S up to 10g/100g water), higher pectin contents (P ~ 0.5 g/100g water) and the same amounts of the different pectins (R = 1).

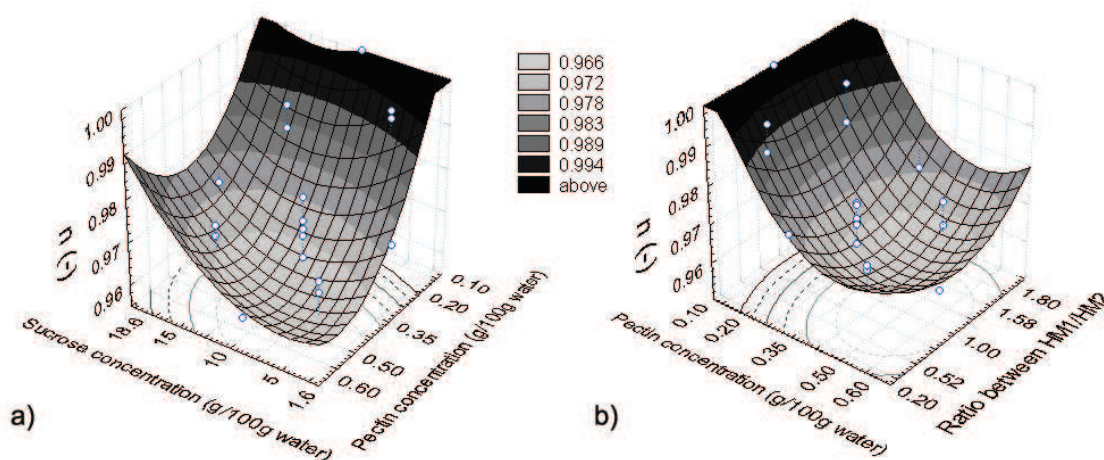


Fig.4 - Response surfaces for the flow index behaviour n of mixed HM1/HM2 solutions as a function of: a) sucrose and pectin concentrations (R fixed at level 0) and b) pectin concentration and the ratio between the different pectins (S fixed at level 0).

At low pectin concentrations, structuring due to hydrophobic interactions between pectin ester-methyl groups must be more pronounced, which is favoured by the amount of added sucrose that bonds with the water, reducing polymer-water interactions and hence favouring hydrophobic interactions (Oakenfull & Scott, 1984). On the other hand, as the pectin concentration increases and the amount of sucrose remains constant, hydrogen bonds will prevail over the hydrophobic interactions, leading to a more shear thinning system. In this way, one could speculate that a structure formed predominantly by hydrophobic interactions is less subject to shear ordering, i.e. is less shear thinning (n closer to 1) than structures formed with a majority of hydrogen bonds. This effect was more pronounced for systems with a HM1/HM2 ratio near to 1 or slightly lower (more HM2). In this case, the higher the amount of HM2 in comparison to HM1 ($R < 1$) the lower the DE of the system, i.e. with less methyl-ester groups or increased hydrogen bonds.

In order to validate the models fitted in 0, samples at three random conditions were prepared within the range studied. The experimental conditions and rheological

parameters fitted for the power law model of the different systems are shown in Table 4. The differences between the calculated and experimental k values were lower than 15% at all points, the greatest difference being close to the axial points. For the flow index behaviour n, the variation between the predicted and experimental data was lower than 2.5%, indicating that the proposed models were predictive for the rheological properties studied, within the range studied.

Table 4 - Validation conditions for the experimental design with HM1/HM2 mixtures.

	Coded values			k (Pa.s ⁿ)			n (-)		
	S	P	R	Model -fitted	Experimental	Error (%)	Model -fitted	Experimental	Error (%)
1	0	1	0	0.0095	0.0101	6.42	0.9608	0.9610	0.01
2	1	0	-1	0.0071	0.0067	6.03	0.9726	0.9715	0.12
3	1.5	1.5	0	0.0119	0.0136	14.29	0.9758	0.9526	2.38

HM1/LM mixture

All the HM1/LMA mixtures showed a good fit to the power law model ($R^2 > 0.93$), with n ranging from 0.49 to 0.87. The quadratic statistical model allowed for the prediction of the rheological properties studied at a 95% confidence level, with a coefficient of determination higher than 0.97 and F_{model} at least 36 times higher than F_{tab} (Table 5). For mixed HM1/LM systems, all the rheological parameters were influenced by the pectin concentration in the same way as observed for the HM1/HM2 systems, in addition to the ratio between the different pectins ($p < 0.05$), which was not observed for the mixture of different HM pectins. When compared to the HM1/HM2 systems (0), the fitted models for the HM1/LMA solutions indicated the possibility of obtaining k, η_{10} and η_{100} values of up to 60, 20 and 7 times higher, respectively, and n with half the value of that obtained for the HM1/HM2 systems, within the range studied. On the contrary of

what was observed for the HM1/HM2 mixtures, the sucrose concentration had no significant influence on the rheological properties of the mixed HM1/LMA solutions ($p < 0.05$). In this case, the range of sucrose concentrations studied was not large enough to influence the rheological parameters, probably due to its weak influence on the rheology of these systems, when compared to the influence of LMA.

The quadratic statistical model also allowed for the prediction of the final pH of the acidified solutions at a 95% confidence level, with satisfactory R^2 and $F_{\text{model}}/F_{\text{tab}}$. As observed for the HM1/HM2 mixtures, the pectin concentration (P) exerted a positive effect ($p < 0.05$) on the final pH of the acidified solutions, while the increase in R (more HM1) led to more acidic solutions.

Table 5 - Fitted model for the rheological parameters and pH of acidified mixed HM1/LMA solutions: coefficient of determination (R^2) and F-model/F-table. P: coded pectin concentration; R: coded ratio between HM1/LMA.

	Model	R^2	$F_{\text{model}}/F_{\text{tab}}$
k =	$0.0997 + 0.1142 * P + 0.0232 * P^2 - 0.0810 * R + 0.0386 * R^2 - 0.0654 * P * R$	0.9728	36.06
n =	$0.6356 - 0.0789 * P + 0.0291 * P^2 + 0.0597 * R - 0.0185 * R^2$	0.9803	101.79
$\eta_{10} =$	$0.0427 + 0.0391 * P + 0.0069 * P^2 - 0.0224 * R + 0.0098 * R^2 - 0.0169 * P * R$	0.9759	41.45
$\eta_{100} =$	$0.01839 + 0.0132 * P + 0.0020 * P^2 - 0.0054 * R + 0.0022 * R^2 - 0.0039 * P * R$	0.9752	39.31
pH =	$2.81 + 0.06 * P - 0.04 * R$	0.7255	11.08

Fig.5 shows the response surfaces for the rheological parameters evaluated, k and n as a function of the pectin concentration and the HM1/LMA ratio. An analysis of the surfaces indicated a tendency to reach minimum n and maximum k values at low R (more LMA) values and maximum pectin concentrations, leading to more viscous and shear-thinning systems, while an increase in the amount of HM pectin in the systems

(increase in R) with the same pectin and sucrose concentrations, reduced k and increased n.

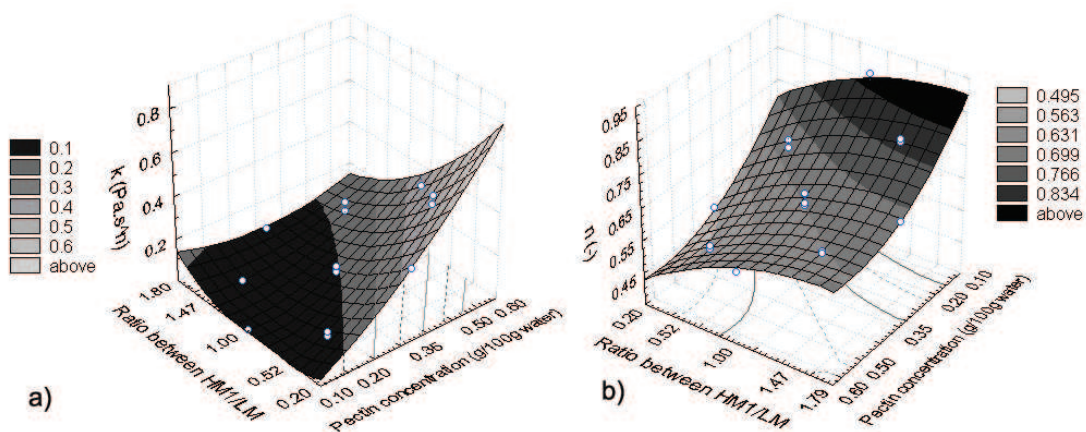


Fig.5 - Responses surfaces of the rheological properties for the mixed HM1/LMA solutions as a function of pectin concentration and the ratio between the different pectins (S fixed at level 0): a) consistency index k and b) flow index behaviour n .

In order to validate the quadratic models obtained for the HM1/LMA mixtures (Table 5), three random points were chosen within the range studied, and the rheological properties were measured (0). In general, the results showed an acceptable deviation from the responses obtained using the prediction equation. The consistency index values showed the highest error (deviation) between the experimental and predicted values, but evaluating the n values, the fitted models were very predictive, with a maximum error of 1.23%.

Table 6 - Validation conditions for the experimental design with HM1/LMA mixtures.

	Coded values			k (Pa.s ⁿ)			n (-)		
	S	P	R	Model -fitted	Experiment al	Error (%)	Model -fitted	Experiment al	Error (%)
1	0	1.5	-1.5	0.6788	0.6996	3.07	0.4517	0.4479	0.84
2	-1	0	1	0.0572	0.0654	14.32	0.6769	0.6686	1.23
3	0	-1	0	0.0087	0.0098	12.92	0.7437	0.7368	0.92

Evaluating the response surfaces (Fig.5), it can be seen a tendency to obtain the minimum viscosities and consistency indexes values with the same amount of both pectins (ratio between HM1/LMA = 1), while maximum n values would be achieved. Fig.5 also shows that an increase in pectin concentration led to a higher k value, especially with a lower HM1/LMA ratio.

Influence of pH on the rheological parameters

The pH of pectin solutions seems to affect their conformation and consequently their rheological properties, which has already been exploited in the literature (Lootens et al., 2003; Gilsenan et al., 2000; Holst et al., 2006). It is known that a lowering of the pH reduces the amount of charged groups and thereby the electrostatic repulsion between polymer chains, causing the attractive forces to become more dominant and leading to a more structured system. However, Fig.6 shows the opposite tendency, indicating that the value for k tended to decrease and n to increase exponentially with decreasing final pH. Lootens et al. (2003) observed that for low-methoxy non-amidated pectin, the elastic modulus increased with decreasing pH, reaching a maximum at pH ~ 3.0, after which it decreased. According to Gilsenan et. al (2000), although protonation of a certain proportion of the carboxyl groups may be an important factor in stabilising the intermolecular association of pectin chains, hydrogen bonds formed with ionised

carboxyl groups as the receptors are stronger than those involving groups that carry only a partial negative charge (hydroxyl or protonated carboxyl), because the electrostatic attraction will be greater. Thus, more structured systems reflect the optimum balance between the facilitation of intermolecular association by charge suppression and the loss of enthalpic stability due to hydrogen-bonding to ionised carboxyl groups, as the pH is reduced.

In general, the final pH of mixed HM1/LMA systems was higher than for HM1/HM2 systems, and the rheological properties of HM1/LMA solutions were more influenced by pH variation (Fig.6b), which can be associated with the ability of LMA to bind the amide groups via hydrogen bonds.

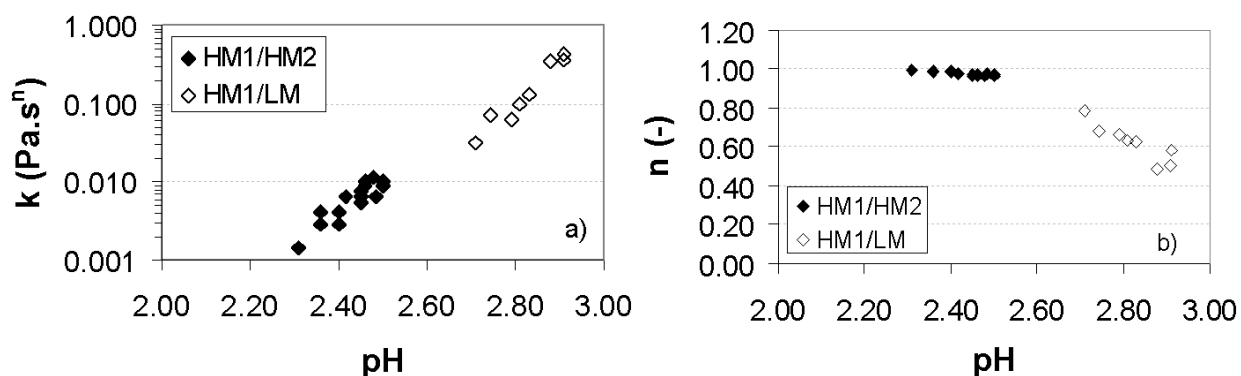


Fig.6 – The influence of pH on the rheological parameters: a) consistency index and b) flow index.

Influence of the ratio between the pectins on the rheological behaviour

In order to evaluate the quadratic effects of the ratio between the different pectins (HM1/HM2 and HM1/LMA), samples were prepared with constant sucrose, pectin and citric acid concentrations (10, 1.25 and 0.5 g/100 g water, respectively), but with expanded proportions between the different pectins (Table 7) as compared to the

conditions studied in the experimental design. Moreover, it is important to emphasize that the pectin concentration was twice as high as the maximum amount used in the experimental design.

Table 7 - Ratio of the different pectins added for the evaluation of the effect of the ratio between the polysaccharides.

HM1/HM2 systems				HM1/LMA systems			
Sample	HM1	HM2	HM1/HM2	Sample	HM1	LMA	HM1/LMA
1HH	0.00	1.00	0.00	1HL	0.00	1.00	0.00
2HH	0.25	0.75	0.33	2HL	0.25	0.75	0.33
3HH	0.50	0.50	1.00	3HL	0.50	0.50	1.00
4HH	0.75	0.25	3.00	4HL	0.75	0.25	3.00
5HH	1.00	0.00	∞	5HL	1.00	0.00	∞

The mixture of two high methoxyl pectins (HM1/HM2) led to systems with similar rheological characteristics (Fig.7a and c), except for the pure HM1 systems (5HH). With the same sucrose, citric acid and pectin concentrations, it can be seen that the increase in HM1 pectin content led to systems with lower pH, increased pseudoplasticity (lower flow behaviour index - n) and lower viscosity, which can be directly related to the consistency index k. However, the mixture of HM1 and LMA pectins showed a synergistic influence on the rheological properties (Fig.7b and d), which was not possible to observe in the evaluation of the response surface shown in Fig.5. It can be seen that systems with approximately 50% of each pectin (3HL) showed the highest k and lowest n values, indicating a more viscous and pseudoplastic behaviour when compared to systems with other HM1/LMA ratios. Löfgren & Hermansson (2007) observed that the kinetic behaviour of a mixed HM/LM pectin gel in the absence of calcium showed characteristics of both HM and LM pectin gelation at pH 3. It is important to emphasize

that such behaviour was not observed in the experimental design (section **Mixed pectin solutions: HM1/LM mixture**), since the ratio between HM1/LMA studied previously, ranged from 0.20 to 1.80, i.e., closer to the conditions for 2HL and 3HL, which showed similar k and n values. Moreover, the effect of the HM1/LMA ratio on the system viscosity was more pronounced at higher pectin concentrations (Fig.5). Thus, the higher pectin concentrations used in this section allowed one to discriminate the effect of the HM1/LMA ratio on the synergy of these polysaccharide mixtures. Such a result illustrates the importance of hydrogen bonding between the amide groups of LMA when this pectin is predominant, and up to approximately 50% of each pectin. When HM1 is predominant, weaker hydrophobic interactions begin to prevail, reducing the k and increasing the n values. Even though the contribution from hydrogen bonding is twice that from hydrophobic interactions in stabilizing the junction zones between pectins (Oakenfull & Scott, 1984), the results shown in Fig.7b and d emphasize the importance of the presence of hydrophobic interactions between methyl ester groups (lower k for 1HL and higher for 3HL) in addition to the stronger hydrogen bonding for junction zone stabilization.

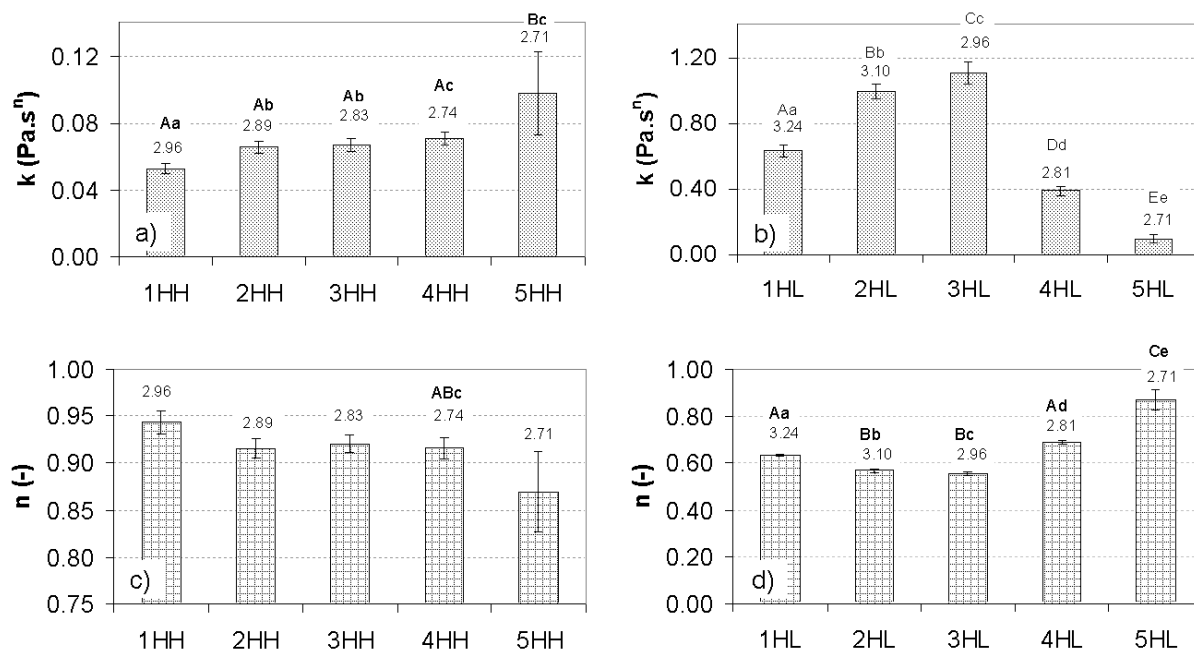


Fig.7 - Influence of the ratio between the different pectins on the rheological parameters: a) k for HM1/HM2; b) k for HM1/LMA; c) n for HM1/HM2 and d) n for HM1/LMA. The numbers above the columns indicate the final pH of each sample. Different letters indicate significant differences at $p < 0.05$. Capital letters: difference between the rheological properties. Small letters: difference between the pH values.

4. CONCLUSIONS

This study allowed for the evaluation of the effect of mixtures of pectins with different characteristics (amidation and degree of esterification) on the rheological behaviour of dilute pectin solutions. The sucrose and pectin contents were shown to be significant variables in the rheological behaviour of mixed HM1/HM2 systems, as described in the literature for more concentrated systems, while the ratio between these two pectins did not exert significant influence in this property. In this case, the increase in sucrose content contributed to a more viscous and structured solution due to its effect of reducing the water activity of the system, which favoured hydrophobic interactions between the pectin methyl ester groups. For the HM1/LMA mixtures, the significant

variables for the rheological parameters were pectin concentration and the ratio between the different pectins, which showed a synergistic effect when mixing HM1 and LMA in the same proportions, this effect being more pronounced at higher polysaccharide contents. Such results indicated the importance of the presence of hydrophobic interactions between the methyl ester groups in addition to the stronger hydrogen bonding in junction zone stabilisation. Furthermore, more pseudoplastic systems were observed under conditions in which hydrogen bonds were favoured over hydrophobic interactions. Thus, depending on the kind and content of pectin added it is possible to obtain different synergistic or antagonistic effects, providing a means to manipulate the texture of beverages and other liquid processed foods.

5. ACKNOWLEDGEMENTS

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**CAPÍTULO 4 – COMPORTAMENTO
REOLÓGICO DE SUSPENSÕES-
MODELO**

Parte 1. Efeito da viscosidade e polaridade da matriz dispersante

**INFLUENCE OF DISPERSING MEDIA AND PARTICLE
CHARACTERISTICS ON RHEOLOGICAL BEHAVIOR
OF RIGID SUSPENSIONS**

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ABSTRACT

Model systems were studied in order to evaluate the effect of viscosity (high and low viscous) and polarity (polar and non-polar) of continuous matrix on the flow behavior of suspensions. Silica particles and cellulose fibers (medium and long fibers) were used in the preparation of the dispersions to evaluate the effect of particle characteristics. Suspensions were prepared by adding particles to the continuous matrices with increasing solids volume fraction up to 0.20, and their steady state rheological properties were evaluated. In general, the increase in solids volume fraction exerted higher influence for larger cellulose fibers and less viscous matrices, due to larger particle-particle interaction. Evaluation of matrix polarity allowed the assessment of particle-solvent interactions, indicating higher interaction for particles dispersed in the polar

matrices. Results indicated that in addition to particle characteristics, suspending matrix properties strongly influence the rheological behavior of suspensions.

Keywords: rheology, suspensions, polarity, viscosity, interaction

1. INTRODUCTION

Suspensions are multiphase systems in which solid particles are dispersed into a liquid medium. Polymers with fillers, pharmaceuticals, ceramic pastes, concrete, blood, food and cosmetics are some examples of suspension products in the most diverse industries. Controlling the structure and flow properties of suspensions is often crucial to the consumer acceptance of the product or/and to its manufacture. In each particular case, suspensions have distinct characteristics, which rule their rheological behavior.

The simplest suspension consists of a diluted dispersion of non-Brownian, non-interactive rigid spheres in a Newtonian fluid, which was studied by Einstein over 100 years ago. Rigid repulsions are the only interactions between the particles dispersed in these suspensions. In this case, particles are widely separated and hydrodynamic interactions may be neglected, its rheological behavior being mainly controlled by the continuous phase [1]. However, in most real situations, the suspended particles tend to be non-spherical and are frequently found in not so diluted systems, so that hydrodynamic interactions are observed. As solids volume fraction (ϕ) increases, the movement of each particle is affected by the disturbance caused by other particles (hydrodynamic interaction), and its movement is directly influenced. Thus, as ϕ increases, interaction between suspended particles becomes important, and may strongly influence the suspension behavior [2]. As ϕ approaches the maximum packing fraction (ϕ_m), the role of particles in viscosity becomes much more effective until there is

no longer sufficient fluid in the system to lubricate the relative motion of particles, with viscosity tending to infinity [3, 4]. In this case, factors such as particle size/dimension, shape and particle size distribution influence the maximum packing fraction, therefore directly affecting suspension rheology. Hence, more than 100 papers within the last five years have been published about the effect of particle characteristics on the rheological behavior of suspensions. However, only a few papers deal with the effect of the continuous phase, and most of them evaluate the influence of polymer addition or the dispersing matrix elasticity on suspension properties [5-7]. Moreover, besides elasticity, the knowledge of the influence of the dispersing matrix characteristics such as viscosity and polarity may be of interest of distinct areas. Thus, the present study focused on the study of model systems, in order to evaluate the effect of the suspending phase properties (viscosity and polarity) on the steady state rheological behavior of rigid particle suspensions with different sizes, shapes and structures.

2. MATERIAL AND METHODS

2.1. Material

Silica particles (S) (S4133) and cellulose fibers of medium (CM) (C6288) and large (CL) (C6663) sizes were obtained from Sigma (Sigma-Aldrich, St. Louis, MO, EUA). Glycerol (Synth - Labsynth, Brazil), sucrose (Synth - Labsynth, Brazil), silicone oil (Boss – Accumetric Inc., Elizabethtown, KY, EUA) and commercial soy oil (Bunge Alimentos S.A., Brazil) were used to prepare the dispersing matrices.

2.2. Methods

Characterization of particles

Density, size, size distribution and morphology of particles were characterized. Particle density was determined by helium pycnometry, using an AccuPyc II 1340 V1.20

(Micrometrics, USA), with at least 20 measurements of each sample. Particle size distribution of different samples was evaluated by laser diffraction (LD) using a Mastersizer S model MAM 5005 (Malvern Instruments Ltd., U.K.), with distilled water as dispersing medium and 5 replicates of each sample. Optical microscopy (OM) was used to evaluate particle morphology and size characterization. In this case, particles were placed on microscope slides, covered with glass cover slips and observed at 40x magnification using a Carl Zeiss Model mf-AKS 24 x 36 EXPOMET optical microscope (Zeiss, Germany). Images were analyzed with the public domain software Image J v1.36b (<http://rsb.info.nih.gov/ij/>). The pixel-scale values were converted into microns by a scaling factor and at least 200 units of each sort of particle were measured. For the silica particles, 3 dimensions (diameters) of each unit were measured. The length (L) and the width (d) were the dimensions determined for the cellulose fibers, and the aspect ratio (a_r) was calculated by $a_r = L/d$, considering the width as the fiber diameter. For the OM analysis, particles were visualized as dry powder and dispersed in the different continuous matrices used in this study. The distributions obtained by laser diffraction and by image analyses were statistically compared using the non-parametric Kolmogorov-Smirnoff test, with the Statistica v.5.0 software (StatSoft Inc., Tulsa, USA).

Continuous phase characterization

Suspending matrices were characterized at 25°C with respect to their flow characteristics and density. Flow behavior was evaluated through steady state rheological measurements (section ***Rheological Measurements***) and density characterization was obtained using a 10 ml picnometer in five replicates.

Continuous phases were separated into two categories, according to their viscosity and polarity. In the first case, suspensions were classified into low and high

viscosity solutions; soybean oil, 82% glycerol aqueous solution and 60% sucrose aqueous solutions were the low viscosity matrices, while silicone oil and 98% glycerol aqueous solution were the high viscosity suspending phases. According to polarity, systems were classified as polar (aqueous systems: 98 and 82% glycerol and 60% sucrose solutions) and non-polar (oily systems: soybean and silicone oils), based on their chemical structure.

Dispersions preparation

Silica particles or cellulose fibers were added to the different matrices at different concentrations, with volume fraction up to 0.20. Systems were magnetically stirred for at least 10 minutes before rheological measurements were performed.

Rheological measurements

Steady state rheological properties were obtained in triplicate on a Carri-Med CSL² 500 controlled stress rheometer (TA Instruments Ltd., Surrey, England) at 25°C. Stainless steel cone-plate geometry (6 cm diameter and 2 degrees) was used for continuous phase characterization, while a 4 cm plate-plate geometry with roughed surface was used for suspensions. Measurements with plate-plate geometries were performed with a 1.0 mm gap, determined in preliminary tests (data not shown). Steady state rheological measurements were carried out with shear rate ranging from 0 to 300 s⁻¹, in 3 sweeps (up, down and up-cycles) to eliminate thixotropy. The data obtained in the third sweep were fitted to different equations (Newtonian, Power Law and Herschel-Bulkley) to find the best suitable model, through the Quasi-Newton iterative method, using the Statistica v.5.0 software (StatSoft Inc., Tulsa, USA).

Mathematical modeling

Based on particles and dispersing matrices properties, the dimensionless Péclet (Pe) number was calculated, according to Eq. (1).

$$Pe = \frac{6\pi\eta_0 a^3 \dot{\gamma}}{kT} \quad (1)$$

where: η_0 = viscosity of dispersing matrix (Pa.s);

$2a$ = characteristic dimension of particles (m);

k = Boltzmann constant ($1.38 \times 10^{-23} \text{ kg.m}^2.\text{s}^{-2}.\text{K}^{-1}$)

T = absolute temperature (K)

Influence of solids volume fraction (ϕ) on the relative viscosity (η_r) at 100 s^{-1} (typical food processes and consumption magnitude order) of the studied suspensions were evaluated using different models found in literature (0). Except for the Einstein equation, which was developed for diluted non-interactive systems maximum packing fraction (ϕ_m) was obtained by fitting each equation to the experimental data.

Table 1 Models used for correlation between solids volume fraction and relative viscosity of studied suspensions.

Einstein	$\eta_r = (1 + k_E \cdot \phi)$	
Maron-Pierce [8]	$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-2}$	
Krieger-Dougherty [2]	$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-\phi_m[\eta]}$	$1.4 \leq (\phi_m \cdot [\eta]) \leq 3$
Eilers [9]	$\eta_r = \left(1 + \frac{\frac{1}{2}[\eta]\phi}{1 - \frac{\phi}{\phi_m}}\right)^2$	

Where: η_r = relative viscosity ($\eta_r = \frac{\eta}{\eta_s}$)

ϕ = solids volume fraction;

k_E = adjustable parameter (2.5 for non-interactive rigid spheres);

ϕ_m = maximum packing fraction;

$[\eta]$ = intrinsic viscosity

η = suspension viscosity;

η_s = viscosity of suspending matrix.

3. RESULTS AND DISCUSSION

3.1. Particles characterization

Laser scattering (LD) analyses indicated a monomodal particle size distribution of silica particles, while both types of cellulose fibers showed a minor second peak at larger sizes (Fig.1). Such distribution of cellulose fibers could be attributed to a deviation from the ideal circular shape of these particles, since laser scattering theories are based on spheres, causing the measured particle size distribution of fibrous particles to convert into a widened distribution with a smoother second peak [10]. Statistical analyses of particle size distribution obtained by LD measurements indicated that cellulose fibers (Fig.1) did not show significant differences ($p < 0.05$) between the particle size distribution

(PSD) of medium (CM) and large (CL) fibers, although their volume mean diameter ($D[4,3]$) showed significant difference ($p>0.05$), being that CL was about 15% larger than CM (Table 2).

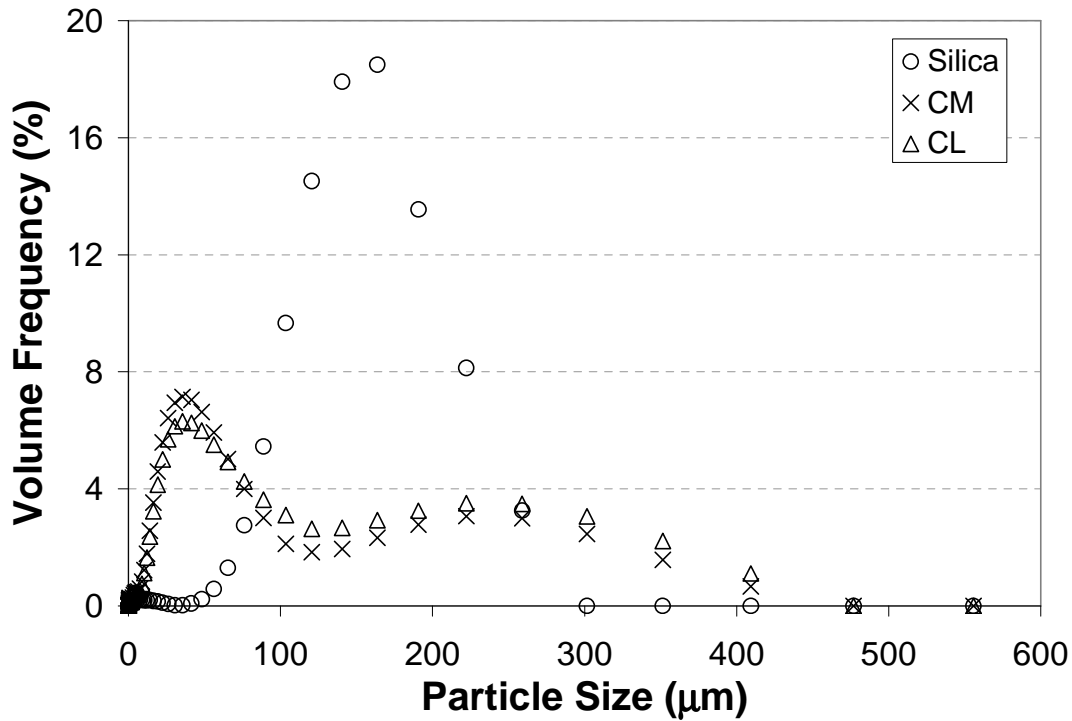


Fig.1 - Particle size distribution of silica and cellulose with medium (CM) and long fibers (CL).

Table 2 – Density and laser scattering measurements of volume mean diameter ($D[4,3]$) and median ($D(v,0.5)$) from silica particles and medium and long cellulose fibers.

	D[4,3] (µm)	D(v,0.5) (µm)	Density (g/ml)
Silica	144.31 ^a	142.91 ^a	2.01
CM	75.59 ^b	42.64 ^b	1.82
CL	86.31 ^c	45.70 ^b	1.86

Different letters indicate significant differences between measured diameters ($p>0.05$) within the same column.

Considering that different particle sizing techniques measure different particle physical properties, it would be advisable to use more than one technique to evaluate particle size distribution of a sample [11]. In this sense, besides light scattering, particles were analyzed through image analysis obtained by optical microscopy. It should be emphasized that LD measurements are based on the light energy scattering pattern of a sample, while image analysis obtained by microscopy is based on the projected sample areas. Thus, optical microscopy allows for morphology evaluation of the different particles (Fig.2) and for determination of fiber diameter and length and, consequently, their aspect ratio (a_r) (Table 3). As expected, silica particles showed to be more spherical, even though a little bit irregular, while the aspect of both types of cellulose fibers approached that of rods, with similar width (Fig.2).

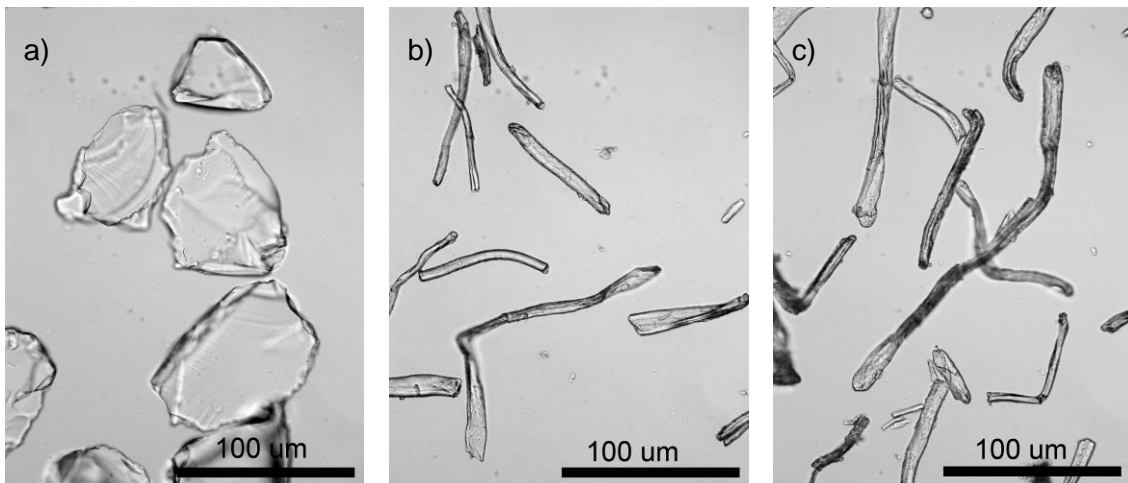


Fig.2 - Optical microscopy images from a) silica particles, b) cellulose medium fibers and c) cellulose long fibers.

As particle shape differs from a sphere, larger differences between the diameters obtained by different methods are expected. Comparing optical microscopy (OM) data (Table 3) with the laser diffraction (LD) ones (Table 2), it is observed that the use of different techniques provided distinct particle sizing results ($p < 0.05$), even for silica

particles, whose shape is more spherical, compared to fibers. It should be considered that LD methodology is largely affected by the choice of the refractive index in converting the experimentally determined scattering pattern into a particle size distribution [11], which could lead to deviation in the real particle size measurement [12, 13]. Moreover, such differences between particle sizes observed for LD and OM techniques could also be attributed to the fact that laser scattering techniques are based on the volumetric distribution, while microscopy analysis is a numeric distribution, based on the particle projected area.

Optical microscopy (Table 3) indicated that both types of cellulose fibers showed similar diameters ($p>0.05$) but CL length was about 50% larger than CM, resulting in a larger aspect ratio (a_r) of the long fiber (CL). Moreover, CM length was similar to the diameter of silica particles.

Table 3 - Particle dimensions measured by image analysis obtained from optical microscopy.

		Diameter (μm)	Length (μm)	a_r
Silica	Dry Powder	55.57	-	-
	Polar matrices	68.20	-	-
	Non-polar matrices	65.18	-	-
CM	Dry Powder	6.64	57.81	8.71
	Polar matrices	8.21	73.96	9.01
	Non-polar matrices	7.51	69.99	9.32
CL	Dry Powder	6.68	86.99	13.02
	Polar matrices	8.28	108.74	13.13
	Non-polar matrices	7.48	100.04	13.37

Polar matrices: 82 and 98% glycerol and 60% sucrose aqueous solutions.

Non-polar matrices: soybean and silicon oil.

Evaluating particle dimensions from particles dispersed in different matrices, microscopy analyses showed that all studied particles immersed in the different matrices “swelled” (Table 3), which could be attributed to particle porosity, leading to a dimension

increase of around 25 and 15% for the polar and non-polar media, respectively. Despite their different structures, silica particles and cellulose fibers had their size increased in the same proportion when immersed in the same matrices (aqueous or oil).

Comparing the increased size within the different matrices, particles immersed in the polar matrices were not more than 10% larger than the particles immersed in the non-polar medium, leading to a similar displacement of curves obtained for particles dispersed in all matrices. Thus, in this study, the solids volume fraction (ϕ) was considered to be the volume of particles added to the suspensions, i.e. of the dry particles.

3.2. Continuous phase characterization

Once particle densities (Table 2) were much higher than the observed for the matrices or continuous phases (Table 4), highly viscous solutions were chosen as suspending medium in order to avoid particle sedimentation during the flow curves assays [2].

Rheological analysis indicated that all continuous phases used in this study showed Newtonian behavior and the viscosity of the different suspending phases can be observed in Table 4. According to viscosity, these suspending matrices were separated into low and high viscosity solutions, with approximately 0.05 and 0.5 Pa.s, respectively. Moreover, solutions were classified as polar (glycerol and sucrose solutions) and non-polar (soybean and silicone oil). In this case, considering the chemical structure and/or composition of compounds, the polarity of matrices was ordered as follows: Silicone oil < Soybean oil < Glycerol 98% < Glycerol 82% < Sucrose 60%

Table 4 - Viscosity and density of continuous phases or suspending matrices.

Matrix	Density (g/ml)	Viscosity (Pa.s)
Soybean oil	0.9177 ± 0.0098	0.052 ± 0.001
Silicone oil	1.1075 ± 0.0149	0.505 ± 0.022
Glycerol 82%	1.2053 ± 0.0120	0.052 ± 0.001
Glycerol 98%	1.2485 ± 0.0222	0.497 ± 0.018
Sucrose 60%	1.2840 ± 0.0113	0.047 ± 0.001

3.3. Rheological behavior of suspensions

All suspensions with low solids volume fraction showed Newtonian behavior (Table 5). In this case, no interaction between the suspended particles should occur and the rheological behavior is determined by the continuous phase, with suspensions classified as diluted systems [1, 14]. Non-Newtonian characteristics were observed with increasing solids volume fraction (ϕ) for most of the suspensions. These systems could be classified as semidiluted or concentrated, depending on the interactions between suspended particles [15].

For most of the studied systems, a shear thinning behavior was observed for solids volume fractions much lower than 0.40, differently from what has been stated in literature [16] (Table 5). As solid content increases, suspensions become more structured systems, with higher consistency index (k) and pseudoplasticity (lower n), but no yield stress (σ_0) was observed.

Table 5 - Rheological parameters of suspensions obtained from fitting of the Power Law model ($R^2 > 0.950$).

	ϕ	Soybean oil		Silicone oil		Glycerol 82%		Glycerol 98%		Sucrose 60%	
		k (Pa.s ⁿ)	n (-)	k (Pa.s ⁿ)	n (-)	k (Pa.s ⁿ)	n (-)	k (Pa.s ⁿ)	n (-)	k (Pa.s ⁿ)	n (-)
Silica	0.005	0.044	1.00	0.485	1.00	0.048	1.00	0.413	0.98	0.042	1.00
	0.01	0.036	1.00	0.499	1.00	0.050	1.00	0.472	0.98	0.045	1.00
	0.05	0.056	1.00	0.601	1.00	0.067	0.98	0.541	0.99	0.059	1.00
	0.10	0.077	1.00	0.911	1.00	0.097	0.97	0.732	0.98	0.093	1.00
	0.15	0.179	0.97	2.011	0.97	0.192	0.97	1.406	0.96	0.199	1.00
	0.20	0.363	0.96	3.387	0.94	0.593	0.95	4.382	0.87	0.603	1.00
CM	0.004	0.046	1.00	0.434	1.00	0.053	1.00	0.473	0.98	0.048	1.00
	0.008	0.036	1.00	0.512	1.00	0.055	1.00	0.448	0.98	0.052	1.00
	0.025	0.076	0.96	0.724	0.98	0.123	0.94	0.794	0.95	0.111	0.94
	0.042	0.118	0.93	1.193	0.95	0.395	0.88	1.526	0.88	0.287	0.91
	0.067	0.357	0.87	4.579	0.83	4.019	0.74	7.524	0.73	5.291	0.67
	0.084	1.078	0.79	8.422	0.76	10.190	0.70	32.890	0.58	23.034	0.55
	0.101	2.973	0.71	27.910	0.52	-	-	-	-	-	-
CL	0.004	0.048	1.00	0.479	1.00	0.054	1.00	0.453	0.97	0.058	1.00
	0.008	0.052	1.00	0.567	1.00	0.060	1.00	0.503	0.96	0.069	1.00
	0.024	0.127	0.95	1.747	0.91	0.421	0.82	1.250	0.89	0.414	0.82
	0.041	0.348	0.86	4.736	0.82	1.576	0.74	5.568	0.75	2.450	0.70
	0.066	1.439	0.76	17.705	0.67	20.680	0.60	30.890	0.60	25.366	0.48
	0.082	4.951	0.72	-	-	-	-	-	-	-	-

The influence of solids volume fraction (ϕ) on the rheological behavior of the different suspensions was lower for silica systems than for the cellulose ones (Table 5). It should be considered that the chemical structure of silica (SiO_2) would indicate a more rigid structure, with consequent lower particle-particle interaction when compared to cellulose. Thus, considering such characteristic as well as the shape, which could be approximated to a sphere, the lower influence of silica on flow behavior of the studied suspensions would be expected [17]. Tsai et al. [18] concluded that van der Waals

interparticle attraction between non-colloidal silica sand particles dispersed in non-polar medium is negligible, and that Newtonian behavior was observed for solids volume concentration up to 0.60, while for aqueous matrices, van der Waals attraction was significant, imparting shear thinning behavior of suspensions at lower ϕ . In the present study, non-Newtonian behavior was observed for lower ϕ even for matrices with non-polar characteristics, as compared to the silica sand, used by Tsai et al. [18]. Evaluating cellulose fiber suspensions, it could be observed that influence of the polar (glycerol and sucrose solutions) matrices on suspension rheology was greater than for the soybean and silicone oils. At a same ϕ , higher pseudoplasticity was observed for the cellulose suspended in the glycerol and sucrose solutions, which could indicate higher interaction of these fibers with the suspending phase. Such result could be also correlated comparing the n values obtained for the high viscosity matrices (silicone oil and glycerol 98%), with different polarity but allowing for similar behavior of particle mobility. In this viscosity condition, particle-particle interaction (as will be observed in section 3.4) is reduced, and the highest n showed by the non-polar matrix emphasizes that the higher influence of the polar matrices on pseudoplasticity would be associated with enhanced particle-solvent interactions.

For diluted non-spherical suspensions, the particles rotate around the so called Jeffery orbits, and the increase on concentration disturbs such rotation [19]. Thus, fibers in a diluted suspension would be free to rotate, with no hydrodynamic interaction between them. As ϕ increases, hydrodynamic interactions would be predominant with some physical contact between the fibers, but with a random orientation (semidiluted systems) [2]. When fiber-fiber interaction is observed, the dynamic properties of the suspension may be severely affected and the system is classified as concentrated [15].

Usually, fiber suspensions are more viscous and elastic than spherical particle suspensions of equal volume concentration due to the larger excluded volume of the first ones. Therefore, the interaction between fibers is strong even at low concentrations [20], leading to a higher influence of this kind of particle on the rheological properties of the suspensions. When subjected to flow, non-spherical particles dispersed in a Newtonian matrix can develop preferred orientations. The resulting anisotropy causes non-Newtonian behavior [6]. This is more remarkable as the fiber aspect ratio becomes larger, due to the higher degree of particle alignment, as could be observed comparing the CM and CL systems. At a similar solids volume fraction, CL suspensions were more shear thinning (lower n) than CM ones (Table 5). For particles of higher a_r or higher ϕ , transitions to nematic phases or other ordered microstructures may occur, leading to more significant effect of aspect ratio on viscosity [21]. In addition, in order to achieve higher thermodynamic stability, fibers with larger aspect ratio tend to flocculate instead of remaining individual particles [20], influencing even more the rheological behavior, specially with high solids content. At elevated solids concentration, particle motion may be restricted and particle jamming may occur, leading to a solidlike behavior which will prevent the system to flow [21], thus avoiding flow curves measurements at high solids volume fraction. For the cellulose particles, it was not possible to evaluate systems with ϕ as high as obtained for silica systems, since for most CM suspensions 0.10 of solids volume fraction could hardly be achieved, while for CL this value was even lower, not much higher than 0.08.

In this way, Eberle et al. [15] defined ranges of fiber concentration which allows classifying the suspensions into categories, depending on the particle aspect ratio. According to this classification, suspensions would be in the diluted regime when $\phi < a_r^{-2}$. The concentrated regime would be achieved for $\phi \geq a_r^{-1}$ while a semidiluted suspension

would have a solids concentration between these two limits. Based on such definition, the cellulose suspensions studied in the present research would be considered diluted for volume fractions (ϕ) up to ~ 0.01 and 0.005 for medium and long fibers, respectively, which could be associated to the Newtonian behavior of these suspensions. A further increase on fiber concentration would lead to a semidiluted regime, with particles interaction with network formation, responsible for the non-Newtonian behavior [14]. Solids content close to 10 and 7% would define the limit between the semidiluted and the concentrated regime for medium and long fiber suspensions, respectively. Indeed, such values would be close to the maximum concentration that could be achieved for the aqueous suspensions (Table 5).

3.4. Effect of continuous phase characteristics on rheological behavior of model suspensions

In order to compare the influence of particle concentration on the rheological behavior of suspensions, Fig.3a and 3b show the effect of solids volume fraction suspended in continuous phases with different viscosities, but grouped according to their polarity. As observed previously (Table 5), CL suspensions were the systems most influenced by solids concentration, followed by CM suspensions. Silica suspensions were less influenced by ϕ , leading to increase on viscosity of dispersing phase not higher than 10 times, within the entire range of concentration studied (up to 20%). In this case, only a slight difference was observed between the more and the less viscous solutions, independently the polarity, differently from what occurred with fibrous suspensions. For both cellulose systems, increasing the solids volume fraction in the less viscous matrices led to a considerable increase in suspension viscosity (Fig.3c), which was mainly observed as ϕ increased. For the fibers dispersed in the more viscous solutions (Fig.3d),

such increase was more discrete, which could be attributed to the lower mobility of particles reducing their interaction, due to the high viscosity of the continuous matrices.

The effect of continuous phase polarity on relative viscosity of different suspensions is shown in Fig.3c and d. For the highly viscous matrices, only a small difference between the relative viscosity of aqueous (polar) and oily (non-polar) suspensions was observed (Fig.3d). In this case, it was not possible to achieve an increase in suspension viscosity (η_r) much higher than 10 times, within the concentration range studied. For the low viscosity matrices, the viscosity of suspensions dispersed in more polar solutions was clearly more influenced by the increase on solids volume fraction, since no significant difference was observed between the 82% glycerol and the 60% sucrose suspensions ($p>0.05$). Such results could be associated with higher “swelling” observed for particles immersed in the more polar matrices (Table 3). Such results emphasize the fact that fluid binding properties with the solids dispersed are important for the suspension rheological properties [22], and thus, together with other properties such as particle characteristics and solution viscosity, should be considered in their flow behavior evaluation.

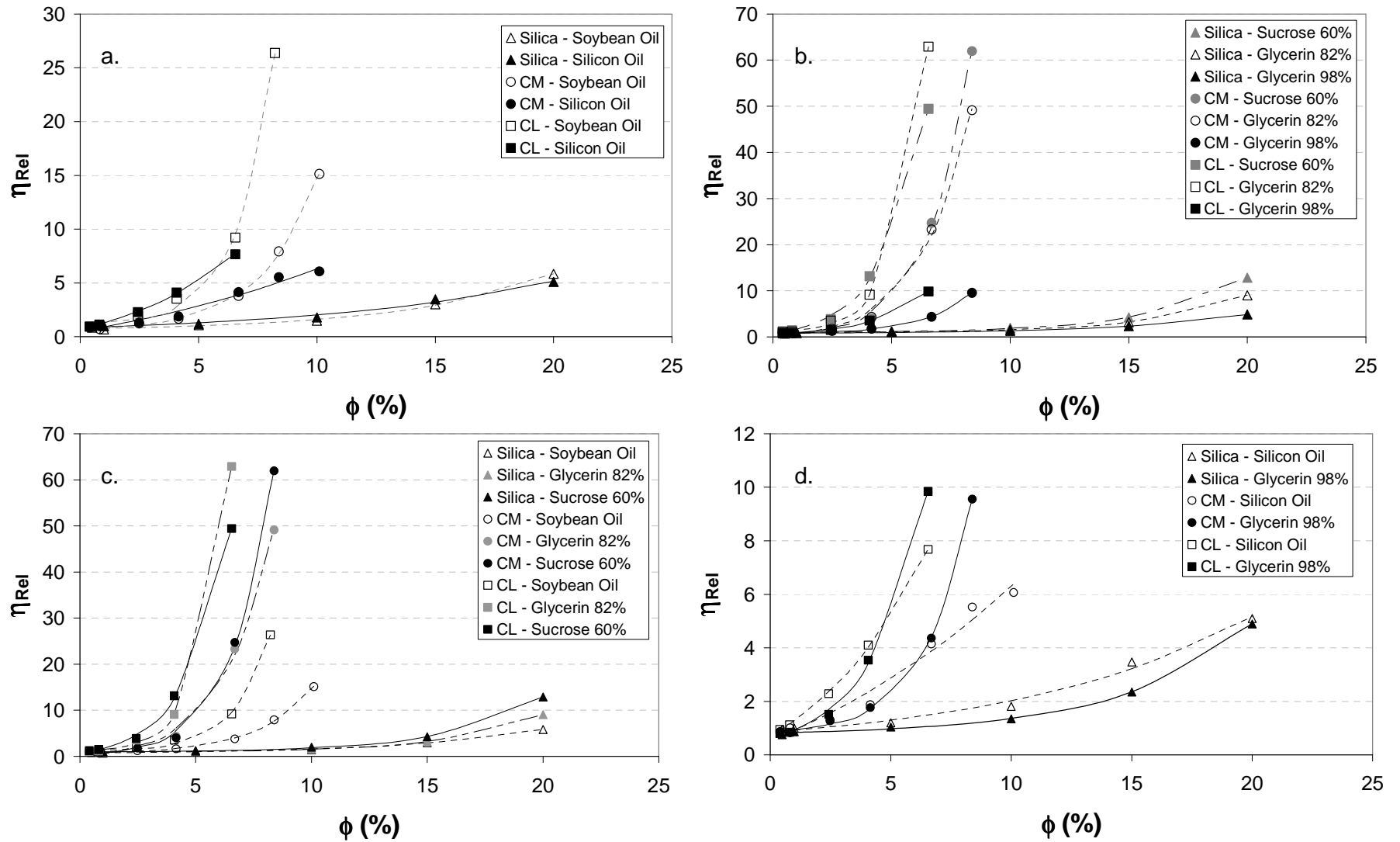


Fig.3 - Influence of solids concentration on relative viscosity of suspensions. Data grouped by polarity (a. non-polar and b. polar character) and by viscosity (c. low (~0.05 Pa.s) and d. high (~0.5 Pa.s) viscosity dispersing matrices).

3.5. Maximum packing fraction

Numerous models are found in literature in order to correlate relative suspension viscosity (η_r) with solids volume concentration (ϕ). Thus, Table 6 shows the comparison with different models proposed for such correlation (0). A higher deviation in model fitting of experimental data occurred for systems with solids volume fraction close to the maximum packing fraction (ϕ_m), decreasing models accuracy [4]. Generally, it was observed that Eilers and Krieger-Dougherty equations showed better fit of the experimental data, probably due to the increased number of model parameters as compared to the Einstein and Maron-Pierce equations. Despite the fact that the latter were developed for monomodal spherical suspensions, experimental data of all systems were satisfactorily fitted. The Einstein model was adjusted within the diluted and semidiluted concentration range, showing better fitting for silicone and glycerol 98% media (Table 6). The increased viscosity of these solutions should reduce particle interaction, as previously observed (section 3.4), leading to a better fit for this model developed for non-interacting rigid spheres.

Evaluating the ϕ_m fitted by different models (Table 6), it is observed that a higher ϕ of silica particles is necessary to achieve the maximum packing fraction, as compared to the cellulose fibers, which could be related to the larger excluded volume of these latter particles, as previously stated. Comparing the different matrices, it is observed that the maximum packing fraction was higher for the non-polar systems (soybean and silicon oils). Besides the maximum packing fraction (ϕ_m), Eilers and Krieger-Dougherty models allowed for the fitness of the suspensions intrinsic viscosity ($[\eta]$). While ϕ_m represents the maximum ϕ at which suspended particles completely “fill up” the space throughout a suspension [23], intrinsic viscosity is defined by the limiting value of specific

viscosity at zero concentration, i.e., they could be associated with a concentrated and diluted system, respectively.

Intrinsic viscosity obtained for silica suspensions was smaller than for the cellulose ones, since the larger the size, the larger the $[\eta]$ value. Considering that $[\eta]$ is in fact a measure of the hydrodynamic volume occupied by a molecule, it is observed that cellulose suspensions dispersed in non-polar matrices showed lower intrinsic viscosity, indicating that fibers could be agglomerated in these matrices, consequently reflecting in higher maximum packing fraction. In these cases, higher solids volume fraction would be achieved, not only because particles swell less in the non-polar matrices, but mainly due to the fiber-fiber interactions, reducing their binding properties with dispersing matrix.

1 Table 6 - Model fitted for ϕ versus relative viscosity (at 100s^{-1}) plots.

		Einstein		Maron-Pierce		Krieger-Dougherty			Eilers		
		k_E	R^2	ϕ_m	R^2	ϕ_m	$[\eta]$	R^2	ϕ_m	$[\eta]$	R^2
Soybean Oil	Silica	0.004	0.856	34.731	0.995	28.187	0.050	0.996	28.798	0.042	0.995
	CM	0.035	0.880	16.344	0.801	20.018	0.150	0.852	14.215	0.166	0.997
	CL	0.323	0.738	10.109	0.998	11.009	0.222	0.999	10.544	0.233	1.000
Silicone Oil	Silica	0.167	0.920	35.578	0.979	47.448	0.063	0.985	40.398	0.064	0.985
	CM	0.178	0.919	13.942	0.987	17.771	0.161	0.993	15.409	0.163	0.993
	CL	0.464	0.966	10.122	0.959	13.078	0.229	0.972	10.148	0.295	0.995
Glycerol 82%	Silica	0.268	0.742	30.147	0.989	25.271	0.055	0.998	25.141	0.041	0.999
	CM	0.298	0.882	11.515	0.770	13.377	0.224	0.834	15.456	0.611	0.990
	CL	1.075	0.773	7.479	0.996	8.719	0.344	0.998	8.682	0.529	1.000
Glycerol 98%	Silica	0.132	0.832	37.326	0.982	29.789	0.047	0.992	25.221	0.025	0.992
	CM	0.058	0.877	13.968	0.883	17.561	0.171	0.918	11.069	0.125	0.999
	CL	0.159	0.915	9.504	0.971	12.154	0.247	0.987	9.194	0.229	0.993
Sucrose 60%	Silica	0.396	0.743	27.766	0.998	24.381	0.061	1.000	25.721	0.058	1.000
	CM	0.297	0.777	8.370	1.000	8.393	0.240	1.000	8.376	0.240	1.000
	CL	1.085	0.872	6.696	0.978	7.906	0.376	0.994	7.402	0.881	1.000

A number of studies attempts to correlate the relative viscosity of suspensions with their solids volume concentration, but the shear rate effect evaluation has not been the focus of these studies [16]. Thus, fitting the relative viscosity (η_r) correlations with the solids volume concentration (ϕ) at different shear rates leads to different values of maximum packing fraction, since ϕ_m is higher for higher shear rates, according to a power law fit (data not shown). Such result could be associated with particles alignment during flow, which is increased with increasing shear rate [24], leading the arrangement of particles to a more ordered/nematic structure. Moreover, as $\dot{\gamma}$ approaches zero ($\dot{\gamma} \rightarrow 0$), the obtained $\phi_{m,0}$ value represents the solids volume fraction contained in a cluster [25], and the exponent of the power law model (b) would be an indicative of how much ϕ_m values would be influenced by the shear rate, i.e., an indirect indicative of particles alignment. Generally, higher matrix viscosity was associated with a higher exponent value (b) (Table 7). In this case, the low viscosity matrices would “allow” the fibers to be arranged in a more aligned direction in their initial position, while for the highly viscous matrices the alignment would most likely occur with shearing.

Table 7 – Fitting parameters to the power law model ($\phi_m = \phi_{m,0} \dot{\gamma}^b$) from maximum packing fraction obtained by Eilers model versus shear rate.

		$\phi_{m,0}$	b	R ²
Soybean Oil	Silica	27.154	0.014	0.993
	CM	10.419	0.012	0.970
	CL	8.142	0.013	0.941
Silicone Oil	Silica	35.013	0.044	0.987
	CM	13.292	0.075	0.959
	CL	7.202	0.080	0.971
Glycerol 82%	Silica	25.160	0.000	0.953
	CM	12.835	0.015	0.999
	CL	8.087	0.017	0.999
Glycerol 98%	Silica	26.364	0.000	1.000
	CM	10.425	0.038	0.984
	CL	8.179	0.086	0.957
Sucrose 60%	Silica	23.854	0.017	0.989
	CM	10.059	0.025	0.997
	CL	9.422	0.020	0.929

3.6. Dimensionless number analysis

The Péclet number is a dimensionless number relating the viscous forces, induced by the applied shear flow, with Brownian motion in colloidal suspensions. For non-colloidal particles, Brownian motion may be neglected, since kT could be considered as a convenient energy scale, and the Pe number would be associated with a “diffusional relaxation time”, i.e. the time required for a particle to diffuse a distance comparable to its radius in an aggregated system [18]. Thus, the Péclet number may be related to the structure of suspensions together with factors such as particle size distribution, particle morphology and interparticle forces [16].

For non-colloidal suspensions, the Pe number has been used in literature to correlate particle size with relative viscosity (η_r) [26, 27]. In Fig.4, the behavior of the studied systems may be observed as a function of Pe for $\phi = 0.07$. In such concentration, particle interaction should be observed in cellulose suspensions (semidiluted/concentrated regime), while for silica suspensions a higher solids volume fraction (Table 5) would be needed. Thus, for silica particles the effect of relative viscosity as a function of Pe was also evaluated for $\phi = 0.20$ (detail in Fig.4). As observed for silica suspensions at 0.07 (Fig.4), relative viscosity for all suspensions within the diluted regime (**APÊNDICE I**) were independent of Pe, with no correlation among the different systems. As solids concentration increased, it was observed that the influence of relative viscosity with Pe was higher for sucrose solutions (higher slope), followed by glycerol 82%, while for the non-polar matrices the influence was smaller. A similar behavior was observed for fiber suspensions. Such results highlight the effect of suspending matrix on particle interaction.

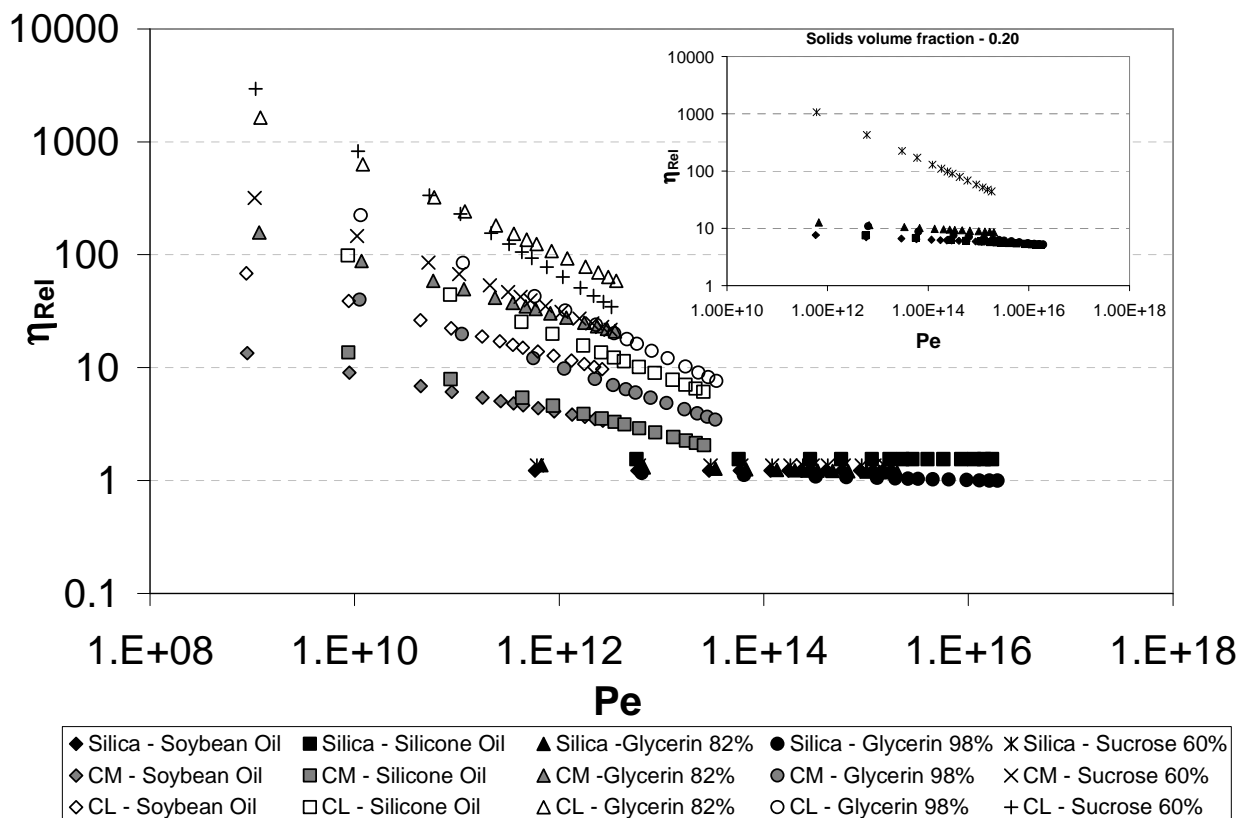


Fig.4 - Péclet number calculated for 0.07 solids volume fraction and 0.20 (in detail).

4. CONCLUSIONS

Suspension viscosity was more strongly affected by cellulose fiber presence as compared to silica particles, allowing a higher packing fraction with the latter. Relative viscosity increased exponentially with ϕ , with such influence being higher using polar and less viscous matrices. The lower viscosity of the suspending phase facilitated particle movement and interaction, while a higher interaction between fluid and particle was observed for the polar matrices. Results indicated that in non-polar matrices, cellulose fibers tended to agglomerate/interact, reducing particle-matrix interaction. It was also observed that the maximum packing fraction depended not only on particle geometry

and arrangement, but also on the characteristics of the suspending matrix properties and the interaction between them.

5. ACKNOWLEDGEMENTS

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***Parte 2. Efeito do comportamento
não-Newtoniano da matriz***

RHEOLOGICAL BEHAVIOR OF SUSPENSIONS DISPERSED IN NON-NEWTONIAN MATRIX

To be submitted to Applied Rheology

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ABSTRACT

Suspensions composed with silica particles or cellulose fibers dispersed in xanthan and glycerin aqueous solutions were formulated with solids volume fraction varying up to 15 and 10% for silica and cellulose dispersions, respectively. Xanthan was added to the aqueous solutions (82% glycerin + water) at concentrations of 0.005%, 0.1 and 0.2% to impart non-Newtonian character to matrices, and results were compared to the Newtonian systems, without xanthan addition. Increasing cellulose particles concentration led to an increase on the suspension pseudoplasticity, while for silica particles such increase was more discrete. Generally, increasing the solids volume fraction led to an increase on the suspensions relative viscosity, with cellulose influence more pronounced than silica. For most of glycerin-xanthan matrices, a more structured behavior was observed, on the contrary of suspensions in pure xanthan solutions.

Keywords: suspension, rheology, non-Newtonian matrix

1. INTRODUCTION

Suspensions are multiphase systems in which solid particles are dispersed into a liquid medium. Within the industrial area, suspensions comprise a wide class of materials, which may be encountered in the form of raw materials, intermediate and final products. Thus, among the complex fluids, the rheological study of suspensions plays an important role for process engineering in the most diverse industries. Controlling the structure and flow properties of these systems is fundamental for commercial success of the product and/or of its manufacture (Larson, 1999).

Once the density of the particles is usually higher than that of the suspending phase, the use of food additives in suspensions aims mainly to improve their stability, which is closely related to product quality, processing conditions and consumer acceptance. Therefore, a number of food ingredients are used as thickeners, gelling agents and emulsifiers in a broad variety of products including sauces, beverages and confectionery (Clegg, 1995).

Generally, the addition of hydrocolloids can promote a modification on the continuous phase, frequently imparting a non-Newtonian and viscoelastic character to such a phase and, consequently, enhancing the complexity of the system. The normal stresses, resulted from viscoelastic behavior, influence the orientation of suspended particles and thereby have an indirect effect on the suspensions hydrodynamic (Iso et al., 1996). In this case, particle rotation may be suppressed affecting the orientation so that particles may organize in different manners and thus, particle shape becomes even more important in this sort of fluid (Mewis & Wagner, 2009). Moreover, rheological properties of suspending fluid may also interfere on the flow-induced structuring of particles (Scirocco et al., 2004). Hence, it is of interest to understand the role of viscoelasticity of suspending matrix and how it is affected by the presence of the particles with different characteristics (Eberle et al., 2008).

Thus, the aim of the present study was to evaluate the effect of non-Newtonian matrices on the rheology of non-colloidal model suspensions. Different concentrations of xanthan gum were added to glycerin-water solutions in order to evaluate the effect of the shear thinning and elasticity of suspending matrix on the rheological behavior of model particles with different shape and characteristics.

2. MATERIAL AND METHODS

2.1. Material

Silica particles (S) (S4133) (mean diameter = 55.57 μm ; density = 2.01 g/cm^3) (Fig.1a) and cellulose fibers (CM) (C6288) (mean length = 57.81 μm ; mean diameter = 6.64 μm ; density = 1.82 g/cm^3) (Fig.1b), obtained from Sigma (Sigma-Aldrich, St. Louis, MO, EUA), were used as suspended particles. Xanthan gum (X) (Sigma-Aldrich, St. Louis, MO, EUA) was added to impart non-Newtonian behavior on the suspending phases, while glycerin (G) (Synth - Labsynth, Brazil) was used to increase the viscosity of the suspending phase, retarding particles sedimentation, specially at solutions with small amounts (0.005%) or no xanthan addition.

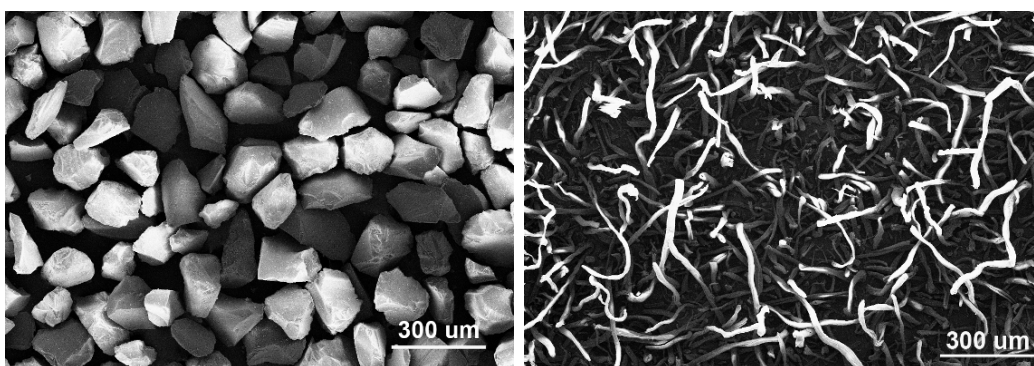


Fig.1 - Micrographs of a) silica and b) cellulose obtained by scanning electron microscopy.

2.2. Methods

Dispersing matrices preparation

A 3% xanthan stock solution was prepared, by vigorous mechanic stirring, at room temperature. Stock solution was stored at 10 °C overnight for complete hydration. Xanthan stock solution, glycerin and deionized water were weighed, magnetically stirred, to obtain final solutions with the concentrations showed in Table 1, stored at room temperature for at least 1 hour before suspension preparation.

Table 1 - Ingredients composition (g) of solutions (100g) used as dispersing matrices. X: xanthan; G: glycerin.

	X (g)	G (g)	Water (g)
G82	-	82	18
G82X005	0.005	82	18
G82X01	0.1	82	17.9
G82X02	0.2	82	17.8
X01	0.1	-	99.9
X02	0.2	-	99.8

Sample preparation

Silica particles or cellulose fibers were added to the different continuous phases, at volume fraction varying from 0.5 to 15%. Systems were magnetically stirred for at least 10 minutes at room temperature before rheological measurements of dispersions.

Rheological measurements

Rheological properties of suspending matrices and their respective suspensions were obtained in triplicate on a rheometer Physica MCR301 (Anton Paar GmbH, Germany), at 25 °C. Glass parallel-plate geometry was used for measurements (43 mm diameter). All measurements were performed with a 1.0 mm gap. Steady state measurements were carried out within shear rate range from 0 to 300 s⁻¹. Results were fitted to different flow equations (Newtonian, Power Law and Herschel-Bulkley) to find the best suitable model, through the Quasi-Newton iterative method, using the software

Statistica v.5.0 (StatSoft Inc., Tulsa, USA). A CCD camera coupled with a microscope tube with a 50x objective (Mitutoyo, Japan) was attached to the rheometer (Rheo-Microscope – Anton Paar GmbH, Germany) allowing evaluating the effect of shearing on the suspended particles. Pictures were taken for suspensions before and after shearing.

Stress sweep tests were performed at a frequency of 0.1 Hz to determine the range of linear viscoelastic response (limit of linearity - σ_{olim}) under oscillatory shear conditions. Frequency sweep measurements were performed within the linear viscoelastic region, in the range of 0.1 – 10 Hz, to obtain the mechanical spectrum. The dynamic storage (G'), loss (G'') and complex modulus ($G^*=(G'^2+G''^2)^{1/2}$) were evaluated. All measurements were performed at least in triplicate at 25°C.

Data analysis

Steady state data of suspensions were normalized with the characteristics of each matrix in order to compare the effect of solids concentration in solutions with distinct rheological characteristics. Thus, the reduced shear viscosity or relative viscosity (η_r) was calculated by dividing the suspension viscosity (η) with the viscosity of the suspending medium (η_0) at constant temperature, pressure, and shear rate (Eberle et al., 2008). Reduced shear viscosity data were fitted to Eilers (Eq. 1) (Ferrini et al., 1979) and Krieger-Dougherty (Eq. 2) (Larson, 1999) models for obtaining the maximum packing fraction (ϕ_m) of each suspension.

$$\eta_r = \left(1 + \frac{\frac{1}{2}[\eta]\phi}{1 - \frac{\phi}{\phi_m}} \right)^2 \quad (1) \quad \eta_r = \left(1 - \frac{\phi}{\phi_m} \right)^{-\phi_m[\eta]} \quad (2)$$

Where: $\eta_r = \eta/\eta_0$ is the relative or reduced viscosity;
 ϕ = solids volume fraction;
 ϕ_m = maximum packing fraction;
 $[\eta]$ = intrinsic viscosity.

3. RESULTS

3.1. Continuous matrices characterization

Low and high deformation rheological measurements were performed in order to characterize the dispersing matrices used in the present study. Frequency sweep of G82X01, G82X02 and X02 solutions are showed in Fig.2. For other matrices, it was not possible to measure the linear viscoelastic region to obtain the mechanical spectra, probably due to the lack of sensibility of measurements due to their low elasticity.

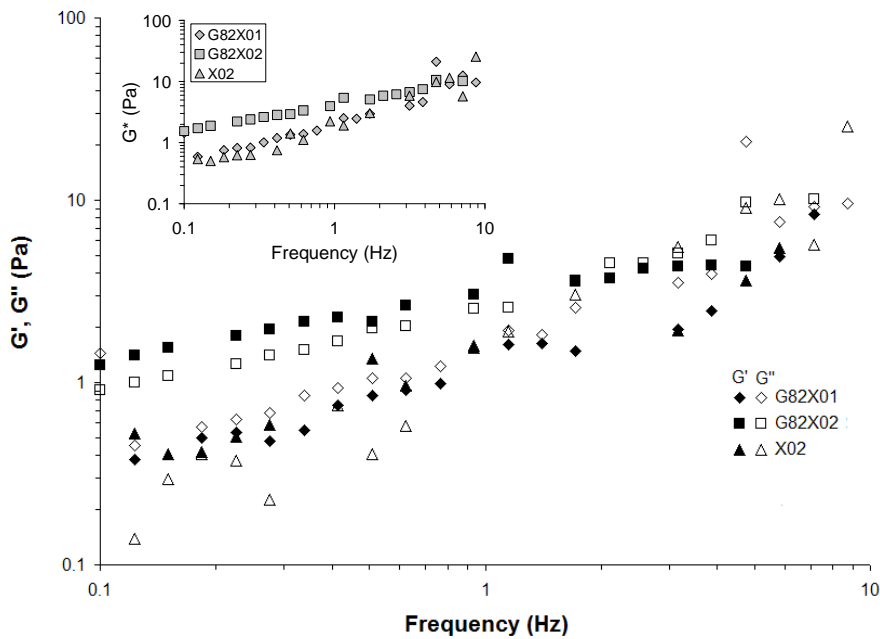


Fig.2 - Storage (closed symbols) and loss (open symbols) moduli as a function of frequency for dispersing matrices. In detail: Complex modulus for dispersing matrices.

Evaluating the mechanical spectra of dispersing solutions, it was possible to observe that the G82X02 solution was the more structured, when compared to other matrices, with higher complex modulus (G^*) (detail in Fig.2), and G' slightly higher than G'' , indicating a solid-like behavior. Same trend was observed for X02 solutions, but with lower G^* , indicating a less structured system when compared to G82X02.

Evaluating the G82X01 mechanical spectrum, it was observed that the lower xanthan concentration as compared to G82X02 was not enough to impart the solid-like behavior ($G' < G''$), even though the G^* was higher than X02 solution. Such result indicates that the glycerin and xanthan addition would contribute in distinct forms for the rheological behavior of solutions, imparting “structuring” and “elasticity” to the solutions, respectively.

Such contribution of the different components could be also visualized by the evaluation of the steady state properties (Fig.3). In this case, increase on xanthan concentration led to lower n values (higher pseudoplasticity), while the addition of glycerin was responsible for increase of the viscosity. In the latter, even with the same xanthan concentration as the pure xanthan-water solutions, glycerin plus xanthan solutions were much less shear-thinning. Same behavior was observed by the addition of xanthan in wheat syrup, in which xanthan molecules seemed to behave as rigid or semirigid rods due to the high viscosity of the solvent (Zirnsak et al., 1999). As observed at the oscillatory measurements, steady state analysis also indicated a solid-like behavior for G82X02 matrix, which was the only sample to present yield stress (σ_0).

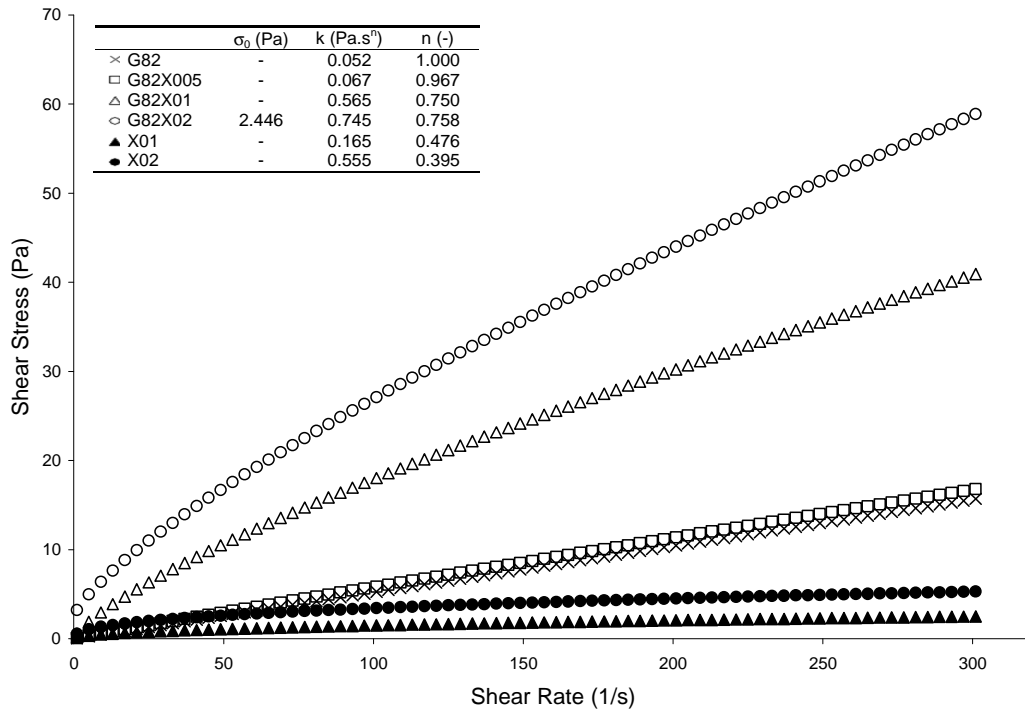


Fig.3 - Flow curves and parameters of model fitted ($R^2 > 0.998$) for dispersing matrices.

Oscillatory rheological behavior of suspensions

The influence of particle concentration on the limit of linearity of studied suspensions is observed in Fig.4. The influence of solids volume fraction on σ_{0lim} depended mainly on the composition of dispersing matrix and of particle nature. At general, it is observed that the increase on solids content led to a decrease on σ_{0lim} value of glycerin-xanthan dispersions (Fig.4a) for both particles, with larger influence of cellulose fibers. In this case, the addition of a low amount of solids led to a high decrease on σ_{0lim} as compared to silica at the same concentration. On the other hand, distinct behavior was observed for particles dispersed in pure xanthan solutions (Fig.4b). In this case, the increase on cellulose content led to an increase on σ_{0lim} , indicating a stronger structure (bears higher stresses without irreversible deformation),

while the limit of linearity obtained for the silica remained almost constant with increasing solids content.

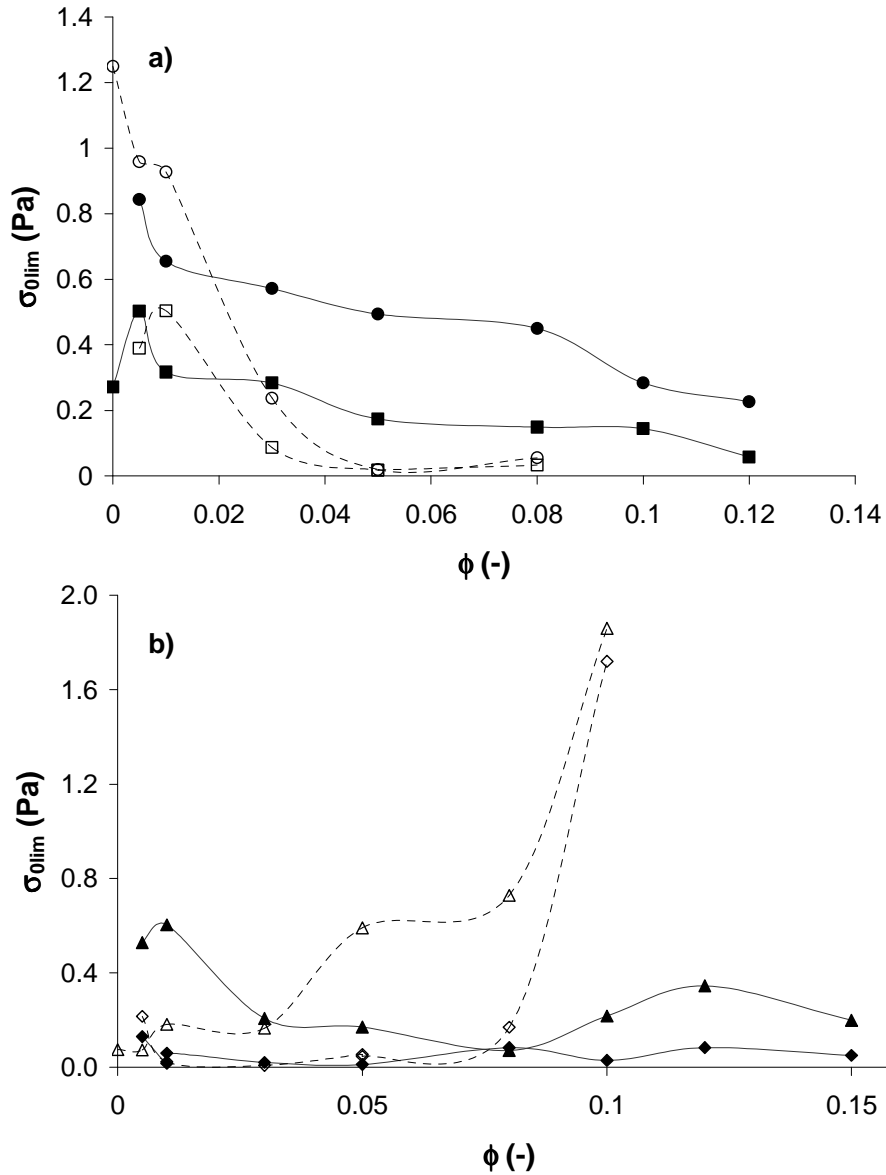


Fig.4 - Limit of linearity as a function of solids volume fraction (ϕ) of suspensions of silica (closed symbols) and cellulose (open symbols) dispersed in: a) glycerin-xanthan solutions (\square, \blacksquare) G82X01; (\circ, \bullet) G82X02 and b) pure xanthan solutions (\diamond, \blacklozenge) X01; ($\triangle, \blacktriangle$) X02.

Mechanical spectra of different suspensions obtained within the linear viscoelastic range were evaluated. Fig.5 shows the typical behavior of the storage and

loss moduli (G' and G'') for the silica and cellulose suspensions. As observed for G82X02 in Fig.5, all suspensions (**APÊNDICE II**), independently of the suspending matrix, showed G' values slightly higher than G'' within all concentration range studied, indicating that the suspensions were more elastic than viscous.

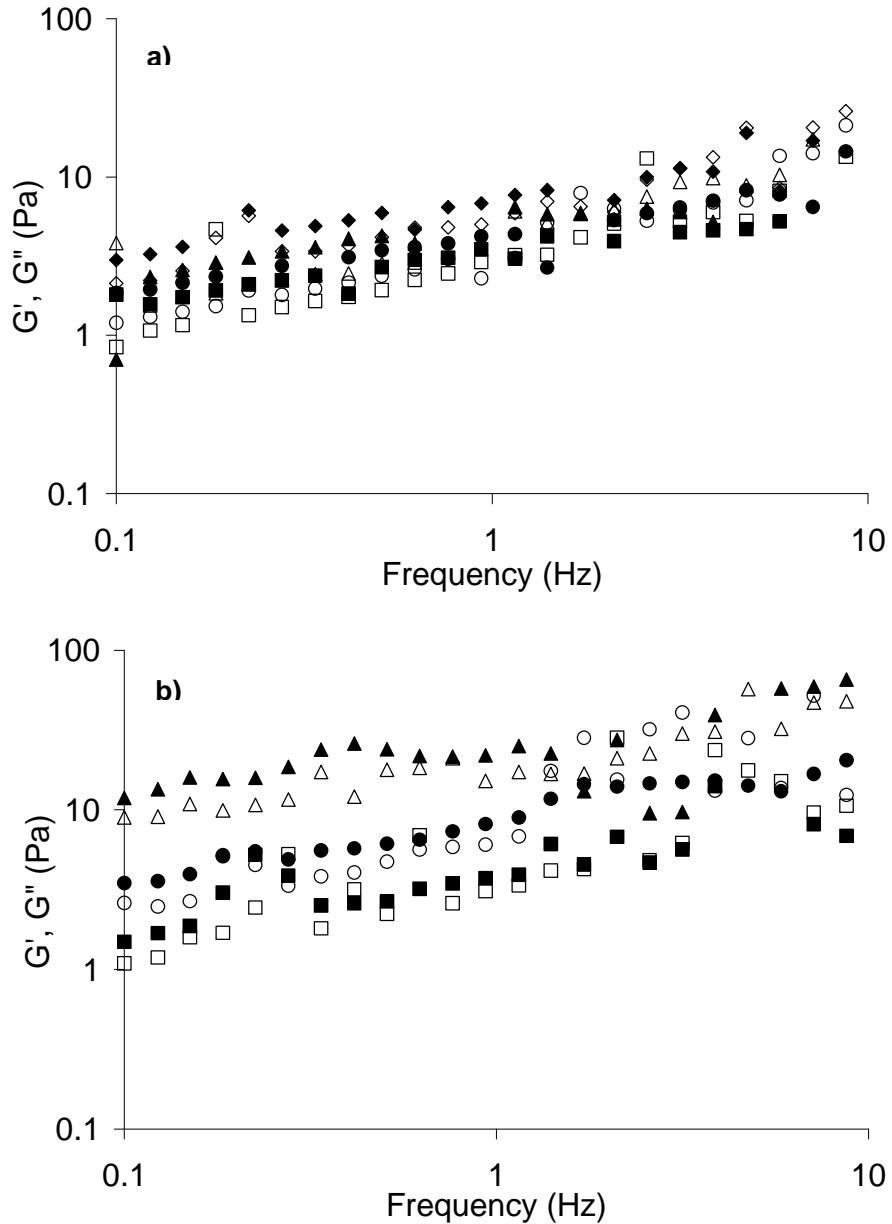


Fig.5 - Storage (closed symbols) and loss (open symbols) moduli of G82X02 suspensions of: a) silica and b) cellulose with increasing solids volume fraction: (\square, \blacksquare) 0.01; (\circ, \bullet) 0.05; ($\triangle, \blacktriangle$) 0.08; (\diamond, \blacklozenge) 0.12.

For all concentrations, relation between G'' and G' ($\tan \delta = G''/G'$) at 1.5 Hz remained close to 0.5 for most of suspensions in pure xanthan solutions (cellulose in X01 and X02 and silica in X02) and to 1 for other suspensions. Concentrated solutions show typical viscoelastic response, with $\tan \delta$ value of 1.19 at 10 rad/s, while for gels or solid suspensions the response is predominantly elastic, with $\tan \delta$ close to 0.07 (Steffe, 1996; Tadros, 1996). Thus, viscoelastic responses of the suspensions evaluated in this study showed behavior more similar to concentrated solutions.

The complex moduli (G^*) of silica and cellulose suspensions are showed in Fig.6 and Fig.7, respectively. As previously observed (section 3.1), some samples (G82 and G82X005) could not be analyzed by oscillatory measurements due to lack of sensibility. However, despite the fact that the solution X01 could not be analyzed by oscillatory measurements, its corresponding suspensions showed linear viscoelastic region, for particle concentration over 0.005 and 0.01, of silica and cellulose respectively.

For silica suspensions (Fig.6), within the concentration range studied, only a slight trend on increasing G^* with solids volume fraction (ϕ) may be observed. On the other hand, cellulose addition led to a more significant increase of complex modulus value (Fig.7), even with lower solids concentration, indicating higher structuring of these particles within all studied media. Comparing the dispersing matrices, increasing solids concentration on G82X02 led to a much smaller variation on G^* value, as compared to other matrices.

Generally, slope of G^* was higher for pure xanthan solutions, reflecting the higher dependency of complex modulus with frequency. Particularly, such behavior was more pronounced for silica suspensions and for low concentrated cellulose suspensions.

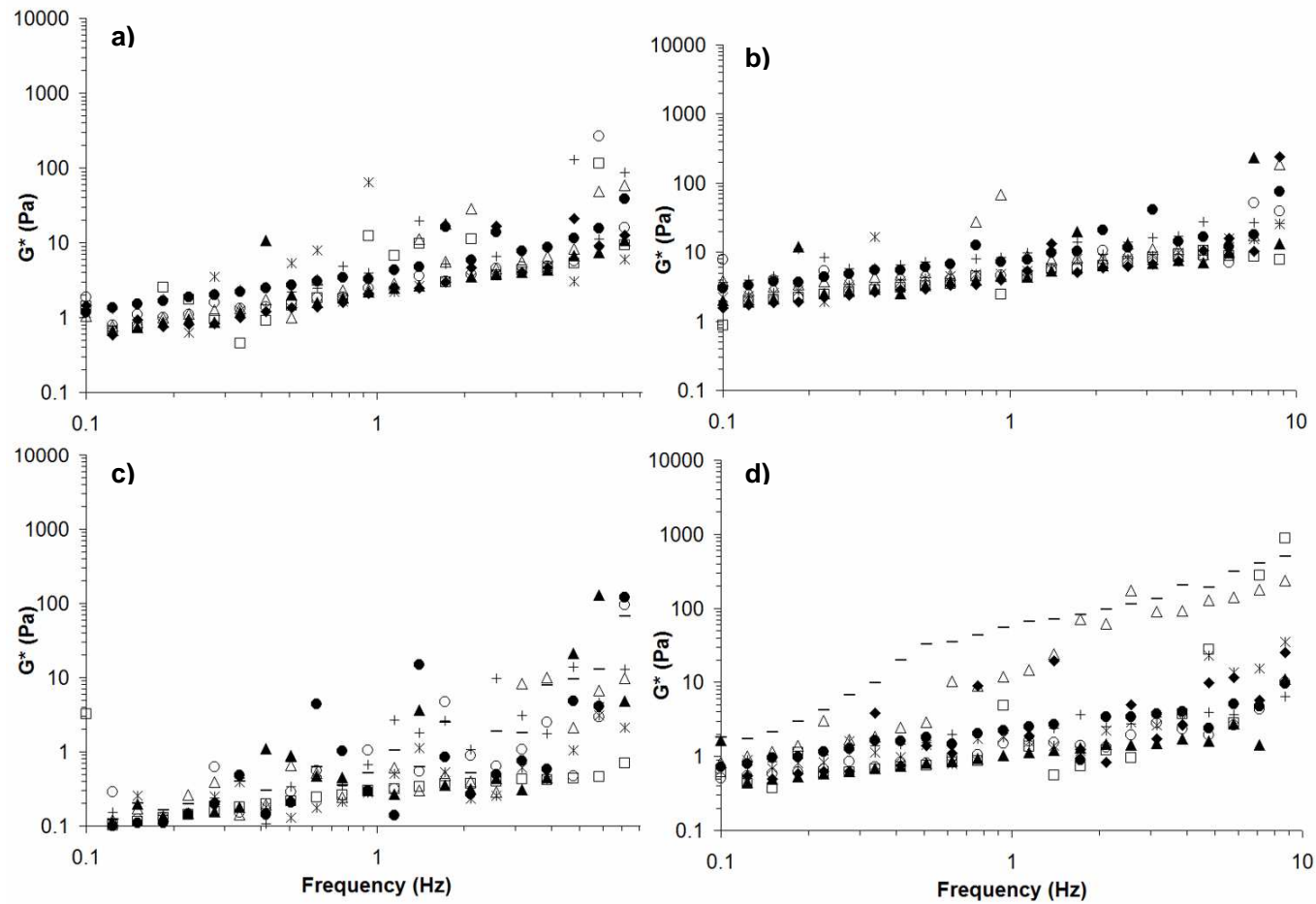


Fig.6 - Complex modulus (G^*) of silica suspensions dispersed in different matrices with increasing solids volume fraction: a) G82X01; b) G82X02; c) X01; d) X02. Solids volume fraction: (\blacklozenge) 0.00 (pure matrix), (\square) 0.005, (\blacktriangle) 0.01, (\circ) 0.03, (\times) 0.05, (\triangle) 0.08, (\bullet) 0.10, ($+$) 0.12, ($-$) 0.15.

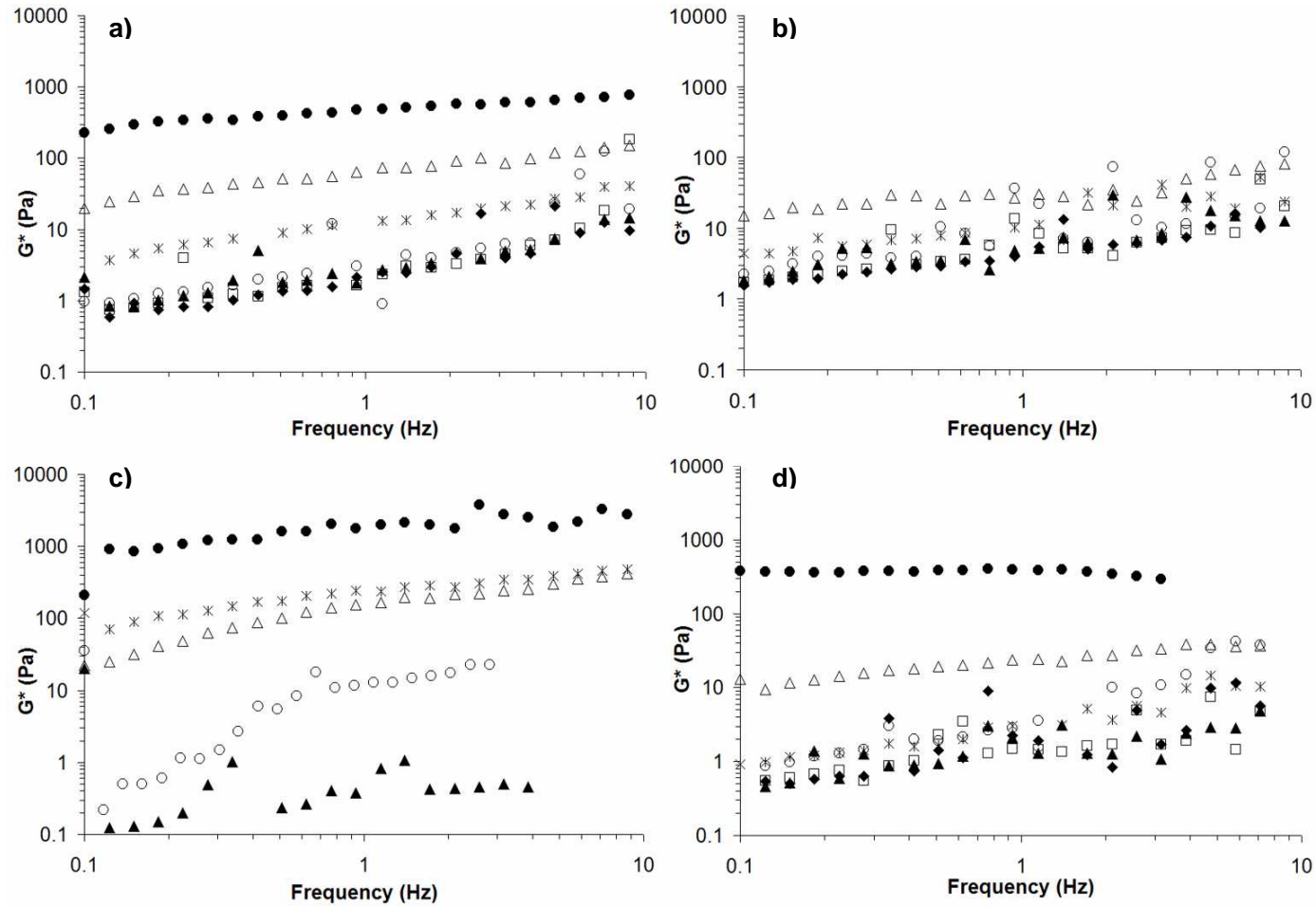


Fig.7 - Complex modulus (G^*) of cellulose suspensions dispersed in different matrices with increasing solids volume fraction: a) G82X01; b) G82X02; c) X01; d) X02. Solids volume fraction: (◆) 0.00 (pure matrix), (□) 0.005, (▲) 0.01, (○) 0.03, (✱) 0.05, (△) 0.08, (●) 0.10.

Steady state rheological behavior of suspensions

Fig.8 shows the relative viscosity behavior as a function of solids volume fraction for all studied suspensions. In order to evaluate the effects of pseudoplasticity, η_r was calculated for low ($10s^{-1}$) and high ($300s^{-1}$) shear rates.

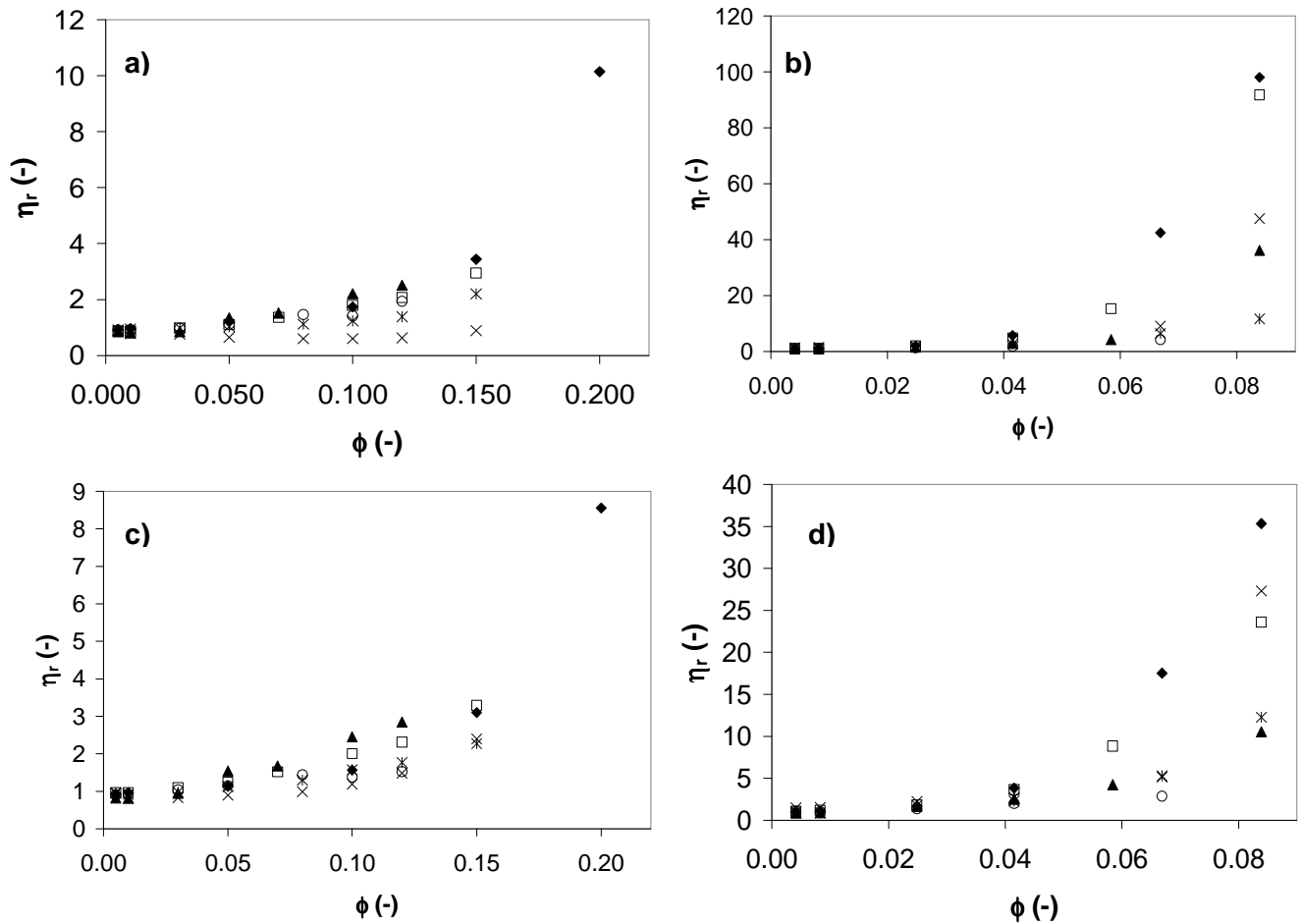


Fig.8 - Relative viscosity (η_r) as a function of solids volume fraction (ϕ) of: a) silica at $10s^{-1}$; b) cellulose at $10s^{-1}$; c) silica at $300s^{-1}$; d) cellulose at $300s^{-1}$, dispersed in different dispersing matrices: (\blacklozenge) G82; (\square) G82X005; (\blacktriangle) G82X01; (\circ) G82X02; (\times) X01; (\ast) X02.

It may be observed that cellulose addition (Fig.8b and d) led to a higher increase on relative viscosity as compared to silica (Fig.8a and c), achieving much higher η_r ,

values at similar concentrations. As can be observed in Fig.9, for suspensions in X01 matrix, after shearing cellulose fibers agglomerates, independently the dispersing phase, which was more evident at higher ϕ . Such agglomeration was not observed for silica particles, which showed similar structure before and after shearing. Such result was observed for all matrices, indicating that rod-like particles exert higher influence on the flow behavior of suspensions as compared to spheres, independently of the dispersing matrix.

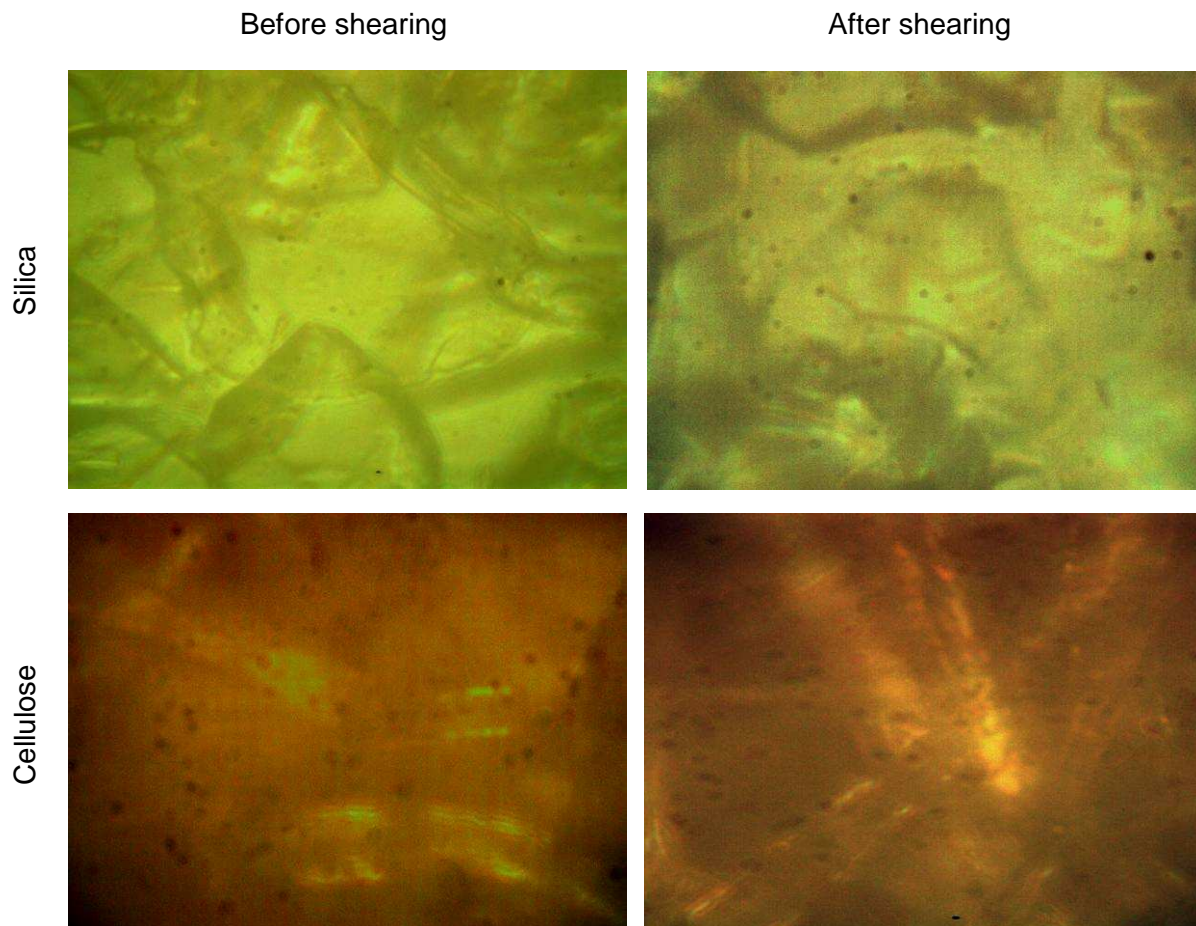


Fig.9 - Pictures of silica and cellulose particles before and after shearing at $\phi = 0.10$.

In general, increasing the solids volume fraction (ϕ) of silica dispersed on different matrices led to a similar influence on η_r behavior, independently on the suspending matrix. However, pure xanthan solutions (X01 and X02) showed values of relative viscosity slightly lower as compared to the glycerin-xanthan suspensions. Increase on xanthan concentration on cellulose suspensions, within each sort of matrix studied (pure xanthan and glycerin-xanthan solutions), led to a reduction of relative viscosity (η_r), despite the differences on the flow index behavior (n). Thus the Newtonian matrix (G82) showed the highest influence of ϕ on η_r . Such result is in disagreement to the observed for short fibers (Sepehr et al., 2004), since the steady shear viscosity increase was more markedly for a viscoelastic Boger fluid than for a Newtonian matrix. It should be considered that the Boger fluid is an elastic fluid but with constant viscosity, i.e. with no shear thinning observed (James, 2009), differently from the matrices evaluated in the present study.

Evaluating the flow index behavior (n) of suspensions with increasing solids content (Fig.10), it is observed that for cellulose suspensions, increasing ϕ reduces n value, indicating higher ability of structural organization with shearing. Such reduction is better observed evaluating the glycerin-xanthan suspensions. On the other hand, n values of silica suspensions remained practically constant and close to 1 (Newtonian) when dispersed in the glycerin-xanthan solutions, while a slight increase was observed for n of pure xanthan solutions, within all concentration range studied.

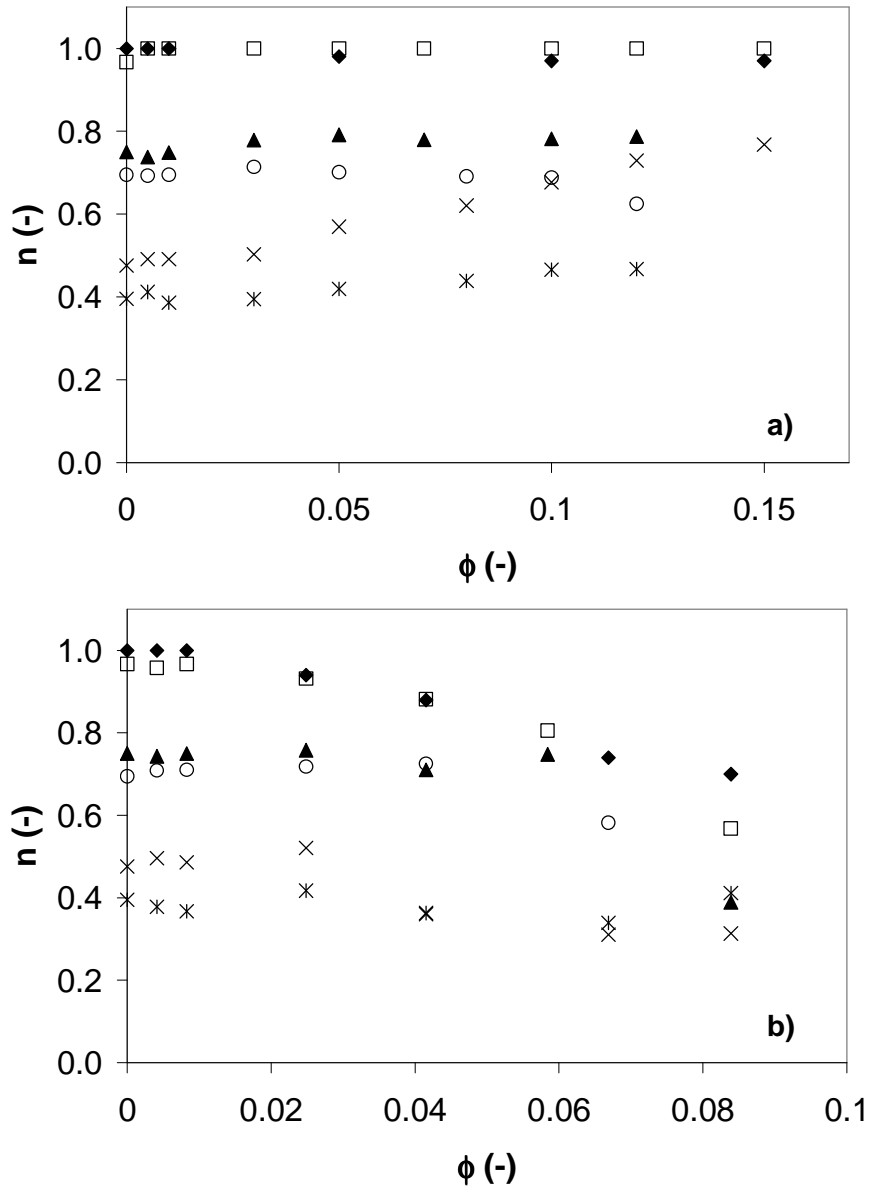


Fig.10 - Flow index behavior (n) of suspensions of a) silica and b) cellulose dispersed in different matrices: (◆) G82; (□) G82X005; (▲) G82X01; (○) G82X02; (×) X01; (✱) X02.

Table 2 shows comparison of the parameters fitted by Krieger-Dougherty and Eilers models, initially proposed for correlating the relative viscosity (η_r) with solids volume fraction (ϕ) for suspensions dispersed in Newtonian matrices. Models were fitted

at different shear rates, indicating similar trend independently of the shear rate. It should be considered that at higher shear rates, the particles arrangement should be more ordered/nematic (Capítulo 4 – Parte 1). Thus, in order to reduce effect of shear thinning, models were fitted for viscosity values at 300 s^{-1} . Even evaluating non-Newtonian matrices in the present work, a quite good agreement was observed for the fitted values of both equations, for most of suspensions studied. Maximum packing fraction fitted for silica and cellulose dispersed in the glycerin solutions G82, G82X005 and G82X01 remained approximately constant and close to 0.26 and 0.14, for silica and cellulose, respectively. In general, it is observed that a higher ϕ of silica particles is necessary to achieve the maximum packing fraction (ϕ_m), as compared to the cellulose fibers, mainly due to the difference in the aspect ratio (a_r =length/diameter) of both particles, once, ϕ_m tends to be lower as particles differs from the spherical shape (larger aspect ratio) (Chang & Powell, 2002). In the present study, silica particles should present a_r close to 1, while cellulose a_r was 8.70.

For other dispersing matrices, higher discrepancy between fitted parameters of the different models was observed. In these cases, the high shear thinning and the high viscosity of the pure xanthan (X01 and X02) and G82X02 solutions, respectively (Fig.3) led to different behavior with increasing solids content that could not be precisely predicted by the fitted models.

Table 2 - Model fitted for relative viscosity (at 300s⁻¹) as a function of ϕ .

		<i>Krieger-Dougherty</i>		<i>Eilers</i>	
		<i>Silica</i>	<i>CM</i>	<i>Silica</i>	<i>CM</i>
G82	ϕ_m (%)	25.271	13.016	25.141	13.948
	$[\eta]$	0.055	0.250	0.041	0.472
	R^2	0.998	0.965	0.999	0.995
G82X005	ϕ_m (%)	26.272	12.848	27.247	14.112
	$[\eta]$	0.053	0.233	0.049	0.374
	R^2	0.998	0.984	0.996	0.997
G82X01	ϕ_m (%)	25.819	15.290	26.703	13.363
	$[\eta]$	0.066	0.194	0.065	0.200
	R^2	0.969	0.999	0.968	0.999
G82X02	ϕ_m (%)	47.928	22.329	22.609	24.654
	$[\eta]$	0.029	0.134	0.019	0.152
	R^2	0.993	0.985	0.967	0.990
X01	ϕ_m (%)	39.184	9.262	16.804	9.497
	$[\eta]$	0.036	0.151	0.008	0.118
	R^2	0.845	0.997	0.966	0.999
X02	ϕ_m (%)	35.093	11.400	24.771	11.557
	$[\eta]$	0.040	0.165	0.027	0.164
	R^2	0.990	0.999	0.987	0.999

4. DISCUSSION

Rheological measurements of suspensions with different solids concentration indicated an overall trend on structuring with increasing solids volume fraction (ϕ), which is reflected by the increase on the dynamic moduli and viscosity of suspensions (sections ***Oscillatory rheological behavior of suspensions*** and ***Steady state rheological behavior of suspensions***). In general, at lower concentration of suspensions, neither the rheological parameters obtained in oscillatory shear, nor the

ones obtained at steady state shear showed difference when compared to the behavior of suspending matrix. In this case, suspensions are classified as diluted, once particles do not suffer interference from other particles, so that the rheological behavior is basically defined by the continuous phase (Ferguson & Kemblowsky, 1991; Pawlik et al., 2004).

As the concentration of particles increases, rheological behavior of suspensions diverges from the suspending matrix, indicating a more structured system in most cases, which was reflected by the higher values of complex moduli (G^*) (Fig.6 and Fig.7), viscosities ($\eta_r \gg 1$) (Fig.8) and pseudoplasticity (lower n) (Fig.10). In this case, the increase on ϕ enhances the hydrodynamic interactions relevance, and some physical contact between the particles should occur (semidiluted systems) (Larson, 1999; Pasquino et al., 2008). A further increase on solids concentration leads to increased particle-particle interactions, and some structure takes place so that the dynamic properties of the suspension may be severely affected and the system becomes concentrated (Marti et al., 2005; Eberle et al., 2008). Such interactions are more evident for fiber suspensions than for spherical ones. In diluted systems, non-spherical particles rotate around the so called Jeffery orbits, and the increase on concentration disturbs such rotation (Lindström & Uesaka, 2008). As fiber content increases, transitions to nematic phases or other ordered microstructures may occur, which is more pronounced the higher the aspect ratio (Meng & Higdon, 2008). Thus, besides the rigid repulsions observed for idealized rigid spheres, increase on concentration of fibrous suspensions leads to hydrodynamic and even particle-particle interactions, resulting in a higher influence of addition of rod like particles, which is clearly reflected by presented results, which shows the higher influence of cellulose fibers as compared to silica in the evaluated rheological properties

Evaluating the effect of the suspending matrix, some characteristics behavior may be observed. Generally, complex moduli of suspensions of both particles on glycerin matrices (G82, G82X005, G82X01) were more independent on frequency, reflecting a better structuring of such suspensions. For the high viscous G82X02 matrix, distinct behavior was observed, mainly for cellulose suspensions. In this case, the increase on solids concentration promoted lower variation on G^* and η_r , when compared to other matrices. The reduced mobility of particles due to the high viscosity of the dispersing matrix would reduce particles interaction and thus, their influence on the rheological behavior of the suspension (*Capítulo 4 – Parte 1*). Such effect would be more discrete for silica suspensions, once interaction between silica particles is small, independently the dispersing matrix. Other characteristic behavior was observed for pure xanthan solutions, particularly when silica particles were added. In this case, a slight “loss of structure” was observed with increasing solids addition, which was reflected by the higher dependency of G^* on frequency and by the reduction of pseudoplasticity (higher n) with increasing solids content. When suspended in shear thinning viscoelastic fluids, spherical particles form strings in both steady state and oscillatory measurements (Lyon et al., 2001). Such strings would be oriented in the flow direction, which corresponds to a quantitative reduction in the measured shear stress (Lyon et al., 2001; Scirocco et al., 2004). However, beyond the organization of the spherical particles into strings, it is believed that the biopolymer should also influence on the “loss of structure” observed on the suspensions of silica on xanthan solutions. In this case, the xanthan solutions would in fact behave as a xanthan dispersion. Thus the biopolymer molecules should stretch, aligning themselves, so that biopolymer-particle strings layers would be formed (Fig.11). Such organization would avoid the hydrocolloid molecules to entangle at the same time as it would form paths that would facilitate particles movement. Such

distinct behavior could be responsible by the larger discrepancies between fitted parameters of Krieger-Dougherty and Eilers Equation (Table 2), indicating that such models are not able to predict properly interactions between particles and matrices for suspensions dispersed in complex fluids.

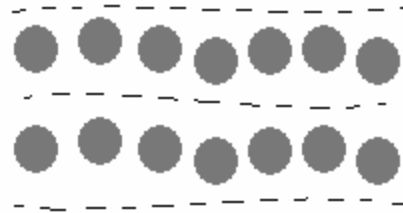


Fig.11 - Formation of layers of silica strings (represented by the gray circles) and stretched xanthan molecules (continuous line).

Even though cellulose could also form layers when dispersed into biopolymer solutions, rod-like particles would still rotate when subjected to flow in viscoelastic matrices, albeit slower than in Newtonian solutions (Gunes et al., 2008). Such rotation would interfere in the organized structure, so that the effects observed for the silica suspensions would be more pronounced than the observed for the cellulose ones.

5. CONCLUSIONS

As particle concentration increased, the rheological behavior of suspensions diverged from the suspending matrices, which was not observed for systems with small amounts of solids. Generally, cellulose influence was higher than the silica, which was reflected by the higher values of complex moduli, viscosity and pseudoplasticity of suspensions. Evaluating the dispersing matrices effects, it was observed that the high viscosity matrix (G82X02) reduced particles interaction, while suspensions dispersed in other glycerin-xanthan matrices were more structured. Pure xanthan matrices, which showed higher pseudoplasticity, behaved differently from others, once a slight loss of

structure was observed with increasing solids concentration. Thus, besides particles characteristics, the rheological properties of the suspending matrix may be crucial for determining the structuring and flow properties of suspensions.

6. ACKNOWLEDGEMENTS

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CAPÍTULO 5 *CONCLUSÕES*

O estudo dos sistemas-modelo visando uma maior compreensão do comportamento de sistemas reais como as polpas de frutas, mostrou que diversos fatores influenciam a reologia de suspensões. A princípio, sistemas-modelo de soro de polpas de frutas foram avaliados através do estudo da influência da concentração de sacarose e de pectina, além da mistura de diferentes tipos de pectina no comportamento reológico dos sistemas. A partir dos ensaios de curvas de escoamento, foi possível observar que pectinas com diferentes características (graus de metoxilação) apresentaram comportamento reológico distintos, sendo que:

- A adição de sacarose favoreceu a interação entre os grupos hidrofóbicos de pectinas de alto teor de metoxilação, levando a um sistema mais estruturado;
- A adição de pectina amidada de baixo teor de metoxilação (LM) levou a uma maior alteração no comportamento reológico dos sistemas-modelo de soro de polpas de frutas do que as pectinas de alto teor de metoxilação (HM) estudadas, resultando em soluções mais viscosas e pseudoplásticas, que permitiram ressaltar o efeito sinérgico de diferentes tipos de ligação;
- A mistura de pectinas de alto e de baixo teor de metoxilação levou a um efeito sinérgico, resultando em sistemas mais viscosos e pseudoplásticos do que os sistemas compostos por pectinas puras nas mesmas concentrações de sacarose e pectina, o que enfatiza a importância da presença de interações hidrofóbicas junto às pontes de hidrogênio na estabilização das zonas de junção.

Deste modo, os diferentes efeitos observados nesta etapa ressaltam a complexidade de sistemas reais, uma vez que indicam que dependendo do tipo e concentração do biopolímero presente é possível obter produtos com texturas/consistências bastante variadas.

Posteriormente, a influência da concentração de partículas com diferentes formatos e características (sílica e celulose), assim como a sua interação com o meio

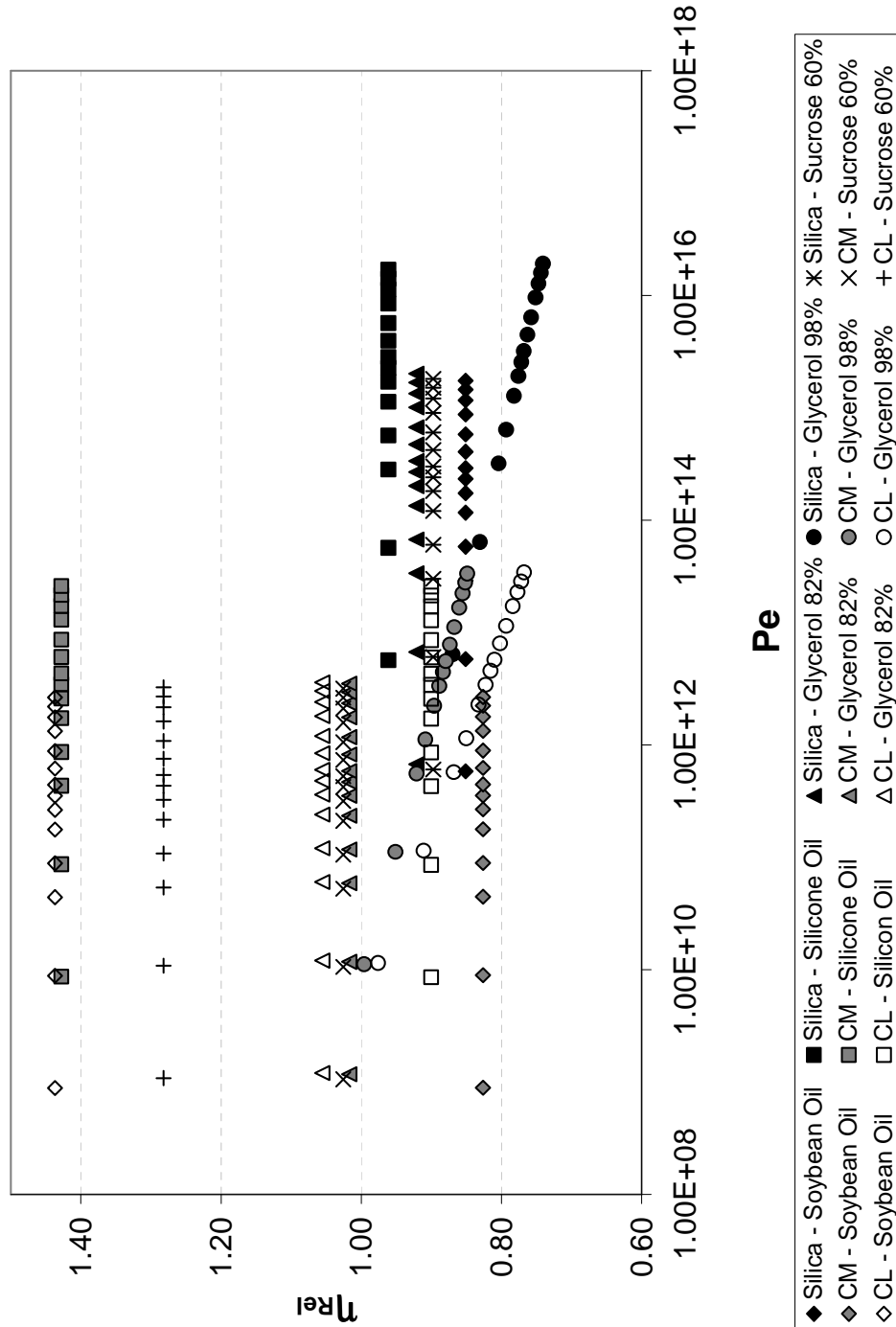
contínuo foram avaliadas através de ensaios reológicos de suspensões-modelo. Foram estudados meios com diferentes polaridades, viscosidades, além de sistemas com caráter não-Newtoniano, sendo que foi possível observar que:

- De um modo geral, a alteração no comportamento reológico das suspensões-modelo foi atribuída às interações entre partículas e partícula-solvente;
 - Interações foram maiores para as suspensões de fibras, sendo que quanto maior o comprimento das fibras (*aspect ratio*), maior a influência no comportamento reológico;
 - A utilização de matrizes de alta viscosidade e não polares resultaram em menor interação entre as partículas e partícula-solvente;
 - Adição de maior quantidade de sólidos em sistemas com menos interações (maior ϕ_m);
- A adição de partículas em meios não-Newtonianos com glicerina e xantana (viscosos e levemente pseudoplásticos) levou à formação de suspensões mais estruturadas, enquanto que a adição de sólidos em soluções puras de xantana (altamente pseudoplásticas) indicou tendência a desestruturar a suspensão;
- Falta de modelos matemáticos que correlacionem o comportamento reológico com a fração de sólidos em suspensões dispersas em matrizes não-Newtonianas.

Assim, pode-se concluir que o aumento no teor de sólidos (concentração), o tipo de partícula presente e as características do meio dispersante podem apresentar grande influência nas propriedades reológicas de suspensões, aumentando ainda mais a complexidade destes sistemas. Além disso, o estudo dos sistemas-modelo no presente trabalho pode contribuir para o entendimento do comportamento de sistemas reais, em especial as polpas de frutas, já que estas apresentam características distintas dependendo da sua composição.

APÊNDICE

APÊNDICE I – Viscosidade relativa (η_{rel}) em função do número de Péclet para as diferentes suspensões em regime diluído: $\phi = 0.005$ (0.5%).



APÊNDICE II – Espectro mecânico das suspensões de sílica e celulose dispersas em matrizes não-Newtonianas.

