**Particle additives in liquid and solid performance materials**

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**FUMED SILICA FOR RHEOLOGY CONTROL IN ADHESIVES AND SEALANTS**

Formulators use particles to enhance the functionality of existing polymer matrices for adhesive and sealant products. Fumed silica is commonly used as a rheology control additive; for providing sag resistance, anti-settling of fillers, and shear-thinning viscosity. The generic term “fumed silica” defines a broad range of products with different surface chemistries, from hydrophilic to hydrophobic.

These products have differing compatibility to polymer systems. This enables formulators to fine-tune the rheology performance. At the same time, formulators can enhance the viscoelastic response of liquid systems by controlling particle-particle interactions and particle–matrix interfacial adhesion. Such interactions can yield desirable viscoelasticity and provide a means of securely incorporating hard materials, which lengthen fracture paths, and dissipate energy at interfacial junctions. These properties strengthen films. This article presents recent application development data, which illustrates the benefit of these interactions to scientists and engineers developing new adhesives and sealants.

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**LA SILICE PIROGENICA COME MATERIALE DI RINFORZO IN ADESIVI E NEI SIGILLANTI**

In addition to the well-documented benefits in rheology control, fumed silica also enhances the strength of cured adhesives. Below are three examples where fumed silica provides reinforcement of a polymer, resulting in a higher performing adhesive or sealant.

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**LA SILICE PIROGENICA PER IL CONTROLLO DELLA REOLOGIA NEGLI ADESIVI E NEI SIGILLANTI**

I formulatori utilizzano le particelle per apportare migliorie alla funzionalità delle attuali matrici polimeriche per i prodotti adesivi e sigillanti. La silice pirogenica è comunemente utilizzata come additivo di controllo della reologia per garantire la resistenza alla colatura, la non-sedimentazione dei riempitivi e la viscosità di taglio. Il termine generico “silice pirogenica” definisce una vasta serie di prodotti dotati di differenti processi chimici superficiali, da idrofili a idrofobi. Questi prodotti presentano una differente compatibilità con i sistemi polimerici e ciò consente ai formulatori di adattare ad hoc la prestazione reologica. Nello stesso tempo, i formulatori riescono a migliorare la risposta viscoelastica dei sistemi liquidi tenendo sotto controllo le interazioni particella-particella e l’adesione nell’interfaccia particella-matrice. Queste interazioni possono fornire la viscoelasticità desiderata fornendo il modo per incorporare con sicurezza i materiali duri che allungano le linee di frattura dissipando energia nei giunti d’interfaccia. Queste proprietà rinforzano i film. In questo articolo si presentano i dati dei recenti sviluppi applicativi illustrando i vantaggi arrecati da queste interazioni agli scienziati e agli ingegneri che sviluppano i nuovi adesivi e sigillanti.
EXAMPLE 1 – TRANSPARENT SILYL-TERMINATED POLYMER (STP) ADHESIVES AND SEALANTS

High-clarity STP adhesives and sealants for the “do it yourself” (DIY) market are preferred by consumers. In Europe, manufacturers of these products have switched to clear packaging to highlight this benefit. Additives such as waxes, clays, and calcium carbonates are commonly used for rheology control and reinforcement of STP adhesives and sealants. The selection of these reinforcing aids typically results in an opaque product because the refractive index of these products does not match the matrix. By contrast, the index of refraction of fumed silica closely matches the transparent polymers commonly used in these products. Fumed silica is widely used to provide reinforcement in transparent STP adhesives and sealants.

Formulators using hydrophilic fumed silicas in moisture curing systems such as STP or polyurethane face premature curing of these systems due to the large water adsorption capacity of hydrophilic silica. Several options are available to solve this challenge, including adding process steps (pre-drying hydrophilic silica or removing water during compounding via heat and vacuum) or adding additional components (chemical dryers). A better option is replacing the hydrophilic silica with a hydrophobic silica that can greatly reduce or eliminate the need for these extra process steps.

Two hydrophobic additives, Cab-o-sil® TS-610 and Cab-o-sil TS-720 fumed silicas, were compounded in a model formulation consisting of MS Polymer™ SAX 400 silyl-terminated polyether, diisononyl phthalate and an organotin catalyst. The effect of fumed silica surface chemistry on rheology is clearly observed in this system.

Fig. 1 Viscosity vs shear rate for uncured STPE measured on controlled stress rheometer
The less hydrophobic additive, Cab-o-sil TS-610 fumed silica, with stronger particle-matrix interaction, provides a Newtonian rheology. In contrast, the more hydrophobic additive, Cab-o-sil TS-720 fumed silica, with weaker particle-matrix and hence stronger particle-particle interaction, provides thixotropic rheology resulting in a system with a yield stress or sag resistance and viscosity that shear-thins as shown in Figure 1.

With either of these fumed silicas, the particle-matrix interaction is sufficient to result in increases to the tensile strength of the system as shown in Figure 2 and a greater than 3x increase in elongation at break. With increased loading of fumed silica both tensile strength and elongation at break increase but usage at very high loadings is limited by the corresponding increase in viscosity.

**EXAMPLE 2 – ONE-COMPONENT POLYURETHANE ADHESIVES AND SEALANTS**

High surface area carbon blacks and fumed silica are more efficient on an equal weight basis as a reinforcing agent than other rheology control additives. Carbon black is used to build viscosity, provide sag resistance, and increase cohesive strength of automotive windshield adhesives. Coated precipitated calcium carbonates (PCCs) are used for rheology control of STP and polyurethane adhesives and sealants. Those PCCs with hydrophobic coatings (e.g. fatty acid, or stearic acid) do yield a shearthinning rheology in polyurethane systems and have the added benefit of providing modest increases in adhesive strength.

Figure 3 shows the increase of lap shear strength of a moisture-curing, one-component polyurethane adhesive, consisting of a polyurethane prepolymer with NCO...
content <2%, diisononylphthalate plasticizer, ground calcium carbonate filler, and organotin catalyst, with the addition of either a hydrophobic fumed silica or a coated PCC. On an equal weight basis, treated fumed silica provides significantly more adhesive strength, as shown in Figure 3, than the PCC in this system. Compounding the benefit of lower loading, fumed silica has a lower specific gravity than calcium carbonate and thus contributes far less to adhesive weight, which can be a benefit in applications where adhesive weight is a concern (e.g. automotive lightweighting).

**EXAMPLE 3 – PRESSURE SENSITIVE ADHESIVE**

Fumed silica aggregates are commonly used to improve the processing and performance characteristics of films formed from natural rubber, polychloroprene, acrylates, and many other water-based latex emulsions. These submicron, high specific surface area particles can decrease drying times, mitigate crack formation by modulating the capillary pressure, and enhance the mechanical properties of the final product. Predispersed fumed metal oxides, such as Cab-o-sperse® dispersions, provide an easy and effective “pour-in” means of incorporating these particles into the adhesive films.

Cabot’s Application Development team has observed significant improvements in cohesive shear strength and thermo-mechanical properties of water borne pressure sensitive adhesives due to the incorporation of highly dispersed fumed silica. Adhesive films with fumed silica content ranging from 0 to 15 weight percent (dry weight) were formulated from water-based acrylic emulsions designed for pressure sensitive adhesive applications. The plastificante diisononilftalato, di un riempiitivo carbonato di calcio macinato e un catalizzatore organostagno con l’aggiunta o di silice pirogenica idrofoba o di un PCC rivestito.

In condizioni di uguale peso, la silice pirogenica trattata fornisce in questo sistema una tenacità adesiva molto significativa come mostrato in Figura 3 rispetto al PCC. Sommando il vantaggio di un carico inferiore, la silice pirogenica ha un peso specifico inferiore al carbonato di calcio influendo meno sul peso dell’adesivo e rappresenta un beneficio in quelle applicazioni in cui il peso dell’adesivo gioca un ruolo importante (ad es. nella riduzione del peso in campo automobilistico).

**ESEMPIO 3 – ADESIVI PRESSOSENSIBILI**

Gli aggregati di silice pirogenica sono utilizzati solitamente per apportare migliorie al trattamento e alle
films were formed by drawing down the emulsions on Mylar backing, and drying the wet films in a \(~110^\circ C\) oven for 20-40 minutes. The dry films were cooled at room temperature, backed with waxed release paper, rolled with a 17 lb. weight at a controlled rate, and then incubated for 24 hours at room temperature prior to test. The dry films were 1.0 to 1.3 micron dry film thickness (DFT).

Film shear strength was measured as function of shear force (1.1 to 4.4 psi) and temperature (room temperature to 100°C) in a two bank, eight position shear oven (Fig. 4).

Four or more adhesive samples from a given draw down were typically evaluated, yielding relative standard deviations in time to failure of \(~15\%\) or less. The film shear strength enhancement was calculated as the mean time to failure of the film normalized by the mean time to failure of the films without particle reinforcement. Shear measurements show significant increases in shear

![Fig. 4 Interior of two bank, eight position shear test oven. Top bank: Pressure sensitive adhesive with CAB-O-SPERSE dispersions reinforcement is maintaining bond against applied shear force. Bottom bank: Pressure sensitive adhesive with no reinforcement has failed. (Note cohesive failure leaves film on stainless steel adherent)](image-url)
strength enhancement with fumed silica loading as low as a few weight %. For example at 4 weight %, room temperature evaluation, the adhesive shear strength is increased 8-20x, depending upon shear force. At higher weight % (8-15%) and higher temperatures (e.g. 100°C), the shear strength enhancement as a result of fumed silica addition is even more striking. We typically observe adhesive shear strength increases of more than thousand fold as compared to the films without particle reinforcement. We are currently investigating chemical bond formation in these adhesive films caused by the addition of fumed silica dispersions, as this level of enhancement was unexpected. Regardless of the source of the shear strength enhancement, the increase in film cohesive strength is impressive.

The peel strength of the pressure sensitive adhesive films with and without fumed silica reinforcement was also evaluated (ChemInstruments Adhesion/Release AR-1000 peel tester). A 7 lb. weight was used to roll 10” x 1” adhesive strips onto a stainless steel adherent at a controlled rate; the time lapse between the end of rolling and the peel test was one minute. The reduction in peel strength as a result of fumed silica reinforcement is fairly modest: over a fumed silica weight % of zero to 4 weight %, the peel strength decreases linearly to ~ 75% of its initial value. Between 4 weight % and 8 weight % fumed silica, no further reduction in peel strength is observed. No tackifiers were used in the pressure sensitive adhesive data discussed above. For products requiring high adhesion via tackifier addition, we have also shown that reinforcement via fumed silica more than compensates for the shear strength loss caused by tackifier addition (e.g. Tacolyn 3509). The 20-40% loss in shear strength caused by common tackifier levels, is easily recovered via 2-4 weight % fumed silica reinforcement.

CONCLUSIONS
Balancing the strength of particle-matrix and particle-particle interactions by selection of the appropriate surface chemistry of fumed silica provides the formulator the opportunity to achieve performance targets for the rheology in the uncured state and reinforcement or strength of the cured adhesive or sealant. Fumed silica are multi-functional particles providing performance in a wide range of adhesives, PSA to polyurethanes, and unexpected benefits in reinforcement.

REFERENCES

CONCLUSIONI
Il bilanciamento della tenacità delle interazioni particella-matrice e particella-particella mediante selezione del processo chimico adeguato della silice pirogenica offre al formulatore l’opportunità di raggiungere gli obiettivi prestazionali della reologia nelle condizioni di non indurimento e di rinforzo o tenacità degli adesivi o sigillanti reticolati. Le silici pirogeniche sono particelle polifunzionali che offrono alte prestazioni in una vasta serie di adesivi, PSA, poliuretani e notevoli vantaggi nell’area del rinforzo.