Highly Porous Materials with Unique Mechanical Properties from Smart Capillary Suspensions

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Capillary suspensions are three-phase fluids comprising a solid and two immiscible liquid phases. Addition of a small fraction of the secondary liquid phase to a suspension of particles dispersed in the so-called primary or bulk phase leads to the formation of a strong sample spanning particle network, even at low particle loadings. This particle network gains its strength from the capillary forces inferred from the added secondary liquid no matter whether it wets the particles better or worse than the primary liquid.1,2 This attractive force is typically orders of magnitude stronger than the ubiquitous van der Waals attraction. Accordingly, capillary suspensions exhibit a paste-like texture and a strongly shear thinning flow behavior. They are highly resistant to sedimentation and flow properties can be tuned in a wide range according to different processing or application demands. Even the flow behavior of methane hydrates turned out to be strongly affected by capillary bridging.3 A broad range of innovative products including novel food formulations, such as heat stable and low calorie chocolate spreads,4 capillary suspensions with an appropriate solvent or swelling agent/plasticizer as secondary fluid. Finally, the mechanical strength of the resulting porous sintered parts can be distinctly increased. 

Beyond that capillary suspensions can be utilized as precursors for highly porous sintering materials to be used as lightweight construction materials, filters, or membranes.10–12 The easiest and most straightforward route to produce porous materials is the partial sintering of a powder compact but the resulting porosities ε are below 50%. Various other methods like sacrificial templating, replica techniques, or using particle stabilized foams13 and Pickering emulsions have been developed to produce macroporous sintering materials.14–16 But especially, the parameter range ε > 50% and dp < 10 µm, with dp is the pore diameter, is hardly accessible using these conventional techniques. The strong particle network in capillary suspensions does not collapse and largely retains its structure even upon removal of the bulk fluid phase (“debinding”). Resulting highly porous green bodies can be sintered and this versatile processing route based on well-established unit operations yields strong solid materials with open porosities ε up to 80% at pore sizes dp between 0.5 and 50 µm as has been demonstrated for α-Al2O3 ceramics.10,12 Recently, glass filters with highly uniform pore structure resulting in a mechanical strength similar to ceramic filters (at given ε and dp) and gas permeability exceeding that of ceramic or commercial glass filters have been manufactured.11 Especially every vitrifiable powder can be easily turned into a highly porous solid using the capillary suspension concept. Examples using metal, polymer, glass, and ceramic powders are shown in the Supporting Information demonstrating the broad applicability of this versatile, low-cost processing route (Figure S1, Supporting Information). Using this approach, porosity and pore size are controlled by the particle size, solid content, amount of secondary liquid phase, and sintering conditions. Lower particle loading typically results in an increased porosity and lower particle size corresponds to a lower pore size. For a constant particle loading at a constant particle size, increasing the amount of secondary liquid phase leads to a coarsening of the structure, i.e., an increase of pore size. Sintering conditions have to be chosen such that neck growth is sufficient to provide the desired mechanical strength and porosity.10,11

Here, we focus on advanced capillary suspension based concepts for manufacturing highly porous materials with unique structural and mechanical features. A targeted choice of the secondary fluid allows for a specific shaping of the particle contact regions resulting in exceptional mechanical strength. We use graphite, polymer, and ceramic model systems to demonstrate the versatility and broad applicability of this concept. Resilient, highly porous solids from graphite which cannot be sintered are obtained from capillary suspensions using reactive resins as secondary fluid. Sintering activity during manufacturing of porous polymeric materials can be drastically increased compared to conventional partial sintering of powders using capillary suspensions with an appropriate solvent or swelling agent/plasticizer as secondary fluid. Finally, the mechanical strength of porous ceramics can be strongly improved using the secondary fluid as carrier transporting appropriate active ingredients to the particle contact zones. Thus, sintering of the neck regions and pore shape can be specifically controlled and the mechanical strength of the resulting porous sintered parts can be distinctly increased.

Micrometer-sized, flaky graphite particles have been suspended in glycerol at a particle volume fraction of 20 vol% and different amounts of reactive epoxy resin were added as secondary fluid. The observed tenfold increase in low shear viscosity upon resin addition indicates the formation of a strong

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particle network within the liquid suspension. The resin was cured at ambient conditions while still surrounded by the bulk fluid. After removing the latter by solvent extraction a durable, load bearing porous solid was obtained for samples including 8 and 12 vol% of resin (corresponding to 24 and 37 vol% resin in the dry membrane) without any sintering. Porosities were in the range 60% < ε < 75%, pore size about 15 µm (cf. pore size distribution in Figure S2a, Supporting Information), and the compressive strength of these membranes was on the order of 0.1–1 MPa. **Figure 1** indicates that this is achieved since the resin is located at the particle contacts resulting in a “point-welding” of the network structure created in the wet state.

Numerous different approaches to fabricate porous carbon membranes with a broad range of different porosity and/or pore size have been described in the literature.[18,19] Here, we restrict ourselves to open, macroporous foams or membranes. In refs.[18] and[19] several examples of macroporous carbon foams including commercial products are listed with porosities around 75% and compressive strength of about 1 MPa but in all these cases the pore size is above 100 µm, i.e., they are similar in mechanical strength but different in microstructure. Pekala and Hopper[20] report about highly porous carbon foams with porosities between 80% and 95% and average pore size of 8 µm. However, the mechanical strength is extremely low (∼100 Pa) due to structural defects and heterogeneities making mechanical test almost impossible. Recently, carbon foams were prepared with pore sizes between 1 and 10 µm but porosity was low and pores were mostly closed as indicated by the provided images.[21] In conclusion, our new approach enables fabrication of previously not accessible self-supporting graphite membranes with open porosities in the range of 70% and median pore size ∼15 µm exhibiting mechanical strength close to what has been observed only for samples with much larger pores. Such self-supporting carbon layers may find application as lightweight construction material, in supercapacitors, or as gas diffusion electrodes in fuel cells or Li-air batteries.[22–25] But more importantly this concept is not restricted to graphite, it may also be applied to various other materials which cannot be sintered at all or in cases where high sintering temperatures have to be avoided. Reactive resins with very different reaction temperature and final crosslink density are readily available. Moreover, appropriate monomers might be used as secondary fluid to be polymerized at the contact areas between particles in order to provide thermoplastic links between solid particles. Further research is warranted to verify whether this concept provides a versatile processing route to tune flexibility and toughness of such highly porous materials.

Often, so-called sintering aids are used to increase the strength and density of sintered parts at reduced sintering temperature. Usually, such active ingredients are introduced as specific coatings or additives facilitating the diffusion processes between particles, thus accelerating the sintering process of the bulk material.[26–28] Here, we use the secondary fluid of a capillary suspension as a sintering aid. Macroporous polymer membranes have been made suspending micrometer-sized ultrahigh molecular weight polyethylene (UHMWPE) particles in glycerol and using m-xylene or paraffin oil as secondary fluid. Addition of these secondary fluids results in a strong increase in yield stress (Figure S3a, Supporting Information) indicating the formation of a capillary suspension with a strong particle network. For the sample with paraffin oil as secondary fluid the capillary bridges could be directly visualized using fluorescence microscopy (Figure S3b, Supporting Information). However, at temperatures above 110 °C these organic solvents act as swelling

![Figure 1](https://www.advancedsciencenews.com/file economide/figures/0150491/1_ADMI201504910_Fig1.png)
agents/solvents. Samples with different amount of secondary fluid were sintered at similar conditions (135 °C, 2 h) in the presence of glycerol thus preventing m-xylene from evaporation during this processing step and all liquid ingredients were removed subsequently via solvent extraction. The open porosity of the resulting dry membranes decreased from \( \varepsilon = 77 \pm 3\% \) without secondary fluid to \( \varepsilon = 62 \pm 3\% \) when 4\% m-xylene was added (Figure 2a). Median pore diameter slightly decreased from 30 µm for the membrane made from the pure suspension to 25 µm for the membrane made from the capillary suspension including 4 vol\% m-xylene. The narrow, monomodal pore size distribution is shown in Figure S2b (Supporting Information). When the sintering temperature is reached, the added secondary fluid starts to penetrate into the particles, this increases the mobility/diffusivity of the polymer chains in particular at the particle contact zones where swelling commences and thus locally increases the sintering activity of the polyethylene without temperature increase. Dissolution of capillary bridges and diffusion of secondary liquid into the polymer particles takes place simultaneously with sintering, i.e., the interdiffusion of polymer chains in the particle contact zones. The increased sintering activity also shows up in the faster decrease in porosity over sintering time when capillary suspensions with m-xylene as secondary fluid are compared to a pure suspension of UHMWPE (Figure 2b). Sintering without secondary fluid is still incomplete under these conditions (Figure 2c), whereas the swelling agent at the particle contacts induces a smooth pore structure with well-developed sintering bridges (Figure 2d). Evaporation of m-xylene at elevated temperature seems not to be an issue, the difference between membranes made with and without secondary fluid is striking and the membranes made with m-xylene and the nonevaporating paraffin oil exhibit similar properties. The sample made from the pure suspension is not self-supporting whereas the samples sintered in the presence of a swelling agent provide durable, flexible membranes with Young’s moduli between 2 and 6 MPa. Commercial UHMWPE membranes are obtained from sintering compacted powder at temperatures above 180 °C resulting in porosities typically well below 50%. High porosity foams were made from UHMWPE gels exposed to extensional flow but the samples did not appear in bulk form and mechanical strength could not be determined. So the smart capillary suspension concept not only provides a new processing route but also gives access to UHMWPE membranes with unique properties in terms of porosity and mechanical strength. UHMWPE is a nontoxic material with a high chemical stability and a high abrasion resistance and such highly porous membranes may be used as separators in lithium-ion batteries. Further applications for highly porous UHMWPE may be for medical implants allowing for a good tissue ingrowth. Beyond that, the proposed concept may be applied to other polymeric systems as well.

Utilizing the secondary fluid of a capillary suspension to deposit small particles specifically at the contact regions of the larger particles is another means to increase the sintering activity. But more importantly this approach can be used to increase the mechanical strength of highly porous materials substantially. For a given chemical composition of the solid material the mechanical strength of macroporous sintered parts is mainly controlled by the porosity and strongly decreases with increasing pore volume fraction. At given porosity parts made from

Figure 2. a) Porosity and shrinkage of sintered parts made from UHMWPE suspensions as a function of secondary fluid content. b) Porosity of sintered UHMWPE suspensions versus sintering time at different m-xylene content. In (a) and (b) glycerol was used as bulk and m-xylene or paraffin oil as secondary liquid phase. SEM images of the internal structure of sintered parts made from the c) pure suspension and d) capillary suspension (secondary fluid phase: m-xylene \( \phi_{\text{sec}} = 2 \text{vol}\% \)). Cross sections were obtained cleaving the membranes with a sharp scalpel. Sintering conditions: \( T_{\text{sinter}} = 135^\circ \text{C}, 2 \text{h.} \)
Capillary suspensions exhibit similar properties as those from other processing routes.\cite{12} Increasing the mechanical strength especially at high porosities is still a challenge and would open up new fields of application. Based on the MSA (minimum solid area) model of Rice and Knudsen it has been suggested to use a bimodal particle size distribution in combination with the partial sintering method to improve mechanical strength of porous sintering materials.\cite{37,38} The idea is to place the fine powder fraction at the contact areas of the coarse particles thus achieving a better neck growth and hence better mechanical stability. The fine powder fraction may either be conspecific to the coarse powder fraction or may work as a doping agent.\cite{39,40} In conventional processing (limited to $\varepsilon < 50\%$) the mechanical strength could not be improved so far, since the fine powder fraction could not be preferentially deposited at the contact areas between large particles. Instead, it was distributed uniformly resulting in an increased densification of the powder compact during the sintering procedure or even partially agglomerated because of insufficient processing.\cite{39} However, if the fraction of fine particles or another active ingredient is dispersed in the secondary liquid phase of a capillary suspension, it will be deposited in the contact regions of the large particles which create the sample-spanning network. The corresponding processing scheme is shown in Figure 3a focusing on the case where the secondary liquid phase preferentially wets both powder fractions, i.e., the three phase contact angle is below 90° for both particle species. In step (I) a pure and homogeneous suspension of the coarse powder is prepared. Then in step (II) the secondary liquid phase including the fine particles (or other additives) is added to the pure suspension, drops of this liquid phase are formed and deposited at the contact regions between the particles creating a strong uniform particle network. Subsequent shaping, e.g., extrusion, injection molding, or screen printing (step III) followed by careful debinding and sintering of the precursor leads to a sintered part with a homogeneous pore size distribution and a high open porosity (step IV). Alternatively, a pure suspension of a bimodal powder can be prepared in step (I), then in step (II), when the small secondary liquid droplets are formed, only the small particles will be selectively captured in the droplets and then again be deposited at the interfacial regions between the large particles. The result of such a self-assembling process, with the secondary liquid phase working as a specific carrier for small particles, is shown in Figure 3b. A bimodal mixture of polyvinylchloride (PVC) particles was suspended in water and upon addition of diisononylphthalate (DINP) the small particle fraction is preferentially deposited at the interfacial regions between the large particles. This does not happen in a pure suspension of a bimodal PVC powder, neither in water nor in DINP. This concept leads to a strong increase of the particle coordination number and sintering can then be done at reduced energy or processing cost. But even more importantly, the circularity of the pores and the MSA of the sintering necks is increased finally resulting in an improved mechanical strength. Moreover, the chemical composition of the fine particle fraction can be selected appropriately such that a composite material is created in the sintering regions further increasing mechanical strength. The potential of this new concept is demonstrated for ceramic materials using $\alpha$-Al$_2$O$_3$ as model system. The coarse powder fraction has a median particle size of 5.76 µm, paraffin

![Figure 3.](image-url)
oil was used as bulk phase, and an aqueous sucrose solution as secondary liquid phase. Two different fine powder fractions were used, both about one order of magnitude smaller than the coarse particles: α-Al₂O₃ with a median particle diameter of 0.67 µm was used as conspecific fine powder fraction, tetragonal stabilized (3 mol% Y₂O₃) t-ZrO₂ with a median particle diameter of 0.7 µm was used to modify the sintering necks. Both fine particle fractions are preferentially wetted by the aqueous phase and the corresponding three-phase wetting angles are 66° and 83°, respectively. ZrO₂ was chosen as fine particle fraction since in dense systems doping Al₂O₃ with t-ZrO₂ results in a composite material called zirconium toughened alumina (ZTA-ceramic), characterized by improved mechanical properties like increased strength, fracture resistance, and toughness. Figure 4 shows scanning-electron-microscopy images in backscattering-mode (SEM-BSE) cross-cut images of sintered parts made from capillary suspensions constant with constant amount of secondary liquid phase but different amount and composition of powder mixtures (see figure caption) chosen to result in a constant porosity of ε ≈ 55%. Error bars are the standard deviation calculated from at least three measurements. Note, in the case of the con-specific α-Al₂O₃ mixture with 20% fine particle fraction and 2.5% added secondary fluid the loading of fine particles in the secondary liquid droplets is close to maximum packing.

Figure 4. SEM-BSE cross-cut images and mechanical properties of sintered capillary suspensions made from different powder compositions at a constant amount of secondary liquid phase (2.5 vol%). a) Coarse monomodal α-Al₂O₃ powder, total solids 25 vol%, sintered at 1650 °C for 2 h, b) powder mixture of coarse and fine α-Al₂O₃, total solids fraction 20 vol%, fine particle fraction 20% relative to total solids, sintered at 1550 °C for 2 h, c) powder mixture of α-Al₂O₃ (coarse) and t-ZrO₂ (fine), total solids fraction 15 vol%, fine particle fraction 10% relative to total solids, sintered at 1650 °C for 2 h, due to the difference in electron density t-ZrO₂ appears white and α-Al₂O₃ appears gray in these electron images, d) overview image of the same α-Al₂O₃/t-ZrO₂ sample, e) compressive strength and f) flexural strength of corresponding samples with ε ≈ 55%. Error bars are the standard deviation calculated from at least three measurements. Note, in the case of the con-specific α-Al₂O₃ mixture with 20% fine particle fraction and 2.5% added secondary fluid the loading of fine particles in the secondary liquid droplets is close to maximum packing.
attributed to the targeted deposition of fine particles at the contact regions between coarse particles. This hypothesis is directly confirmed by the SEM-BSE images obtained for the system where t-ZrO<sub>2</sub> was used as fine powder fraction (Figure 4c). Due to the material contrast between t-ZrO<sub>2</sub> and α-Al<sub>2</sub>O<sub>3</sub> it is directly visible that the fine particles are selectively deposited at the contact areas between the large particles and that this leads to an improved circularity of the pores. The overview image in Figure 4d shows, that the t-ZrO<sub>2</sub> is uniformly distributed throughout the sample. In conclusion, the capillary suspension is a stable precursor prohibiting phase separation between different materials and allowing for a targeted design of the sintering necks in macroporous materials.

Formation of these distinct structural features is enabled by the network in the capillary suspension and already shows up in the wet state as can be seen from Figure S4a (Supporting Information). A capillary suspension with a monomodal particle size distribution exhibits an increase in yield stress of at least one order of magnitude, compared to the corresponding pure suspension. This is different for powder mixtures as shown here for the α-Al<sub>2</sub>O<sub>3</sub> with added t-ZrO<sub>2</sub>. In the pure suspension both particle species are homogenously distributed and contribute to the strength of the van der Waals (vdW) network but with increasing fine powder fraction the number of particle–particle contacts increases drastically and this results in the strong increase in yield stress<sup>[31,41]</sup> as shown in Figure S4a (Supporting Information) for a fixed total volume fraction of solids. The situation changes when the capillary suspension system is considered. In this case, the fine particles are deposited at the particle contact regions of the coarse powder fraction forming the network stabilized by capillary bridges. The number of particle contacts contributing to that network is given by the number of large particles which decreases as the finer powder fraction increases (at constant total solids), since the latter do not create own, new network nodes. Accordingly the yield stress also decreases and at a fine powder fraction of 20% it is only slightly higher than for the corresponding pure suspension with its large number of particle contacts controlled by vdW attraction. However, the microstructure is distinctly different and this has a strong impact on structure and mechanical strength of the corresponding sintered parts. At constant sintering conditions, an increasing amount of fine powder always leads to a decrease in porosity of the sintered parts (Figure S4b, Supporting Information). But this reduction in porosity is only weak, when a capillary suspension is used as precursor. In contrast, the porosity of sintered parts made from pure suspensions with a high fraction of fine particles is very low because the weak van der Waals network collapses and the bimodal particle distribution allows for a much denser packing compared to the monomodal system. Although yield stress of the pure and the capillary suspension with a fine particle fraction of 20 vol% (relative to the total solids volume) exhibits almost the same value, the porosities of the corresponding sintered parts differ strongly and only the capillary suspensions can provide high porosities ε > 50%. Although the sinter activity rises when the fraction of fine powder is increased, densification of the capillary suspension system is prohibited by the self-assembled structure with the fine powder fraction located at the contact regions of the coarse particle network.

The dedicated structural features of sintering materials made from capillary suspensions with bimodal particle size distribution have a direct impact on the mechanical bulk properties of sintered parts (Figure 4e,f). Compressive and flexural strength of such parts made from a monomodal coarse powder preparation of α-Al<sub>2</sub>O<sub>3</sub> are compared to corresponding values for samples made from bimodal powder preparations with t-ZrO<sub>2</sub> and conspecific α-Al<sub>2</sub>O<sub>3</sub> as fine powder fraction at a total open porosity of 55%, sintering conditions were adjusted accordingly. The addition of a conspecific α-Al<sub>2</sub>O<sub>3</sub> fine powder fraction leads to a rise of the mechanical strength compared to sintering the monomodal α-Al<sub>2</sub>O<sub>3</sub> coarse powder, even though the sintering temperature was reduced from 1650 to 1550 °C. The flexural strength increases by a factor of about 1.5 from 6.5 ± 1.3 to 9.5 ± 0.7 MPa and the compressive strength by about a factor of 2 from 16.3 ± 3 to 29.1 ± 5.6 MPa. According to theory of brittle materials this is attributed to the improved MSA and the smoother sintering structure resulting from the addition of the fine powder fraction.<sup>[35,36]</sup> Moreover, using t-ZrO<sub>2</sub> as fine powder fraction results in an increase of flexural strength by a factor of 2.5 from 6.5 ± 1.3 to 15.8 ± 0.9 MPa and compressive strength by a factor of almost 3.5 from 16.3 ± 3 to 52.7 ± 11 MPa compared to the monomodal α-Al<sub>2</sub>O<sub>3</sub> coarse powder preparation. This drastic increase in mechanical strength may be due to the formation of a strong ZTA composite like in dense systems. Figure 4c indicates that most of the t-ZrO<sub>2</sub> is encased by α-Al<sub>2</sub>O<sub>3</sub> in the sintered part. The presented examples demonstrate that the targeted deposition of a fine powder fraction on the microscale enabled by the capillary suspension concept is a targeted strategy for tailoring mechanical features on the macroscale and the mechanical strength of highly porous materials can be increased in an inimitable manner. Our concept is a priori not restricted to the particular choice of fine particles investigated so far. Active ingredients forming solid solutions with α-Al<sub>2</sub>O<sub>3</sub> may be suited for a further increase of mechanical strength. This warrants continuing research efforts.

In summary, we have presented an advanced capillary suspension based concept for manufacturing porous materials with exceptional mechanical strength taking advantage of a demand-oriented choice of secondary fluid. Resilient self-supporting highly porous carbon layers have been prepared using a reactive resin as secondary fluid. Polymer membranes have been made using a swelling agent as secondary fluid thus acting as sintering aid enabling membrane manufacturing at drastically lower temperature additionally resulting in membranes with unique properties in terms of porosity and mechanical strength. Highly porous ceramics with threefold mechanical strength compared to the pure reference system have been made using the secondary fluid as a carrier depositing small particles at the contact zones of the large particles in the wet state of processing. Thus, sintering of the neck regions was promoted, and moreover their chemical composition and the pore shape could be specifically tailored in order to control the mechanical properties of the final porous parts.

Our new approach is ideally suited to fabricate highly porous solids from a wide range of materials, even if they cannot be sintered or treatment of elevated temperatures is not feasible. The proofs of concept demonstrated here should stimulate further research and technical developments. Besides reactive resins
appropriate monomers to be polymerized in situ maybe used to tailor the strength and elasticity of porous solids. The composition of the neck regions in porous ceramics may be designed by deposition of appropriate small particles forming solid solutions with the major constituent of the ceramic scaffold thus further improving mechanical strength. Such macroporous materials with their unique mechanical strength offer distinctly advanced specifications in classical fields of application like membranes or filters, lightweight construction materials, thermal insulators, or catalyst carriers but are also suited to enable innovative applications, e.g., as membranes in fuel cells, electrode layers in Li-air batteries, or medical implants.

**Experimental Section**

*Materials and Preparation of Capillary Suspensions: Graphite:* Flaky shaped graphite powder SLP30 \( (x_{0.1} = 15.8 \, \mu m) \) was obtained from Imerys Graphite and Carbon Ltd. (Bodio, Switzerland). Glycerol was used as bulk phase. The commercial two-component epoxy resin SK Resins 152 (S u. K Hock GmbH, Regen, Germany) was employed as secondary fluid. The three-phase contact angle of this resin mixture on graphite was determined to be 130° indicating that this system is in the so-called capillary state.\(^{[1]}\)

Suspensions of 20 vol% graphite particles in glycerol were prepared using a high shear dissolver at 1200 rpm for 10 min. The two-component resin was premixed manually and then added to the pure suspension while stirring at 1000 rpm for 5 min. Three-phase suspensions with resin fractions of 0, 1.6, 4, 8, and 12 vol% relative to the total suspension volume were prepared, filled into aluminum molds (diameter: 39 mm, height: 5 mm), and subsequently cured at room temperature for 120 h. Samples were removed from the mold before glycerol was extracted in an ethanol bath for 2 h and then dried at 65 °C for several hours. Note, that capillary suspensions are obtained here even at resin contents of 8 and 12 vol% corresponding to secondary fluid to solid ratios of 0.4 and 0.6. This is due to the plate-like shape of the graphite particles enabling to accommodate more secondary fluid in capillary bridges without inducing spherical agglomeration than in the case of isometric particles.\(^{[4-6]}\)

**Ultrahigh Molecular Weight Polyethylene:** UHMWPE powder \( (x_{0.3} = 34.3 \, \mu m) \) was received from Ticona GmbH (GUR 2126, Sulzbach, Germany). Glycerol (ROTIPURAN ≥ 99.5%, Carl Roth, Karlsruhe, Germany) was used as bulk phase \( (\eta = 1.48 \, Pa \, s) \) and m-xylene \( (\eta = 0.58 \, Pa \, s) \) and paraffin oil \( (\eta = 0.03 \, Pa \, s) \) both supplied by Carl Roth, Karlsruhe, Germany were added as secondary phase. The three phase contact angles of the paraffin oil on UHMWPE is 43° and of m-xylene on UHMWPE is 29°, indicating that the corresponding capillary suspensions are in the pendular state.\(^{[1]}\)

Pure suspensions of 20 vol% UHMWPE \( (M_w = 4.5 \times 10^7 \, g \, mol^{-1}) \) in glycerol were prepared using a high shear dissolver at 1200 rpm for 10 min. Then m-xylene or paraffin oil was added as secondary liquid phase at 2 and 4 vol% relative to the total suspension volume. This corresponds to the concentration range in which the yield stress exhibits a maximum for isometric particles, at higher secondary fluid content spherical agglomeration sets and leads to a pronounced decrease in yield stress.\(^{[11,13]}\)

Samples were stirred for 2 min at 2000 rpm (droplet formation) and 2 min at 800 rpm (structure formation). The prepared samples were filled in aluminum molds (diameter: 39 mm, height: 5 mm). Sintering was done in an ethanol bath. Samples with paraffin oil as secondary fluid phase were additionally washed with diethyl ether.

**Polyvinylidene fluoride:** Bimodal PVC powder \( (x_{0.3} = 1.88 \, \mu m, \text{particle size distribution provided in Figure S5, Supporting Information}) \) was obtained from Vinnolit GmbH & Co. KG. Water was used as bulk liquid phase and diisononyl phthalate \( (\eta = 75 \, Pa \, s) \) as secondary liquid phase (DINP, Roth, Karlsruhe, Germany).

Pure suspensions (20 vol% PVC particles in water) were prepared using a high shear dissolver at 1200 rpm for 10 min. Then 2.5 vol% DINP was added as secondary liquid phase and stirred for 2 min at 2000 rpm (droplet formation) and 2 min at 800 rpm (structure formation). The three phase contact angle determined for this system is 70.3° and it is considered to be in the pendular state.\(^{[1]}\) Preparated pastes were molded into a sample form (sample size 50 × 10 × 10 mm) and the top face was smoothed using a doctor blade. So molded samples were dried, debindered, and sintered at 90 °C for 3 h.

**Ceramics:** \( \alpha-Al_2O_3 \) as coarse \( (x_{0.03} = 5.76 \, \mu m) \) and fine \( (x_{0.67} = 0.67 \, \mu m) \) powder fraction was obtained from Almatis (CT19FG, CT3000SG, Ludwigsafen, Germany) and t-ZrO\(_2\) as fine powder fraction \( (x_{0.03} = 0.7 \, \mu m) \) was used from Tosoh (TZ-3YS-E, Minato, Japan). The density of \( \alpha-Al_2O_3 \) and t-ZrO\(_2\) is 5.76 and 6.05 kg m\(^{-3}\), respectively. Paraffin oil \( \eta = 0.08 \, Pa \, s \) was used as bulk phase (paraffin oil thin, Carl Roth, Karlsruhe, Germany). Aqueous 1.853 m sucrose solution \( (\eta = 0.08 \, Pa \, s) \) was used as secondary liquid phase (\( \alpha \)-sucrose (\( \alpha+\)) , Carl Roth, Karlsruhe, Germany).

Pure suspensions were prepared using a high shear dissolver at 1200 rpm for 20 min followed by a de-agglomeration step using a ball mill with 25 mm balls for 24 h at 20 °C. Corresponding capillary suspensions were obtained by adding the sucrose solution while stirring with a high shear dissolver at 1000 rpm for 1 min (droplet formation) followed by a second stirring step with a reduced stirring speed of 500 rpm for 1 min (structure formation). Samples with different total volume fractions of ceramic powder between 15 and 25 vol% were prepared, fraction of fine powder relative to total solids volume was varied between 0 and 20 vol%. The amount of secondary liquid phase was held constant at 2.5 vol% relative to the total sample volume corresponding to a maximum yield stress indicating formation of a strong capillary force controlled particle network without spherical agglomeration.\(^{[25]}\) The three phase contact angle of the sucrose solution on \( \alpha-Al_2O_3 \) is 66° indicating that the capillary suspension is in the pendular state.\(^{[11]}\) After structure formation capillary suspensions were homogenized again using a ball mill with 25 mm balls for 24 h at 20 °C. Pastes were molded into a sample form (size 50 × 10 × 10 mm) and the top face was smoothed using a doctor blade. The sample form was placed on an absorbent pad and directly demolded after spreading. Debinding the bulk phase was done by capillary extraction for 5 d at room temperature on the absorbent pad followed by a thermal debinding procedure at 200 °C (30 min), 500 °C (1 h), and 800 °C (15 min) for all samples to ensure a complete and gentle debinding of the sucrose and residuals of the bulk phase. Monomodal coarse \( \alpha-Al_2O_3 \) powder preparations and the bimodal composite preparations \( \alpha-Al_2O_3 + t-ZrO_2 \) were sintered at 1650 °C for 2 h, bimodal \( \alpha-Al_2O_3 + \alpha-Al_2O_3 \) powder compositions were sintered at 1550°C for 2 h.

**Characterization:** Particle size distributions for all investigated particle systems were determined using a commercial Fraunhofer diffraction device Helos H0309 equipped with an ultrasonic wet dispersing unit Quixel (Sympatec, Clausthal-Zellerfeld, Germany) according to DIN EN ISO 13321-13. Corresponding results are provided as Figure S5 (Supporting Information). For the flaky or plate-shaped graphite powder image analysis of scanning electron images was performed to characterize the shape anisotropy and an aspect ratio \( r = \frac{0.14}{0.08} \) of shortest to longest plate dimension was determined in addition to the equivalent sphere diameter \( x_{0.3} \) provided in Figure S5 (Supporting Information).

Three phase contact angles were calculated using the expanded Young–Dupré equation.\(^{[5]}\) The required interfacial tensions were determined using a weight-based tensiometer (Dataphysics, DCAT 11, Filderstadt, Germany) employing a Wilhelmy plate\(^{[56]}\) Contact angles against air on compact substrates made from the investigated powders were measured using the sessile drop method (Dataphysics, OCA15, Filderstadt, Germany), evaluated by a numerical Young–Laplace fit.\(^{[47]}\) In case of graphite, a low porosity plate (Graphite Coava GmbH, Rothenbach, Germany) with composition similar to the used powder was employed for contact angle determination. Rheological characterization was done with a stress-controlled shear rheometer (Thermo Scientific, Mars II, Karlsruhe, Germany) using a vane geometry (Z20 according to DIN 53019-1). Yield stress values were determined from shear stress ramps, according to the tangent method.\(^{[48]}\) An increase of the yield stress
upon addition of the secondary liquid phase by about a factor of 5 or more was considered as indication for the formation of a capillary suspension with a strong particle network, corresponding data are included as the Supporting Information. The porosity of the graphite membranes as well as the sintered ceramic and UHMWPE parts was determined from the Archimedes density according to DIN EN 993-1. Pore size of UHMWPE graphite and graphite parts was measured by mercury intrusion porosimetry (AutoPore III, Micromeritics). Young’s modulus of the UHMWPE membranes was determined via compressive strength tests according to DIN EN ISO 604. Compressive strength tests of graphite samples were performed according to DIN 51104 using rectangular shaped parts. Mechanical properties of ceramic parts were measured following DIN EN 843-1 (flexural strength) and DIN 51104 (compressive strength) using reshaped parts with a rectangular cross section. All ceramic samples for mechanical testing had a porosity of 55%. Sintered ceramic parts were vacuum infused with epoxy resin, mounted on SiC paper and polished with a diamond suspension (Buehler, Düsseldorf, Germany) to obtain cross-cut SEM-BSE (Hitachi, S-4500, Krefeld, Germany). Graphite membranes were fractured and sintered UHMWPE samples were cleaved with a sharp scalpel for SEM images (SEM-SE) of the cross section.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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